# CHAPTER 8

# DYES: THE CHEMISTRY AND APPLICATIONS

## CHAPTER 8 OBJECTIVES

- INTRODUCTION
- COLORANTS
- CLASSIFICATION OF DYES
- TEXTILE FIBERS
- THE APPLICATION OF DYES
- INTERMEDIATES
- MANUFACTURE OF DYES



## INTRODUCTION

- Dyes are colored organic compounds that are used to impart color to various substrates, including paper, leather, fur, hair, drugs, cosmetics, waxes, greases, plastics and textile materials.
- *Indigo*, the oldest known dye was used by the ancient Egyptians to dye mummy clothes.
- *Tyrian purple*, obtained from *Murex* snails found near the city of Tyre, was used by the Romans to dye the togas of the emperors.

# INTRODUCTION

- The dye industry has always been highly competitive; the industry has lately experienced major setbacks in terms of profitability and overall attractiveness particularly in Europe and the United States.
- Major changes have taken place during the last 20 years, and today Asia (India, Japan, Korea and China) has become the largest dyestuff market, accounting for about 42% of the value of the global dyestuff market.
- World demand for dyes and organic pigments is forecast to increase 5.1% per year to more than $ 14 billion in 2004.



# CHAPTER 8 OBJECTIVES

- INTRODUCTION
- COLORANTS
- CLASSIFICATION OF DYES
- TEXTILE FIBERS
- THE APPLICATION OF DYES
- INTERMEDIATES
- MANUFACTURE OF DYES



# COLORANTS

- The two major types of colorants produced today are dyes and pigments.
- Pigments both inorganic and organic types, are almost always applied in an aggregated or crystalline-insoluble form that requires a binder to form a coating on the surface of a substrate.
- Pigments do not interact with the substrate and hence do not destroy the crystal structure of the substrate.

## COLORANTS

- Dyes are normally water-soluble or water dispersible organic compounds that are capable of being absorbed into the substrate destroying the crystal structure of the substance.
- The dye molecules are usually chemically bonded to the surface and become a part of the material on which it is applied.
- The primary use of dyes is in the textile industry, although substantial quantities are consumed for coloring, such diverse materials as leather, paper, plastics, petroleum products, and food.



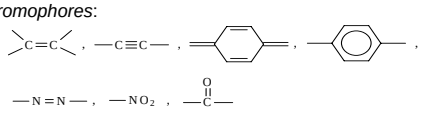
## COLORANTS

- To be of commercial interest, dyes must have high color intensity and produce dyeing of some permanence.
- The color intensity of the dye molecule depends on how strongly it absorbs radiation in the visible region, which extends from 400 to 700 nm.
- It was observed earlier that only some types of organic structures give rise to color.



## COLORANTS

- The partial structures necessary for color (unsaturated groups that can undergo π-π* and n-π* transitions) were called *chromophores*:



- It was also observed that the presence of some other groups caused an intensification of color. These groups are called *auxochromes*.
- The auxochromes are groups that can not undergo π-π* transitions, but can undergo transition of n electrons:

  -OH, -OR, -$NH_2$, -NHR, -$NR_2$, -X

# CHAPTER 8 OBJECTIVES

- INTRODUCTION
- COLORANTS
- CLASSIFICATION OF DYES
- TEXTILE FIBERS
- THE APPLICATION OF DYES
- INTERMEDIATES
- MANUFACTURE OF DYES



# CLASSIFICATION OF DYES

- Dyes may be classified according to their chemical structure or by the method by which they are applied to the substrate.
- The dye manufacturers and dye chemists prefer the former approach of classifying dyes according to chemical type. The dye users, however, prefer the latter approach to of classification according to application method.
- Classification by application or usage is the principal system adopted by the Color Index (C.I.).
- The classification of dyes according to their usage is summarized in Table 8.1, which is arranged according to the C.I. application classification.



# CLASSIFICATION OF DYES

**Table 8.1. Application Classification of Dyes**

| Class | Principal substrates | Method of application | Chemical Types |
|---|---|---|---|
| Acid | Nylon, wool, silk, paper, inks, and leather | Usually from neutral to acidic dyebaths | Azo(including premetalized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso |
| Azoic components and compositions | Cotton, rayon, cellulose acetate and polyester | Fiber impregnated with coupling component and treated with a solution of stabilized diazonium salt | Azo |
| Basic | Paper, polyacrylonitrile, modified nylon, polyester and inks | Applied from acidic dyebaths | Cyanine, hemicyanine, diazahemicyanine, diphenylmethane, triarylmethane, azo, azine, xanthene, acridine, oxazine and anthraquinone |
| Direct | Cotton, rayon, paper, leather and nylon | Applied from neutral or slightly alkaline baths containing additional electrolyte | Azo, phthalocyanine, stilbene, and oxazine |
| Disperse | Polyester, polyamide, acetate, acrylic and plastics | Fine aqueous dispersions often applied by high temperature/pressure or lower temperature carrier methods; dye may be padded on cloth and baked on or thermofixed | Azo, anthraquinone, styryl, nitro, and benzodifuranone |
| Fluorescent brighteners | Soaps and detergents, and all fibers, oils, paints, and plastics | From solution, dispersion or suspension in a mass | Stilbene, pyrazoles, coumarin, and naphthalimides |

