



Dyes and Fibers 4th Year Chemistry Students Faculty of Education 2022/2023 Prepared by Dr/ Entesar A. Hassan

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Introduction

Dyes, can be obtained from natural sources such as vegetable matter, mineral or insects or are manufactured in the factory from petrochemical feedstock. It may, however, be recalled that the first synthetic dye (Mauveine) by Perkin was made from Coal tar. Amongst natural dyes, indigo is well known for its brilliant blue colour and was obtained by fermenting the leaves of a plant. The red coloured lac dye is extracted from lac, a resinous protective secretion of a tiny insect. Dyes are produced either chemically or from plants. An interesting point about them is that unlike paint, they do not build up on the surface of the fiber but are absorbed into the pores of the material. The natural textile fibers meet the requirements for human consumption in terms of the comfort and aesthetic trends. Cotton, wool, and silk were the important natural fibers for human clothing articles. In addition, nowadays the synthetic fibers play an important role in human life.

Dyes

Dyes

Dyes: are organic compounds which are widely used for imparting colour to textiles.

- ***Substance to be used as a dye it must have the following characters
- 1- has a suitable colour.
- 2- it must fix on a fiber by itself or by using other auxiliary agents.
- 3- it can resist the action of light.
- 4- it can resist the action of water, acids, bases and detergents used in washing process.

Wet theory

- The colour of a substance may due to the presence of the following:
- 1- electron withdrawing groups (chromophores), e.g. NO₂, NO₂,...etc the presence of these groups caused the appearance of colour.
- 2- electron donating groups (auxochromes), e.g. $NH_{2,}$ OH,...etc the presence of these groups alone in a substance does not cause the appearance of colour, but these groups work only beside chromophores.
- 3- conjugated system increase the intensity of the colour.

Classification of dyes

Dyes can be classified into two classes according to

- a- their chemical structures.
- b- their application on fibers.
- a- classification of dyes according to their chemical structure.
- 1- nitro NO₂
- 2- nitroso deys NO.
- 3- azo dyes N=N.
- 4- triphenyl methan dyes.
- 5- phthalein dyes.
- 6- anthraqinone dyes.
- 7- indigo dyes.
- 8- azine dyes.

2- Classification of dyes according to their application on fibers

1- direct dyes. 2- acidic dyes.

3- basic dyes. 4- vat dyes.

Classification of dyes according to their chemical structure

1- Nitro dyes

A-Picric acid

B- Naphthol yellow

A-Picric acid

Can be prepared by the nitration of phenol. Used for dyeing wool and silk with yellow colour.

$$\begin{array}{c|c}OH\\ \hline\\OH\\ \hline\\NO_2\\ \hline\\ nitration\\ \hline\\NO_2\\ \hline\\ 2,4,6-trinitrophenol\\ or\\ picric acid\\ \end{array}$$

B- Naphthol yellow

Prepared from α -naphthol, used for dyeing wool and cotton with yellow colour.

$$OH \qquad OH \qquad OH \qquad SO_3H \qquad SO_3H \qquad SO_3H \qquad SO_3H \qquad NO_2$$

$$1- naphthol \qquad SO_3H \qquad SO_3H \qquad NO_2$$

$$0r \qquad \alpha-nahhthol$$

- 2- Nitroso dyes
- A- Resorcine green
- **B- Naphthol green**

A- Resorcine green

Prepared from resorcinol and used for dyeing wool and silk with green colour.

B- Naphthol green

Can be prepared from β -naphthol and nitrous acid. Used for dyeing wool and silk with green colour.

- 3- Azo dyes
- A- Methyl orange
- **B-** Congo red
- C- Besmark brown

A- Methyl orange

Used in dyeing wool and silk with orange colour but it can not fix on fibers so it is used only as indicator.

4-aminobenzenesulfonic acid

B- Congo red

Used for dyeing cotton and as indicator.

