



**Final Exam of First Semester 2016/2017**

**Course:** Chemistry of dyes  
**Code:** PDFW 3104

Second year student  
**Time:** 180 min.  
**(4 pages)**

Textile Printing Dept.  
**Full mark:** (60)

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**First Question: (15 points)**

**I. Put (T) for true and (F) for false answers in the following statements.**

**II. Correct the false ones.**

1. Pigments have affinity for the substrate they are applied to. (F)  
*Pigments have no affinity for the substrate they are applied to.*
2. Coloured material mean that it either reflects or absorbs electro-magnetic radiation in a wide region of the invisible spectrum. (F)  
*Coloured material mean that it either reflects or absorbs electro-magnetic radiation in a narrow region of the visible spectrum.*
3. Conjugated organic molecules absorb specific wavelengths of electro-magnetic radiation. (T)
4. The functional groups on different fibres can give an indication of the type of dye that should be used, as well as suggest ways of developing new dyes. (T)
5. Fading is often caused by the action of sunlight, or by the oxidising action of the atmosphere. (T)
6. The hue refers to the major wavelength or wavelengths transmitted from the material. (F)  
*The hue refers to the major wavelength or wavelengths reflected from the material.*
7. The colour arises when an object does not reflect all the incident white light falling on it. (T)
8. The first part of the dyes name is a trademark used by the particular manufacturer to designate both the manufacturer and the class of dye. (T)
9. The simplicity of the azo dye preparation means that the process can be scaled up or down very easily. (T)
10. Azobenzene, the basic azo chromogen in cis-form is essentially planar in both the solid state and in solution. (F)  
*Azobenzene, the basic azo chromogen in Trans-form is essentially planar in both the solid state and in solution.*

11. Diazotizations are normally conducted in an aqueous medium containing sulfuric acid. (F)

Diazotizations are normally conducted in an aqueous medium containing nitrous acid.

12. When a more reactive system is sulfonated, more stringent conditions are required. (F)

When a more reactive system is sulfonated, less stringent conditions are required.

13. Most dye intermediates are prepared by chemical reactions involving addition processes of one or more of hydrogen atoms of the aromatic compound with  $\text{SO}_3\text{H}$ ,  $\text{NH}_2$ ,  $\text{OH}$ ,  $\text{CH}_3$ , and  $\text{NO}_2$ . (F)

Most dye intermediates are prepared by chemical reactions involving substitution processes of one or more of hydrogen atoms of the aromatic compound with  $\text{SO}_3\text{H}$ ,  $\text{NH}_2$ ,  $\text{OH}$ ,  $\text{CH}_3$ , and  $\text{NO}_2$ .

14. Chlorination of deactivated systems requires lower temperatures. (F)

Chlorination of deactivated systems requires higher temperatures.

15. oleum is used for the sulfonation of activated ring systems. (F)

oleum is used for the sulfonation of deactivated ring systems.

### Second Question: (10 points)

#### Choose the right answer in the following questions:

1. *If a light source is deficient in yellow colour band, the light appears to be coloured in:*

- a. Violet
- b. Blue**
- c. Purple

2. *A bathchromic shift may be caused by:*

- a. Increasing the electron withdrawing power of the chromophore.
- b. Increasing the electron-donating power of the auxochrom.
- c. Both.**

3. *The absorption of light energy by an organic dye or inorganic pigment causes:*

- a. An electron to jump into a higher energy level, thus bringing the dye molecule into an excited state.**
- b. An electron to jump into a lower energy level, thus bringing the dye molecule into an excited state.
- c. An electron to jump into a lower energy level, thus bringing the dye molecule into a stable state.

4. **The chromophore is a group of atoms which:**

- Control the structure of the dye.
- Control the size of the dye.
- Control the color of the dye.**

5. **Molecular excitation may cause the appearance of color due to:**

- Rotation and/or vibration of the molecules.
- Distortion of the metal d-electron shell caused by ligands surrounding the molecules.
- Electronic motion in conjugated organic systems.**

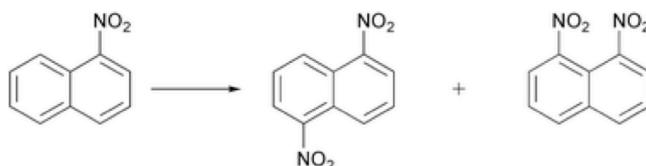
6. **Diazotisation involves a primary aromatic amine, called:**

- The diazo component.**
- The azo component.
- The coupling component.

7. **The Tyrian Purple dye is extracted from**

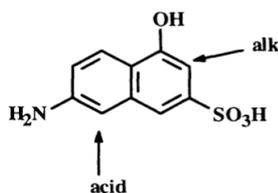
- Plant origin.
- Animal origin.**
- Mineral origin.