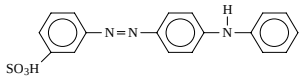
## CLASSIFICATION OF DYES

| | | | |
|---|---|---|---|
| Food, drug, and cosmetic | Foods, drugs, and cosmetics | | Azo, anthraquinone, carotenoid and triarylmethane |
| Mordant | Wool, leather, and anodized aluminum | Applied in conjunction with Cr salts | Azo and anthraquinone |
| Oxidation bases | Hair, fur, and cotton | Aromatic amines and phenols oxidized on the substrate | Aniline black and indeterminate structures |
| Reactive | Cotton, wool, silk, and nylon | Reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline) | Azo, anthraquinone, phthalocyanine, formazan, oxazine and basic |
| Solvent | Plastics, gasoline, varnishes, lacquers, stains, inks, fats, oils, and waxes | Dissolution in the substrate | Azo, triphenylmethane, anthraquinone, and phthalocyanine |
| Sulfur | Cotton and rayon | Aromatic substrate vatted with sodium sulfide and reoxidized to insoluble sulfur-containing products on fiber | Indeterminate structures |
| Vat | Cotton, rayon, and wool | Water-insoluble dyes solubilized by reducing with sodium hydrogensulfite, then exhausted on fiber and reoxidized | Anthraquinone (including polycyclic quinines) and indigoids |

13

## Acid Dyes

- Acid dyes are water-soluble anionic dyes, containing one or more sulfonic acid substituents or other acidic groups. An example of the class is Acid Yellow 36.




- Acid dyes are applied from acidic dye baths to nylon, silk, wool, and modified acrylics. They are also used to some extent for paper, leather, ink-jet printing, food, and cosmetics.
- The dyeing process is reversible and may be described as follows:

$$Dye^- + H^+ + Fiber \rightleftharpoons Dye^- H^+ - Fiber$$

Professor Bassam El Ali 14

## Acid Dyes

- The ionic bonding between the dye and the fiber is the result of reaction of the amino groups on the fiber with acid groups on the dye.
- Generally the fastness of this dye depends on the rate with which the dye can diffuse through the fiber under the conditions of washing.
- Metal complex (cobalt or chromium) acid dyes are used mainly on wool for improved fastness.

Professor Bassam El Ali 15

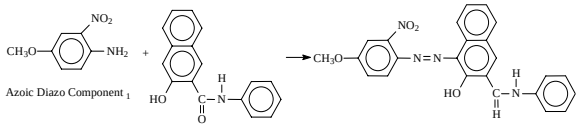
# Azoic Dyes

- Azo dyes contain at least one azo group (-N=N-) attached to one or often two aromatic rings.
- They are produced on textile fibers (usually cotton, rayon and polyester), by diazotization of a primary aromatic amine followed by coupling of the resulting diazonium salt with an electron-rich nucleophile (azo coupling).
- A variety of hues can be obtained by proper choice of diazo and coupling components.



# Azoic Dyes

- The production of bluish red azoic dye from the following two components is an example.




Azoic Diazo Component 1

Azoic Coupling Component 2




Bluish Red Azoic Dye

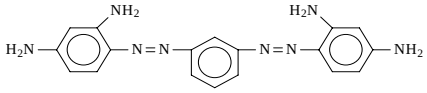


# Basic (Cationic) Dyes

- Basic dyes are water-soluble and produce colored cations in solution.
- They are mostly amino and substituted amino compounds soluble in acid and made insoluble by the solution being made basic.
- They become attached to the fibers by formation of salt linkages (ionic bonds) with anionic groups in the fiber.
- They are used to dye paper, polyacrylonitrile, modified nylons, and modified polyesters.

# Basic (Cationic) Dyes

- In solvents other than water, they form writing and printing inks. The principal chemical classes are triaryl methane or xanthenes.
- Basic Brown 1 is an example of a cationic dye that is readily protonated under the pH 2 to 5 conditions of dyeing.



Basic Brown 1



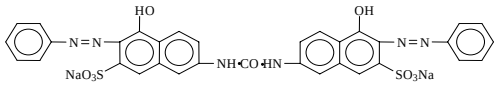
# Direct Dyes

- Direct dyes are water-soluble anionic dyes, but are not classified as acid dyes because the acid groups are not the means of attachment to the fiber.
- They are used for the direct dyeing of cotton and regenerated cellulose, paper and leather.
- They are also used to dye union goods (mixed cotton, and wool or silk) and to a lesser extent nylon fiber.
- Most of the dyes in this class are polyazo compounds, along with some stilbenes, phthalocyanines and oxazines.



# Direct Dyes

- The solubility of the dye in the dye bath is often reduced by adding common salt or Glauber's salt.
- The presence of excess sodium ions favors establishment of equilibrium with a minimum of dye remaining in the dye bath. Direct orange 26 is a typical direct dye.



Direct Orange 26

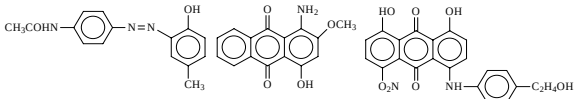
# Disperse Dyes

- Disperse dyes are substantially water-insoluble nonionic dyes for application to synthetic hydrophobic fibers from aqueous dispersions.
- Disperse dyes are applied as very finely divided materials which are adsorbed onto the fibers with which they then form a solid solution.
- Dispersed dyes are primarily used for polyester and acetate fibers. Simple soluble azo, styryl benzodi furanone, and insoluble anthraquinone are the most common disperse dyes.



# Disperse Dyes

- Disperse yellow 3, Disperse Red 4, and Disperse Blue 27 are good examples of disperse dyes:

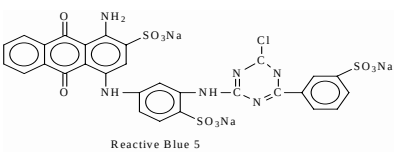



Disperse Yellow 3 Disperse Red 4 Disperse Blue 27



# Fiber-Reactive Dyes

- These dyes react with the cellulosic fiber to form a covalent bond. This produces dyed fiber with extremely high wash fastness properties.
- Cotton, rayon, and some nylons are dyed by this relatively simple dye. The principal chemical classes of reactive dyes are azo, triphendioxazine, phthalocyanine, formazan, and anthraquinone.
- An example of this type is the Reactive Blue 5 dye shown below:




Reactive Blue 5

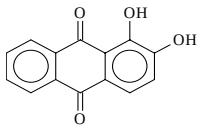
# Mordant Dyes

- Some dyes combine with metal salts (mordanting) to form insoluble colored complexes (lakes). These materials are usually used for the dyeing of cotton, wool or other protein fiber.
- The fiber is first treated with an aluminum, chromium and iron salt and then contacted with a lake forming dye (azo and anthraquinone derivatives).
- The metallic precipitate is formed in the fiber producing very fast colors highly resistant to both light and washing.