C- Besmark brown

Used in dyeing cotton and painting wood with brown colour.

4- Triphenyl methane dyes

- A- Malachite green
- **B- Crystal violet**
- **C-** Gentian violet
- **D- Pararosaniline**

A- Malachite green

Obtained from the reaction of benzaldehyde and N,N-dimethyl aniline. used for dyeing wool, silk and leather.

The effect of acidic medium on malachite green

Two resonance structures 1 or 2 form, this leads to deepness of the colour.

B- Crystal violet

Prepared from Michler ketone and N,N-dimethyl aniline. Used for dyeing wool and silk with brightening violet colour.

The effect of acidic medium on crystal violet

Causes the formation of three resonance structures 1 or 2 or 3 and this leads to deepness of the colour.

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C- Gentian violet

Prepared from diamino diphenyl ketone and N,N-dimethyl aniline and used as antiseptic.

D- Pararosaniline

Can be prepared from the reaction of *p*-aminobenzaldehyde and aniline.

- 5- Phthalein dyes
- A- Phenol phthalein
- **B- Fluorescent dye**
- **C- Phthalein sulphone**
- **D-** Tetrabromo phthalein sulphone
- **E- Mercurochrome**
- F- Eosin
- **G- Erythrosine**

A- Phenol phthalein

Prepared from phthalic anhydride and phenol and used as indicator.

$$\begin{array}{c} & & & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\$$

B- Fluorescent dye

Used as indicator, and in medicine in preparation of Mercurochome which is used as antiseptic.

C- Phthalein sulphone

Has a yellow colour and used in medical purposes.

D- Tetrabromo phthalein sulphone

Prepared from phthailic anhydride sulphone and phenol.

E- Mercurochrome

Has a red colour and used in the medical field as antiseptic.

F- Eosin

Used for dyeing wool and silk with green colour and in medical field in diagnoses of the diseases. It can be prepared by two methods

1- From the reaction of bromoresorcinol with phthalic anhydride

2- From the reaction of dibromoresorcinol with phtalic anhydride.

G- Erythrosine

It does not used in dyeing processes but it can be used in the manufacturing of the medicines and in the colouring of the food with yellow colour.

6-Azine dyesA-Mophine dyeB- Methylene blue

A-Mophine dye

Used for dyeing silk and cotton with reddish violet colour.

B- Methylene blue

Used for dyeing wool and silk with blue colour.

$$(H_{3}C)_{2}N$$

$$H$$

$$S$$

$$H$$

$$N(CH_{3})_{2}$$

$$H_{3}C)_{2}N$$

$$S$$

$$N(CH_{3})_{2}$$

$$N(CH_{3})_{2}$$

$$N(CH_{3})_{2}$$

7- Anthraquinone dyes

A-Alizarine dye

A-Alizarine dye

Used to dye cotton and silk with yellow colour, it can be prepared by two methods.

1- From phthalic anhydride and catechol.

2- From anthracene (commercial method).

- 8- Vat dyes
- A- Indigo dye
- **B-** Thioindigo dye

A- Indigo dye

It can be prepared by two methods.

1- By the halogenation of 2-nitrocinnamic acid with bromine.

2- From the reaction of chlorobenzene with glycine (amino acetic cid).

B- Thioindigo dye

It can be prepared by the reaction of 2-mercaptobezoic acid with phosphorus pentasulfide.