8. **According to the scheme below:**



- Introduction of a second nitro group takes place in the opposite ring since the existing nitro group increases the reactivity of the ring to which it is attached.
- Introduction of a second nitro group takes place in the opposite ring since the existing nitro group reduces the reactivity of the ring to which it is attached.**
- Introduction of a second nitro group takes place in the opposite ring since the existing nitro group reduces the reactivity of the opposite ring.

9. **According to the scheme below of coupling component:**



- Arrows have been used to indicate the coupling positions for the aromatic amine coupler.
- Arrows have been used to indicate the coupling positions for the naphthol-based coupler.**

c. Arrows have been used to indicate the coupling positions for the phenol coupler.

**10. When weakly basic or heteroaromatic amines are used in the synthesis of azo dyes**

- a. H<sub>2</sub>SO<sub>4</sub> is used as the reaction medium, forming nitro-sulfuric acid as the diazotizing agent.
- b. HCl + NaNO<sub>2</sub> is used as the reaction medium, forming Nitrous acid as the diazotizing agent.
- c. HNO<sub>2</sub> is used as the reaction medium, forming Sodium nitrite as the diazotizing agent.

**Third Question: (15 points)**

1. Dyes can be classified According to its chemical structure or according to how it is applied to materials.... Compare

<b>Chemical Classification</b>	<b>Usage Classification</b>
First, it readily identifies dyes as belonging to a group that has characteristic properties, for example, azo dyes (strong, good all-round properties, cost-effective) and anthraquinone dyes (weak, expensive). Second, there are a manageable number of chemical groups (about a dozen). Most importantly, it is the classification used most widely by both the synthetic dye chemist and the dye technologist. Thus, both chemists and technologists can readily identify with phrases such as an azo yellow, an anthraquinone red, and a phthalocyanine blue.	Classification by usage or application is the principal system adopted by the Colour Index. Because the most important textile fibers are cotton and polyester, the most important dye types are those used for dyeing these two fibers, including polyester, cotton blends. Other textile fibers include nylon, polyacrylonitrile, and cellulose acetate.

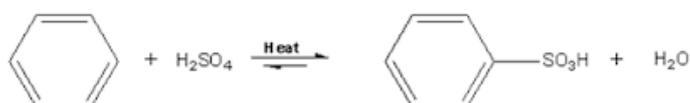
2. Azo dyes are by far the most important class of dyes. They have achieved this prominence for many reasons...Discuss

- 1- They are tinctorially strong (azo dyes are about twice the strength of anthraquinone dyes, the next most important class of dyes);

- 2- They are usually easy to prepare in a multi-purpose chemical plant from cheap, readily available starting materials;
- 3- They cover the whole shade range, in particular oranges, reds and yellows; and they have good fastness properties.

**3. Sulfonation of benzene is a reversible reaction and accompanied by disassociation of water.... Explain**

The sulphonic acid group can be introduced into the aromatic ring by concentrated sulfuric acid  $\text{H}_2\text{SO}_4$ , as shown by (equation 1):



Sulfonation of benzene is a reversible reaction and accompanied by disassociation of water, which results in decrease the sulfuric acid concentration and this led to a decrease in the sulfonation process. Sulfur trioxide readily reacts with water to produce sulfuric acid and heat. Therefore, by adding heat to benzenesulfonic acid in diluted aqueous sulfuric acid the reaction is reversed.

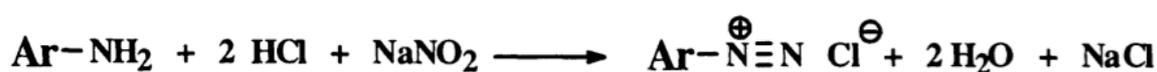
**Fourth Question: (20 points)**

**Write the Equations of the following:**

**1. Synthesis of azo dyes including the two stages.**

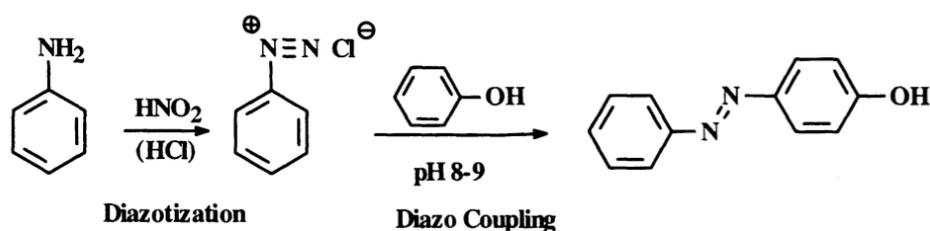
**Stage 1- Diazotization**

This involves a primary aromatic amine, called the diazo component. It is treated in low temperature, acid conditions with sodium nitrite to form an unstable diazonium salt.