# Mordant Dyes

- Alizarin is the best-known anthraquinone derivative as an example of a mordant dye as shown in the following reaction.
- The hydroxyl groups attached to anthraquinone nuclei are capable of reaction with metals in the mordant material (aluminum hydroxide) to form mordant dyes (aluminum "lake").




Mordant Red 11



# Sulfur Dyes

- Sulfur dyes are applied to cotton from an alkaline reducing bath with sodium sulfide as the reducing agent.
- These dyes are water-insoluble but they are soluble in their reduced form and exhibit affinity for cellulose.
- They dye by adsorption but on exposure to air they are oxidized to reform the original insoluble dye inside the fiber.
- They are low cost and have good fastness to light, washings and acids.
- The actual structures of sulfur dyes are largely unknown although it is considered that they possess sulfur-containing heterocyclic rings.

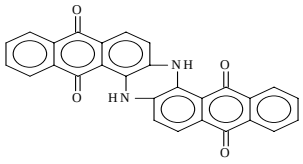
# Vat Dyes

- The vat dyes are insoluble complex polycyclic molecules based on the quinone structure (keto-forms).
- They are reduced with sodium hydrosulfite in a strongly alkaline medium to give soluble leuco forms that have a great affinity for cellulose.
- After the reduced dye has been absorbed on the fiber, the leuco forms are reoxidized to the insoluble keto forms.



# Vat Dyes

- The dyeings produced in this way have high wash and light fastness. An example of a vat dye is Vat Blue 4 (Indanthrene).




Vat Blue 4

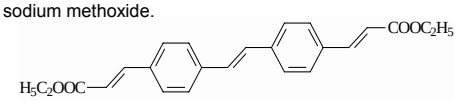


# Solvent Dyes

- These dyes are water-insoluble but soluble in alcohols, chlorinated hydrocarbons, or liquid ammonia.
- They are used for coloring synthetics, plastics, gasoline, oils and waxes.
- The dyes are predominantly azo and anthraquinone, but phthalocyanine and triarylmethane dyes are also used. Perchloroethylene is the preferred solvent.

# Fluorescent Brighteners

- Fluorescent brighteners or fluorescent whitening agents (FWAs) are colorless to weakly colored organic compounds.
- FWAs are used to make yellowish laundry appear dazzling white. These compounds are added to soaps and detergents to produce greater brilliance in laundry washings.
- FWAs are used for improving the appearance of recycled paper.
- An example of a FWAs is 4,4'-bis (ethoxycarbonylvinyl) stilbene, which can be obtained by the reaction stilbene-4,4'-dicarbaldehyde with triethyl phosphonoacetate in the presence of sodium methoxide.





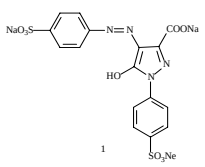

# Food, Drug, and Cosmetic Dyes

- Most synthetic and natural dyes commonly used in food, drug, and cosmetics are carefully controlled materials, regulated by the government agencies in the EEC, the USA, and Japan.
- These currently consist of very few (under 100) dyes and are listed in the approved list.
- Regulations list the approved color additives and conditions under which they may be safely used, including the amounts that may be used.
- The most frequently used synthetic dyes for food, drugs and cosmetics belong to azo, anthraquinone, carotenoid and triarylmethane chemical types.



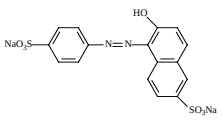
# Food, Drug, and Cosmetic Dyes

- The following two azo series food dyes are good examples:



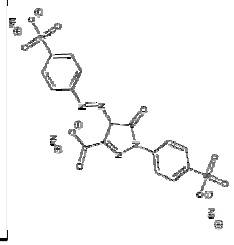

1

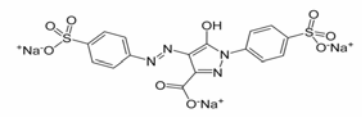
*C.I. Food Yellow 4, 19140* [*1934-21-0*], E 102, Tartrazine




*C.I. Food Yellow 3*, 15985, [*2783-94-0*] Yellow E110, Orange S

# Food, Drug, and Cosmetic Dyes





**Food Yellow 4**

Tartrazine (otherwise known as E102 or FDC Yellow 5) is a synthetic lemon yellow azo dye used as a food coloring



## CHAPTER 8 OBJECTIVES

- INTRODUCTION
- COLORANTS
- CLASSIFICATION OF DYES
- TEXTILE FIBERS
- THE APPLICATION OF DYES
- INTERMEDIATES
- MANUFACTURE OF DYES



# TEXTILE FIBERS

- The world textile industry is one of the largest consumers of dyestuffs.
- The natural fibers may be from plant sources (such as cotton and flax), animal sources (such as wool and silk), or chemically modified natural materials (such as rayon and acetate fibers).
- The synthetic fibers include nylon, polyester, acrylics, polyolefins and spindex.