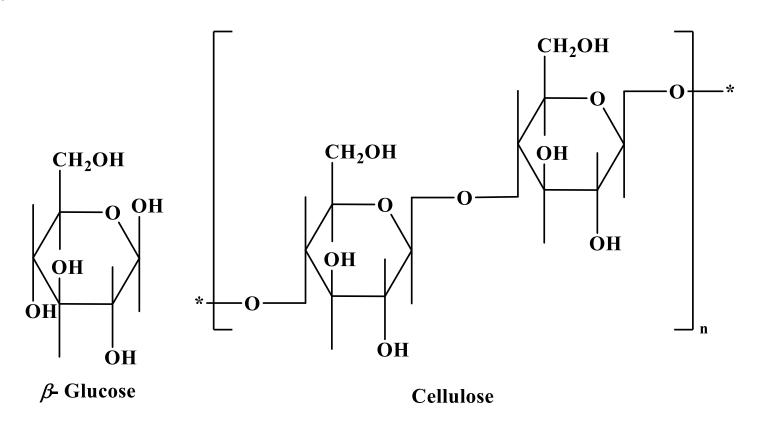
Fibers

1- Cellulose

1- Cellulose

General formula $(C_6H_{10}O_5)_n$

Cellulose consists of several units of β - glucose joined to each other by an oxide bond.



General physical and chemical properties of glucose

- 1- Water insoluble.
- 2- Chars by heating.
- 3-Dissolves in amm. Silver nitrate and calcium chloride solution easily.
- 4- Contains crystals resemble regular parallel chains called crystalline areas.
- 5- Contains irregular and scattered parts called not crystalline areas.
- 6- Cellulose is not reducing agent and doesn't reduce Fehling' solution because CHO group present in glucose units consumed in making the oxide bond between molecules, so it lost its reducing properties.

Effect of different actions on cellulose

1- Effect of acids

A- HCl

Diluted HCl has no effect.

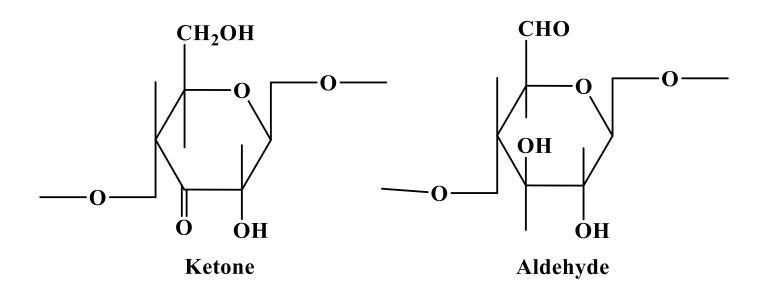
HCl 41% dissolves cellulose and turns it into glucose.

<u>**B- H₂SO**₄</u>

H₂SO₄70% dissolves cellulose and turns it into glucose.

2- Effect of oxidizing agents

Destroy cellulose and transform it into aldehydes, ketones and carboxylic acids.



3- water

Swells when absorbs water and this swelling be in the cross direction because of the presence of OH groups which attract water molecules in the areas which described as not crystalline.

4- Alkalis

- A- Shrinkage.
- **B-** Swilling.
- C- Increasing in transparency.
- D- Increasing the absorbance of dyes.
- E- Increasing in durability and weight.

2- Cotton



Cotton

Description

- Filaments around seed.
- The filament consists of one cell has circular shape tuns into oval shape when it ripens.
- The filament has many twists
- The number of twists in the cotton filament increases as the filament becomes mature.

Chemical composition of the cotton filament

- 1- Cellulose 94%.
- 2- Water 0.8%.
- 3- Wax 0.6%.
- 4- Proteins and pectin (carbohydrate) 2.3%.
- 5- Minerals substances and salts. 1.2%.
- 6- Dyes and other materials 0.3%.
- 7-Organic acids e.g. citric acid and others 0.8%.

1- Cellulose. (already explained)

2- Water.

3- Waxes.

High molecular weights alcohols and fatty acids which can be easily extracted from cotton by benzene, carbon tetrchloride or chloroform.

4- Proteins and pectin

These materials are removed during bleaching processes.

5- Minerals substances and salts

Result after ignition of cotton and turn into white substance called ash.

6- Dyes

Present in some kinds of worthless brown cotton but high-value cotton is colourless.

Cotton types

1-long staple fibers.

