

# CHAPTER 22

## INDUSTRIAL CHEMISTRY

### DYES

Chromogen: colour producing structure

Chromogen is an aromatic body containing a colour giving group called 'chromophore'

Chromophore:

Nitroso group



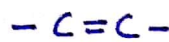
Nitro group



Azo group



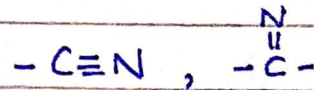
Ethylene group



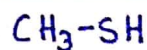
Carbonyl group



Carbon-nitrogen group



Carbon-sulphur group

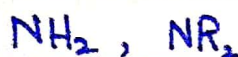


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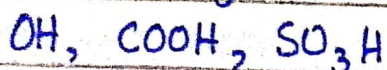
### AUXOCHROME

The part of the dye which causes it to adhere to the material which it colours (usually textiles)

\* Causing Solubility In Acids:



\* Causing Solubility In Basic Solution:



# CLASSIFICATION OF DYES

## 1. ACID DYES

- for dyeing protein fibers such as wool, silk, nylon; also leather and paper
- contain one or more sulfuric acid substituents or other acidic groups
- e.g. Acid Yellow 36 (Metanil Yellow)

## 2. BASIC DYES

- First dye class made synthetically
- "Mauve" was a basic dye.
- used to dye wool or cotton with a mordant but are usually used for duplicator inks, carbon paper and typewriter ribbons. In solvents other than water, they form writing and printing inks
- They are mostly amino compounds soluble in acids and made insoluble by the solution being made basic.

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## 3. AZO DYES

- long-lasting dyes
- used primarily for printing on cotton
- ice-colours

## 4. DIRECT DYES

- dye cotton directly (i.e. without mordant)
- used to dye union goods (mixed cotton and wool or silk)
- These are generally azo dyes and their solubility in dyes bath is often reduced by adding salt

## 5. DISPERSE DYES

- used to dye fibers such as plastic, cellulose acetate, polyesters, nylon fibers.
- These dyes dissolve into the fiber at or near the glass transition temperature of the polymer

## 6. FIBER-REACTIVE DYES

- These dyes form a covalent bond b/w dye and fiber.
- used to dye cotton, rayon and some nylons
- e.g vinyl sulfone (sulfatoethyl sulfone)

## 7. MORDANT DYES (AND LAKES) (Al, Cr, or Fe salt)

- Some dyes combine with metallic salts<sup>↑</sup> to form highly insoluble coloring materials, called lakes. Lakes are usually used as pigments.
- The azo and anthraquinone nuclei, having attached the groups like -OH and -COOH act as mordant dyes.

## 8. SULPHUR DYES (SULPHIDE DYES)

- produce dull shades on cotton
- low costing dyes
- Sulphur dyes are usually colourless when in the reduced form in a sodium sulfide bath but gain color on oxidation

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## 9. SOLVENT DYES

- Sometimes called spirit-soluble dyes
- usually azo, triarylmethane or anthraquinones
- used to color oil, waxes, varnishes, shoe polishes, gasolines.

## 10. VAT DYES

- water insoluble organic pigments
- become water soluble when mixed with powerful reducing agents.
- highly complex chemical structure
- mostly are derivatives of anthraquinone or indanthrone.
- expensive
- most often used on cotton fabrics that are to be subjected to severe conditions of washing and bleaching.
- Best known dye is indigo

## PESTICIDES

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1. Lead Arsenate  $Pb_3(AsO_4)_2$
2. Nicotine sulphate
3. DDT (Dichloro Diphenyl Trichloroethane)

### DDT

- A pesticide that breaks down in nature into harmless products is preferred.
- DDT is a very stable chemical. Its half life is estimated to be 10-15 years.
- The persistence of DDT is more troublesome by its tendency to become concentrated in all forms of animal life (The process is sometimes referred to as biological magnification)
- DDT is water-insoluble
- non-polar
- DDT accumulates in animals and in particular in their fatty tissues.