# TEXTILE FIBERS

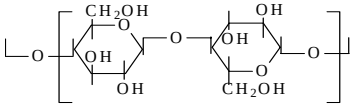
**Table 8.2. Fiber-Dye Property Requirements**

| Fiber name | Type/general classification | Chemical constitution | Ionic nature in dyebath |
|---|---|---|---|
| Cotton, linen, and other vegetable fibers | Natural, hydrophilic | Cellulose | Anionic |
| Viscose rayon | Synthetic, hydrophilic | Regenerated cellulose | Anionic |
| Wool, silk, hair | Natural, hydrophilic | Complex proteins | Cationic |
| Nylon | Synthetic, somewhat hydrophobic | Polyamide | Usually cationic |
| Acrylics | Synthetic, hydrophobic | Modified polyacrylonitriles | Anionic |
| Acetate | Synthetic, hydrophobic | Acetylated cellulose | Nonionic |
| Triacetate | Synthetic, hydrophobic | Acetylated cellulose | Nonionic |
| Polyester | Synthetic, hydrophobic | Polyester | Usually nonionic |
| Polypropylene | Synthetic, hydrophobic | Polyolefin | nonionic |

37

# Cotton

- The cotton fiber is essentially cellulosic in nature and may be chemically described as poly (1,4-B-D-anhyrdoglucopyranose), with the following repeat unit (about 3000 units):



- The structure has primary and secondary alcohol groups uniformly interspersed throughout the length of the polymer chain.
- These hydroxy units impart high water absorption characteristics to the fiber and can act as reactive sites.

Professor Bassam El Ali 38

# Cotton

- The cotton fibers are hydrophilic and swell in water. It is hydrolyzed by hot acid and swollen by concentrated alkali.
- The cotton is treated with caustic soda solution (12-25 %) under tension to develop a silk-luster and stop longitudinal shrinkage. This process is called *mercerization.* Mercerized cotton exhibits increased moisture and dye absorption.
- The dyeing of cotton fiber is accomplished by three principal processes.
- Cotton may be chemically reacted with fiber-reactive dyes in solution.

Professor Bassam El Ali 39

## Cotton

- The dyeing take place by reaction with hydroxyl groups in cotton.
- A second method is the use of substantive dyes which diffuse directly into fiber from a dye solution. The dyeing rate is increased by the addition of electrolytes.
- The third method is referred to as mordant dyeing in which the dye in solution reacts with metals previously applied to the fiber to form insoluble colored compounds on the cotton.
- Vat dyes are another important class of dyes for cotton. These are applied in a soluble reduced form and after application they are oxidized, forming an insoluble molecule.



## Rayon

- Rayon, the first commercial manmade fiber, is composed of cellulose in a quite pure form.
- It is produced by the treatment of wood pulp with alkali and carbon disulfide to form a viscous solution of cellulose xanthate.
- Rayon fibers are easily wetted by water and provide easy access to dye molecules.
- Dying may take place by absorption or by reaction with the hydroxyl groups. Rayon fibers may also be dyed with mordant and vat dyes.

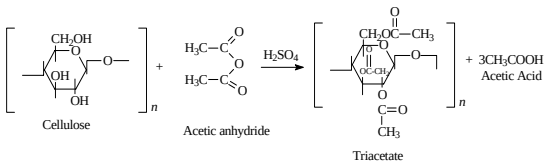


## Cellulose Acetates

- Cellulose acetate is a well-known derivative of cellulose and has found many uses as a fiber.
- Acetate, diacetate, and triacetate are similar in chemical structure with acetate having about 83% of the hydroxyl groups acetylated, and not less than 92% hydroxyl groups are acetylated in triacetate.
- Triacetate and diacetate fibers are manufactured by the acetylation of refined wood pulp or purified cotton linters.

# Cellulose Acetates

- The acetylation reaction is quite simple chemically and may be visualized in the following manner:





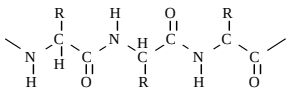

# Cellulose Acetates

- Acetate or diacetate is made by the saponification of one of the acetylated groups, thus restoring some of the hydroxyl in cellulose units.
- The conversion of the hydroxyl group causes these fibers to be hydrophobic and changes their dyeing characteristics drastically from those of cotton and rayon.
- The higher the degree of acetylation the more hydrophobic the acetate becomes. The triacetate is the most hydrophobic.



# Wool and Silk

- Wool is an animal hair from the body of sheep. Silk is a lustrous tough elastic fiber produced by silkworms.
- Both wool and silk fibers are protein substances with both acidic and basic properties.
- The building blocks for these fibers are amino acids. The a amino acids (about 20) in wool are arranged in a polypeptide chain in the following manner:



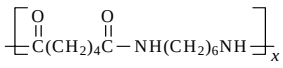
## Wool and Silk

- Silk, like wool, is a protein fiber, but of much simpler structure. It is comprised of six a amino acids, and is the only continuous filament fiber.
- Due to the presence of many amine, carboxylic acid, amide, and other polar groups, wool and silk are hydrophilic in nature, wetted by water and are dyed with either acid or basic dyes through the formation of ionic bonds (salt linkages).
- They may also be dyed with reactive dyes that form covalent bonds with available amino groups.

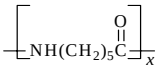


## Polyamides

- Nylon-6,6 was the first synthetic polyamide developed that reached technical importance as a fiber.
- Later, nylon-6 also became a commercial product and has assumed an important position among synthetic fibers.
- In both nylon polymers one chain end consists of an amino group, which can be presented in the free state or in the acetylated form:



nylon 6.6



nylon 6



## Polyamides

- Amino groups are of special importance for dyeing because they form ammonium groups in an acidic dye bath by addition of a proton.
- The depth of color achieved on nylon 6 is somewhat less than that on nylon 6,6. During dyeing a pH below 2.4 should be avoided, because fiber damage occurs at low pH.