The length of the staple is 40-50 ml and they are smoother so they are used in making the finest fabrics e.g. Giza 45.

2- Medium staple fibers.

The length of the staple is 30-40 ml and they are less soft e.g. Giza 30.

3- Short staple fibers

The length of the staple is >30 ml and they are coarse e.g. Ashmoun and Dandara

Some chemical and physical characters of cotton

1- Has no colour and odour.

2- Burns and gives the smell of burnt cotton.

3- The degree of its electrical conductivity increases the higher in humidity.

The importance of cotton in spinning process

- 1- It ranks first in the world.
- 2- It is relatively cheap from other materials.
- 3- Ease of cultivation.
- 4- No need to prepare before spinning
- 5- Easy to spin and weave.
- 6- Cotton, its textiles are very fine.
- 7- Rayon is prepared from cotton.

3- The wool



3- The wool

Constitution

1- Keratin wool 40%.

2- Impurities 20%.

3- Skin secretions 28%.

4- Lanolin grease 11%.

5- Metal materials 1%.

2- Impurities

Wool contains dust and parts of plants which contain thorns. The amount of impurities depends on the type of pasture and the degree of caring for the animal. Impurities can be eliminated by a process called smut where wool is passed in a diluted acid in a low temperaure then it is exposed to a hot weather for the purpose of converting straw into a fragile image which is removed by washing and also it can be removed by diluted sodium sulphate solution.

3- Skin secretions

Results from the sweat glands. These secretions contain fatty acids like stearic and oleic acids.

4- Lanolin grease

It is excreted from the adipocytes and it is made of cholesterol and fatty acids and characterized with.

- 1- It has a waxy texture and a golden yellow color.
- 2- Ointments and cosmetics are made from it because the skin absorbs it.
- 3- It prevents wool from sagging on the back of sheep.
- 4- Contains water 20-25% ratio.
- 5- Removed easily by water and sodium carbonate.
- 6- It decomposes with water and gives cholesterol and fatty acids.

5- Mineral materials

- Sodium oxide.
- Potassium oxide.
- Calcium oxide.
- Aluminium and iron oxides.
- Silica.
- Sulfur oxides.
- Carbonic acid.

Chemical and physical properties of wool

1- Durability

Its durability depends on the inner layer of hair, the scales covered with it, and the healthy animal suit.

2- Flexibility

Very flexible, not wrinkled and bent.

3- The length and diameter of the bristles

Its length is from 1 to 16 inches and the diameter is important in obtaining excellent types of woolen fabrics.

4- Sintering of wool

This occurs because the capillary scales intertwine with each other.

5- Thermal insulation property

It has the ability to thermal insulation as it retains the body heat and prevents it from radiation.

The effect of weather conditions on wool

1- Moisture effect

The most fiber absorbs air humidity, but it gets hardly wet in cold water and the degree of wetness increases with heat, so it is dyed at 65 °C.

2- The effect of heat on wool

It burns at 100 °C, giving the scent of burnt feathers.

3- Acids effect

- A- Dissolves in concentrated acids on cold and HNO_3 is the most effective then conc. H_2SO_4 then conc. HCl
- B- Diluted acids have no effect on the wool.

4- Alkalis effect

- A- The wool dissolves in conc. alkalis like NaOH and KOH so woolen fabrics can't be dyed with vat dyes where this type of dyes depends on the uses of alkalis.
- B- Weak alkalis like ammonia, borax and sodium carbonate has a weak effect on the wool.

5- Oxidizing and reducing agents effect

- Oxidizing agents like H_2O_2 removes colours from wool so they used as bleaching agents for the wool.

- Reducing agents like SO_2 removes colour temporary but it comes again by exposure to atmosphere.

4- Semi-synthetic fibers

Semi-synthetic fibers

There are two types

A- Semi-synthetic cellulosic fibers like rayon.

B- Protein synthetic fibers

Include all fibers which in their manufacturing depend on protein materials like milk and soybean protein.