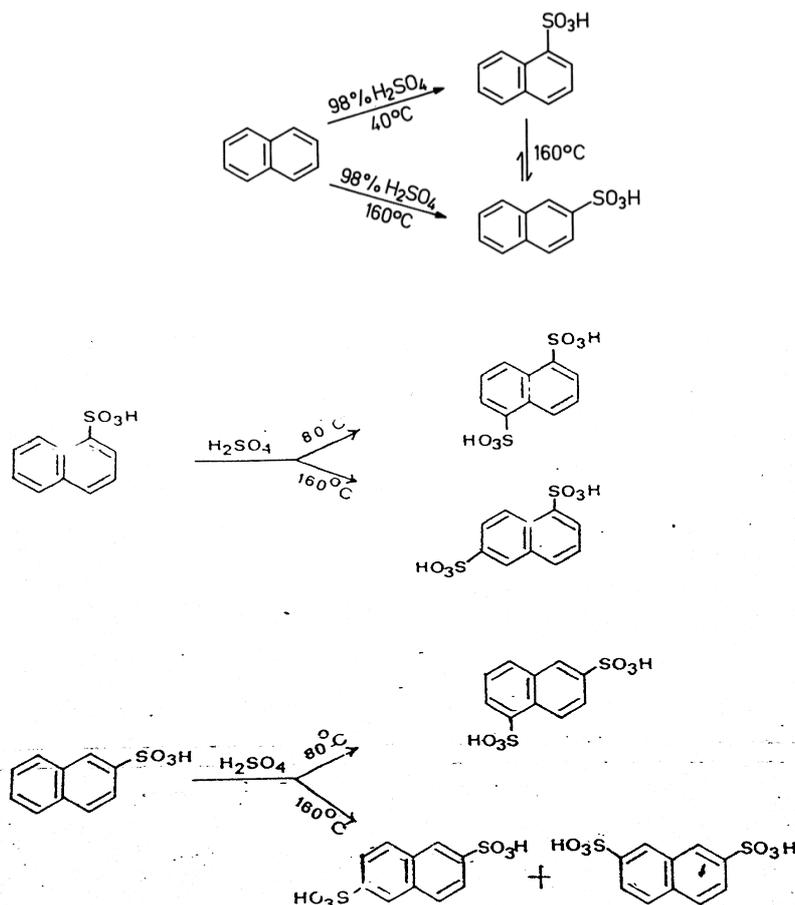
**Stage 2- Azo coupling**

The diazonium salt is reacted with a coupling component (for example a phenol, naphthol or an aromatic amine). This forms the stable azo dye. For example two-step synthesis of an azo dye from aniline and phenol is shown in figure 5

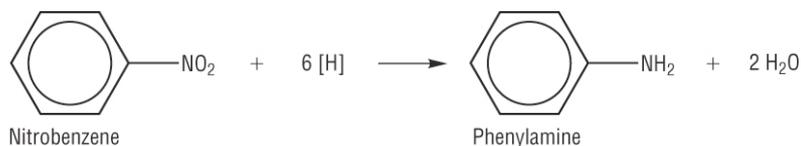


## 2. Sulphonation of naphthalene.

When a more reactive system is sulfonated, less stringent conditions are required. For example, naphthalene is readily sulfonated up to four times without using oleum leads to a mixture of *ortho* and *para* isomers depending on the temperature of the reaction

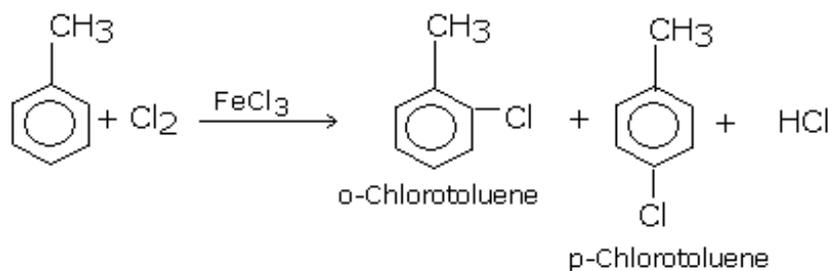


## 3. The reduction of nitrobenzene to aniline.



## 4. Chlorination of toluene.

Toluene is chlorinated to give a mixture of *ortho* and *para-chloro* toluene, which is separated by fractional distillation.



But if chlorine reacts with boiling methylbenzene in the absence of a catalyst but in the presence of UV light, substitution happens in the methyl group rather than the ring and benzyl chloride is formed.