# Acrylics

- Amino Acrylics are produced by the polymerization of acrylonitrile. They have a chemical structure consisting essentially of the repeating unit, $[-CH_2-CH(CN)-]_n$, with up to 15% of the polymer consisting of one or two other monomeric units.
- As comonomers, vinyl acetate and an acrylate or methacrylate ester is used in order to vary the properties of the polymer for both ease of processing into a fiber and for improved fiber properties.
- Acrylic fibers are hydrophobic with excellent chemical stability.



# Acrylics

- Since there are no functional groups present in the acrylics, the fiber producers found ways to modify the basic polymer by incorporating acidic groups in the polymer.
- The acidic group frequently used is the sulfonic acid or its salts which is carried into the polymer chain as a substituent of vinyl benzene, alkoxy benzene, or diamino stilbene monomer.
- Also while the monomer is in the gel state, it can be treated with sulfonic acid derivatives.
- Upon drying and scouring it will retain sufficient acid groups for dyeing with basic dyes.



# CHAPTER 8 OBJECTIVES

- INTRODUCTION
- COLORANTS
- CLASSIFICATION OF DYES
- TEXTILE FIBERS
- THE APPLICATION OF DYES
- INTERMEDIATES
- MANUFACTURE OF DYES

## THE APPLICATION OF DYES

- The process of dye application involves the transfer of dye from a solution in a dye bath to the fiber; the dye preferentially adsorbs onto and diffuses into the fiber.
- In order for a dye to move from the aqueous dye bath to the fiber phase the combination of dye and fiber must be at a lower energy level than dye and water.
- This may be achieved by the proper selection of dye for the particular fiber type.



## THE APPLICATION OF DYES

- The basic operations of dyeing remain the same and include the following:
  a) Preparation of the fiber
  b) Preparation of the dye bath
  c) Application of the dye
  d) Finishing



## THE APPLICATION OF DYES

***Fiber preparation:*** The textile material generally needs a pretreatment before dyeing.

- Wool must be washed to remove wax and dirt and sometimes bleached.
- Cotton must be boiled and bleached to remove pectins and cotton seeds and is mercerized. Sizes and spinning oils must be eliminated.

# THE APPLICATION OF DYES

***The dyeing of fiber*** from an aqueous dye bath depends on the dye-fiber interaction. Depending on the nature of dye and the nature of fiber, the dye is fixed on to the fiber chemically or physically.

- Additives such as wetting agents, salts, carriers, retarders and others may be added to the dye bath along with the dye if required to facilitate the dyeing process.



## CHAPTER 8 OBJECTIVES

- INTRODUCTION
- COLORANTS
- CLASSIFICATION OF DYES
- TEXTILE FIBERS
- THE APPLICATION OF DYES
- INTERMEDIATES
- MANUFACTURE OF DYES



# INTERMEDIATES

- The batch dyeing may be a hand operation by the simple process of moving the fibrous material in an open bath containing the dye liquor.
- In machine dyeing, the yarn or cloth is moved in the dye bath, which is kept stationary except for the agitation of the liquor due to the movement of the yarn or cloth.
- Batch methods for machine dyeing depend on the physical structure of fibers in the textile material to be dyed.
- Continuous dyeing is designed for long runs using a padding machine.

# INTERMEDIATES

- Intermediates in the dye industry are referred to the organic cyclic type compounds used for the manufacture of synthetic dyes.
- The starting raw materials mainly are aromatic hydrocarbons such as benzene, toluene, naphthalene etc., which are derived from petroleum. The products are various dyes.
- The manufacture of a dye from primary raw materials involves a number of prior synthetic stages and transformations, commonly referred to as “unit processes”.
- Such processes include nitration, sulfonation, diazotization, oxidation, reduction, chlorination and others.



# INTERMEDIATES

- The products, precursors of the dyes themselves, are collectively known as “intermediates”.
- Intermediates are produced by a variety of reactions.
- Example the manufacture of a relatively simple intermediate, e.g. N,N-diabenzylaniline disulfonic acid.
- Relatively few reactions are available for direct introduction of substituent groups into the aromatic nuclei:

| | | | |
|---|---|---|---|
| Type 1 (normal) | Nitration<br>Halogenation ($Br_2$, $Cl_2$) | Type 2 (abnormal) | Sulfonation<br>Friedal-crafts acylation<br>Friedal-crafts alkylation |



# INTERMEDIATES
## Sulfonation

- Most aromatic compounds can be sulfonated by the action of concentrated or fuming sulfuric acid to form sulfonic acids. The reaction may be represented as:

$$Ar\text{-}H + H_2SO_4 \longrightarrow Ar\text{-}SO_3H + H_2O$$

- Benzene and toluene can be sulfonated in the cold, whereas anthraquinone requires fuming sulfuric acid and high temperatures.
- Electrophilic substitution reactions of benzene, sulfonation is a readily reversible reaction.
- f water is not removed continuously during the reaction then the hydrolysis of sulfonic acid will lead to the inverse reaction to the starting product containing no sulfonate grouping.

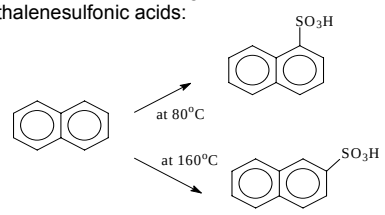
# INTERMEDIATES
## Sulfonation

- Sulfonation of aromatic compounds is very important in the manufacture of dyes.
- Benzene is usually sulfonated by means of fuming sulfuric acid ($H_2SO_4 + SO_3$); a temperature of 80-100°C is used at the end for completing the reaction.
- Toluene reacts more readily than benzene under similar conditions forming a mixture of the o- and p-acids. At low temperatures the o- is the major product, and at high temperatures the p-acids.