A- Semi-synthetic cellulosic fibers

1- Rayon

It is prepared by melting a paste of wood and the most famous of which is the wood of the berries tree (Chardonnet scientist) which was treated with nitric acid and converted to nitrocellulose then dissolve it in a mixture of alcohol and ether.

Types of Rayon

1- Chardonnet rayon

It is the oldest silk made and prepared in several steps

1- Nitration of the cellulosic material.

Where cellulose is treated in pots of clay. It is treated with a mixture of nitric and concentrated sulfuric acid and turns into nitrocellulose, this process takes an hour at a temperature of 39-41 °C.

2- Dissolving nitrocellulose

Nitrocellulose is dissolved in a mixture of alcohol and ether and this takes several hours.

3- Isolation of nitrocellulose solution

- ***This is carried out by two methods
- 1- In it, nitrocellulose is dissolved in a mixture of ether and alcohol in a ratio of 60:40.
- 2- In it, nitrocellulose is dissolved in a mixture of methyl alcohol and ethyl alcohol in a ratio 1:2.

4- Transformation of nitrocellulose into cellulose

Where nitrocellulose (explosive material) is transformed into cellulose by using sodium hydrosulphite $Na_2S_2O_4$ which is reducing agent.

5- Thread washing

Where rayon is washed to remove the chemicals.

6- Thread preparing

This includes the bleaching of the threads and become ready for weaving and dyeing

2- Rayon viscose

1- Preparation of wood pulp

The raw material is wood pulp where the impurities are removed after cutting them into small pieces.

2-Preparation of sodium cellulose

Where previously processed cellulose is treated with caustic soda to give soda cellulose

3- The formation of cellulose xanthines

Where sodium cellulose is treated with carbon disulfide.

4- Preparation of a viscose solution

Where xanthyl cellulose is treated with a dilute caustic solution.

5- Isolation process

Where the viscose solution is pressed, spun and transformed into cellulose xanthate threads.

6- Thread processing with mineral acids

Where these acids transforms viscose into cellulose.

7- Threads washing

Threads are washed with water to remove sulfur materials and the fibers are more shiny and we get the rayon viscose.

5- Synthetic fibers (chemical)

Synthetic fibers (chemical)

It is produced only from the prepared materials or has been laboratory installed.

Chemical reactions on which synthetic fibers are prepared

- A- Condensation reactions in which fibers are prepared
- 1- Polyamides
- 2- Polyurethane
- 3- Polyester
- B- Addition reactions in which the are prepared
- 1- Polyethylene
- 2- Polyvinyl
- 3- Polyacryl
- 4- Polyvinylidine

1- Polyamides

Contains a lot of methylene groups (CH_2) and amide (CONH). Polyamides result from the reaction of carboxylic acids which have two terminal groups of carboxyl COOH and an amine has two terminal amino groups NH₂. These fibers have commercial names accompanied with a certain number. This number composed of two numbers, the fist right number refers to the number of the carbon atoms present in the carboxylic acid, while the second number refers to the number of the carbon atoms present in the amine.

For example

If the number of the fiber 66 it will be
 The number of carbons atoms belong to acid is 6
 and the number of carbon atoms belongs amine is 6 also

If the number of fibers is 610
 The number of carbons atoms belong to acid is 10
 and the number of carbon atoms belongs amine is 6

Examples on polyamides

1- Nylon 66

It results from the condensation of adipic acid (has 6 carbon atoms) with hexamethylene diamine.

The union of amino group with carboxyl repeats to give nylon

$$\label{eq:hooc} HOOC(CH_2)_4[CONH(CH_2)_6NHCO(CH_2)_4]_nCONH(CH_2)_6NH_2$$

$$Nylon$$

Industrially, nylon is prepared by dissolving adipic acid and hexamethylene diamine in methyl alcohol and nylon 66 precipitates of molecular weight 10000-13000 units.

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