# INTERMEDIATES
## Sulfonation

- Naphthalene sulfonates to give a mixture of 1- and 2-naphthalenesulfonic acids:

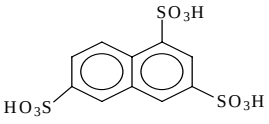



- Further sulfonation at 150-160°C gives rise to di-,tri-, and tetra- sulfonic acids.



# INTERMEDIATES
## Sulfonation

- The important naphthalene-1,3,6-trisulfonic acid can be obtained directly from naphthalene by progressive sulfonation with fuming sulfuric acid first at 40°C, then at 60°C, and finally at 150-155°C.



# INTERMEDIATES
## Sulfonation

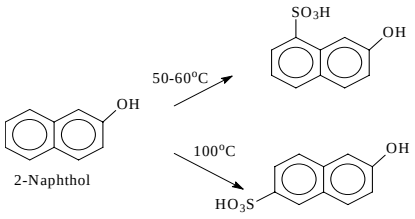
**Table 8.3: Intermediates derived from naphthalene-1,3,6-trisulfonic acid**

| Systematic name | Other name | Class(es) of derived dye(s) |
|---|---|---|
| 1-Amino-8-naphthol-3,6-disulfonic acid | H acid | Azo, Hydroxyketone |
| 1,8-Dihydroxynaphthalene-3,6-disulfonic acid | Chromotropic acid | Azo |
| 1-Naphthol-3,6,8-trisulfonic acid | - | Azo, Hydroxyketone |
| 1-Aminonaphthalene-3,6,8-trisulfonic acid | Koch acid | - |



# INTERMEDIATES
## Sulfonation

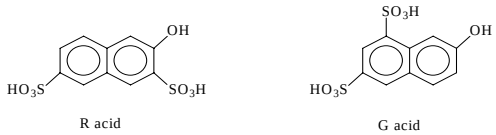
- 2-naphthol undergoes sulfonation to produce two important monosulfonic acids: Schaeffer's acid and Crocein acid. At 100°C Schaeffer's acid predominates; at lower temperatures more Crocein acid is formed.





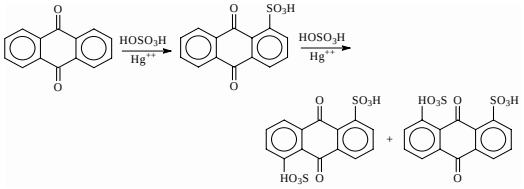

# INTERMEDIATES
## Sulfonation

- Further sulfonation of 2-naphthol leads to the formation of two isomeric disulfonic acids.
- At low temperatures, G acid is preponderant, whereas at higher temperatures R acid predominates. Both R and G acids are important intermediates for azo dyes.



# INTERMEDIATES
## Sulfonation

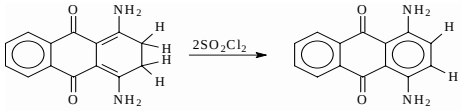
- Anthraquinone is sulfonated by reacting with fuming sulfuric acid at 120-140°C. The product is mostly the 2-sulfonic acid and small quantities of the 2,6 and 2,7-disulfonic acids.
- The presence of mercuric salts in the sulfonation mixtures favors the formation of anthraquinone-1-sulfonic acid; further sulfonation leads to a complex mixture of disulfonic acids chiefly 1,5 and 1,8 with lesser quantities of 1,6 and 1,7-isomers.




67

# INTERMEDIATES
## Halogenation

- The benzene nucleus is readily substituted by chlorine or bromine atoms on interaction with the halogens in the presence of ferric chloride or bromide, aluminum chloride, or iodine.
- Chlorination may also be achieved by reacting with thionyl chloride, phosphorus oxychlorides, phosphorus pentachloride, or sulfuryl chloride.
- For example, the dye Disperse Violet 28 is prepared by the chlorination of Lenco-1,4-diaminoanthraquinone with sulfyryl chloride by the following reaction:

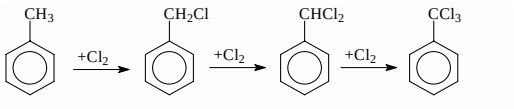



Disperse Violet 28

68

# INTERMEDIATES
## Halogenation

- Toluene undergoes catalyzed chlorination or bromination in the same manner as benzene, with equal quantities of o- and p- chlorotoluenes being produced.
- When the catalyst is omitted and the hydrocarbon is treated with either halogen at the reflux temperature, preferably with exposure to light, the chlorine or bromine atoms enter the methyl side chain rather than the nucleus, with formation of the mono-, di-, and trihalo derivatives.




Toluene Benzyl chloride Benzal chloride Benzotrichloride

69

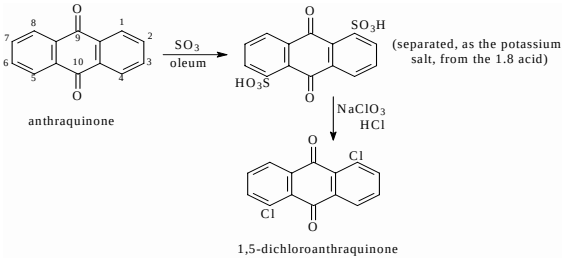
# INTERMEDIATES
## Halogenation

- Benzyl chloride is used in the manufacture of ethylbenzylaniline and dibenzylaniline for triarylmethane dyes.
- The direct chlorination of naphthalenes results in the formation of numerous isomers. This reaction is seldom used.
- In the anthraquinone series an indirect chlorination method is used.



# INTERMEDIATES
## Halogenation

- $-SO_3H$ group may be replaced by –Cl by reacting with hot concentrated hydrochloric acid and 10-15% aqueous sodium chlorate. Such a case is the preparation of 1,5-dichloroanthraquinone.




anthraquinone

1,5-dichloroanthraquinone

# INTERMEDIATES
## Nitration

- Nitration conducted with nitric acid alone or in combination with sulfuric acid, provides an efficient method for preparation of mono-, di-, and trinitro derivatives.
- Nitrobenzene can be produced on a technical scale in yields up to 98% by nitration of benzene with mixed acid. The sulfuric acid serves as a solvent and generates the nitronium ion, which is the attacking electrophile.
- Nitrobenzene itself may be further nitrated with a mixed acid giving m-dinitrobenzene.

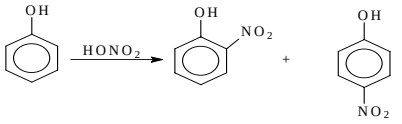
# INTERMEDIATES
## Nitration

- The o- and p- dinitrobenzenes are removed as water-soluble products by treating the nitration product with aqueous sodium sulfite, sodium o- and p-nitrobenzenesulfonates being formed.
- The residual m-nitrobenzene is separated from the aqueous layer, washed with water and finally dried.
- The nitration of toluene is carried out as in the case of benzene, but the temperature is maintained below 20°C to avoid oxidation of the methyl group. A mixture of o-, p- and m-nitrotoluene is obtained in the approximate percentage of 63, 35 and 2.



# INTERMEDIATES
## Nitration

- When benzene derivatives (such as phenols and chlorobenzene) are nitrated, isomers of the desired product are obtained. For example, nitration of phenol by nitric acid gives o- and p-nitrophenol:

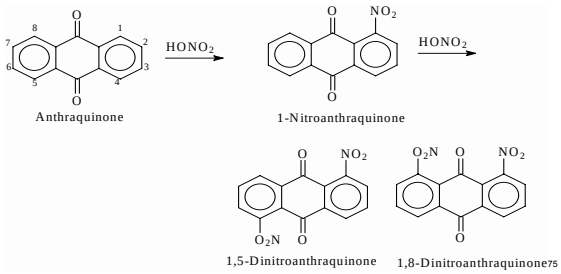



- Mononitration of naphthalene with mixed acid at a temperature of 35-50°C gives a good yield of 1-nitronaphthalene; this is the main source of 1-naphthylamine and its derivatives.



# INTERMEDIATES
## Nitration

- Anthraquinone on nitration at about 50°C gives mainly 1-nitroanthraquinone. At 80-95°C, dinitration occurs to give a mixture of 1,5- and 1,8- isomers.




Anthraquinone — 1-Nitroanthraquinone — 1,5-Dinitroanthraquinone — 1,8-Dinitroanthraquinone

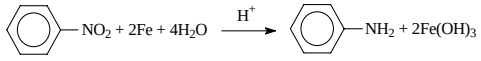
# INTERMEDIATES
## Amination

- The process of making an amine ($RNH_2$) is generally referred as amination.
- The methods commonly used are (a) reduction of a nitro compound and (b) action of ammonia on a chloro, hydroxy, or sulfonic acid compound.
- The main method is nitration followed by reduction.
- Reduction of nitro compounds is accomplished by: (1) catalytic hydrogenation, (2) iron reduction (Béchamp method), (3) sulfide reduction, or (4) zinc reduction in an alkaline medium.

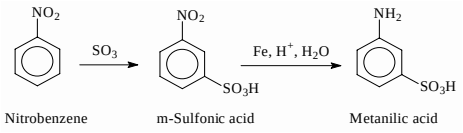


# INTERMEDIATES
## Amination

- The most widely used method of converting nitro compounds into an amine is the Béchamp method, which uses iron turnings in water containing a small quantity of hydrochloric acid.



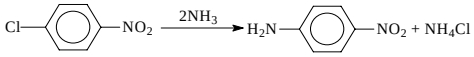

- The Béchamp method can also be used in reducing the nitro derivatives of sulfonic acids. A typical example being the manufacture of metanilic acid and related substances.




77

# INTERMEDIATES
## Amination

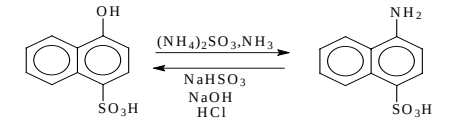
- The conversion of *p*- nitrochlorobenzene to p-nitroaniline. This reaction may be carried out continuously with 40 percent aqueous ammonia under 200 atmosphere at 235 to 240°C.

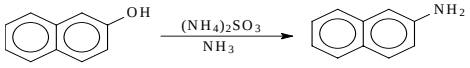



- Aniline can also be prepared by the amination of phenols under a pressure of 15-16 atm at a temperature of 380-385°C in the presence of a silica- alumina catalyst (Halcon process).

# INTERMEDIATES
## Amination

- The Bucherer reversible reaction of conversion of naphthols to anilines by aminolysis. The reaction is used for the replacement of aromatic hydroxy groups by amino groups, in the naphthalene series.

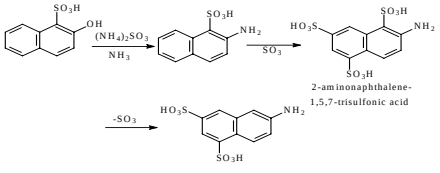


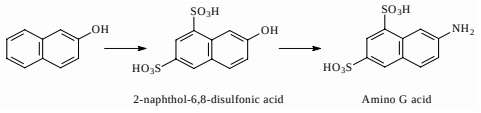






# INTERMEDIATES
## Amination

- Two important azo dye intermediates, Amino J acid and Amino G acid are also produced by the Bucherer reaction represented as follows:






# INTERMEDIATES
## Hydroxylation

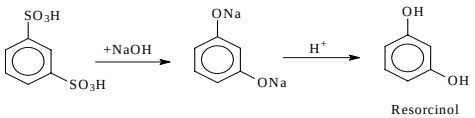
- The main general method for the hydroxylation of aromatic compounds is the alkali fusion of sulfonic acids:

$$Ar—SO_3Na + 2NaOH \longrightarrow Ar—ONa + Na_2SO_3 + H_2O$$

- A second general reaction is hydrolysis of chloro compounds:

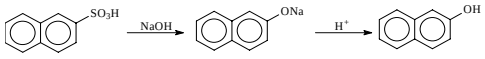
$$Ar—Cl + 2NaOH \longrightarrow Ar—ONa + NaCl$$

- The phenolates thus obtained can be converted to phenol by reaction with an acid. Resorcinol is made by fusion of m-benzene disulfonic acid:



# INTERMEDIATES
# Hydroxylation

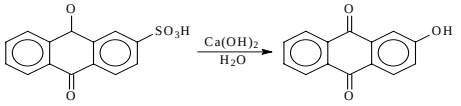
- 2-naphthalene sulfonic acid can be converted to 2-naphthol by the hydrolysis with sodium hydroxide:



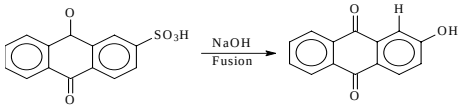



# INTERMEDIATES
# Hydroxylation

- 2-Anthraquinosulfonic acid can be converted to the hydroxy compound by heating with calcium hydroxide in water. Alkaline fusion of the same sulfonic acid gives alizarin.




2-Hydroxyanthraquinone

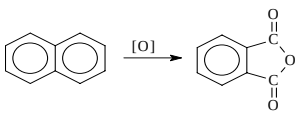



Alizarin



# INTERMEDIATES
# Oxidation

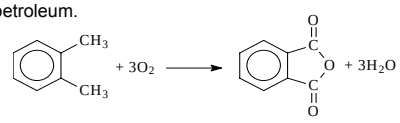
- One of the classical examples is the catalytic vapor phase oxidation of naphthalene to phthalic anhydride. This reaction is carried out over a vanadium pentoxide catalyst at 450°C.




- Phthalic anhydride is used in very large quantities in the plastics industry and plays a significant role in dye chemistry.

# INTERMEDIATES
## Oxidation

- Currently, phthalic acid is mainly produced by the catalyzed oxidation of o-xylene obtained by a cracking process from petroleum.

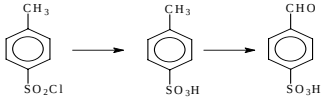



- The oxidation of the methyl group in toluene derivatives to the aldehyde is an important stage in *triarylmethane* dye manufacture.

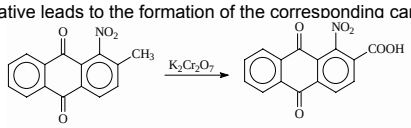


# INTERMEDIATES
## Oxidation

- p-Toluene sulfonyl chloride is first hydrolyzed in concentrated sulfuric acid then subjected to the oxidizing action of a manganese compound to produce benzaldehyde-4-sulfonic acid.




- Similarly, the oxidation of the methyl group in an anthraquinone derivative leads to the formation of the corresponding carboxylic acid.

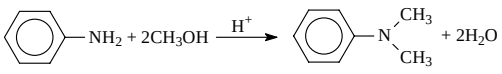



1-Nitro-2-methylanthraquinone 1-Nitro-2-anthraquinonecarboxylic acid



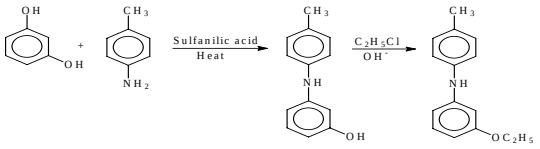
# INTERMEDIATES
## *Alkylation*

- Alkylation on nitrogen and alkylation on oxygen are of some importance in dye chemistry.
- Large quantities of mono- and di- alkylamines are manufactured annually for use in organic chemical industry.
- The usual alkylating agents are methanol, ethanol, methyl and ethyl chlorides, dimethyl and diethyl sulfates.
- N,N-Dimethylaniline is probably the most important of the alkylanilines and is made by heating a mixture of aniline, methanol, and concentrated sulfuric acid.



# INTERMEDIATES
## *Arylation*

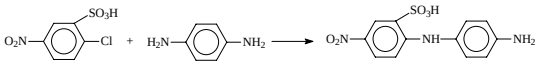
- The introduction of arylamino groups is often needed in the synthesis of intermediates and dyes.
- An important intermediate, 3-ethoxy-4-methyldiphenylamine is prepared from resorcinol and p-methylaniline as follows:






# INTERMEDIATES
## *Condensation and Addition*

- In both condensation and addition reactions, two or more molecules combine by the elimination of a simple molecule (condensation), or the reaction is stopped after the molecules are joined (addition).
- An example of condensation reaction is the formation of the diphenylamine derivative, commonly called Nitro Delta Acid.

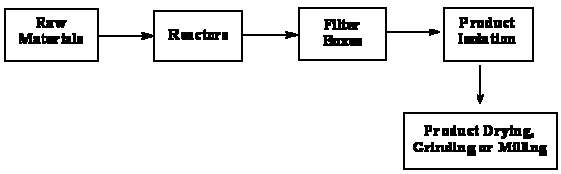



Nitro delta acid



# MANUFACTURE OF DYES

- The general operation sequences in dye and intermediate manufacture are shown in Figure 8.1.



## CHAPTER 8
## OBJECTIVES

- INTRODUCTION
- COLORANTS
- CLASSIFICATION OF DYES
- TEXTILE FIBERS
- THE APPLICATION OF DYES
- INTERMEDIATES
- MANUFACTURE OF DYES