- Almost all chlorinated pesticides including DDT appear to have a variety of undesirable effects.
- Chlorinated Pesticides : Mirex, choldrane, heptachlor, aldrin, dieldrin
- One of the important alternative to DDT is parathion

## PETROCHEMICALS

- First organic chemical made on large scale from a petroleum base was isopropyl alcohol (isopropanol)
- Over ~~80~~ 80% of all organic chemicals are petrochemicals.
- Separating individual species from petroleum involve:
  - i) Distillation
  - ii) Selective adsorption
- 98% of raw material, for aromatic compounds, is obtained from petroleum.

## FRACTIONAL DISTILLATION OF PETROLEUM

- Petroleum in unrefined form is called crude oil.
- Crude oil is first treated to remove sulphur or sulphur compounds that may be present.
- The cleaned hydrocarbon material is then distilled and fractions with various boiling ranges are collected.
- The principal goal of refinery operations is the production of gasoline

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|                    |                   |                             |
|--------------------|-------------------|-----------------------------|
| 1. Refinery Gas    | $C_1 - C_4$       | Below $20^\circ C$          |
| 2. Petroleum Ether | $C_5 - C_6$       | $20^\circ C - 60^\circ C$   |
| 3. Light Naphtha   | $C_6 - C_7$       | $60^\circ C - 100^\circ C$  |
| 4. Gasoline        | $C_7 - C_{10}$    | $80^\circ C - 180^\circ C$  |
| 5. Kerosine        | $C_{11} - C_{15}$ | $160^\circ C - 300^\circ C$ |
| 6. Heavy Oil       | $C_{15} - C_{18}$ | $300^\circ C - 400^\circ C$ |
| 7. Lubricating Oil | $C_{18} - C_{20}$ | $400^\circ C$               |

The residue (solid mass) is still a mixture of higher HCs which is used for making grease, vaseline, waxed paper, candles.

The final residue (with more than  $C_{30}$ ) is a black coal tar and is called asphalt, pitch or bitumen. It is used for metalling roads.

## SYNTHETIC POLYMERS

On the basis of method of formation, polymer may be:

1. Addition Polymers
2. Condensation Polymers

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## 1. ADDITION POLYMERS

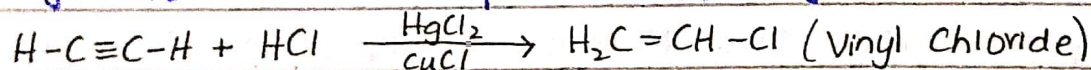
- self-combination of many monomer units
- molecular weight is multiple of monomer
- Empirical formula is same as monomer
- e.g. polyethylene, PVC

### POLYETHYLENE

- A transparent solid polymer obtained when ethylene is heated under pressure
- Average molecular weight: 2000 - 20,000 (depending on temperature and pressure)

### POLY VINYL CHLORIDE (PVC)

- Acetylene forms an addition product with HCl called vinyl chloride in the presence of  $\text{HgCl}_2$  or  $\text{CuCl}$



- Vinyl chloride molecules combine with themselves to produce molecules of very high molecular weight, called PVC.

### PREPARATION OF PVC:

- The liquid monomer is formed into tiny globules by vigorous stirring in water containing a suspending agent
- **Setup:** 100 parts of water, 100 parts of liquid vinyl chloride, 1 part of persulphate catalyst, 1.5 part of emulsifier or sodium lauryl sulphate.
- Autoclave operated at approximately  $50^\circ\text{C}$  for 72 hours (3 days) to give a yield of 90% of polymer with particle size of 0.1 - 1  $\mu\text{m}$ .
- Recovery of these particles may be accompanied by spraying or by coagulation by acid addition.

## 2. CONDENSATION POLYMERS

The polymers formed through a condensation reaction - where molecules join together - losing small molecules as byproducts such as water or methanol.

### NYLON:

Nylon is a condensation polymer, produced by the reaction between a diamine and a dibasic organic carboxylic acid.

If the diamine is hexamethylene diamine (1,6-diaminohexane) and the dibasic acid is adipic acid (hexanedioic acid) then the condensation polymer is nylon (6,6) [six carbon atom in each monomer]  
→ Nylon was the first truly synthetic fiber.

## LIPSTICKS

→ mixture of oils, waxes, pigments, antioxidants and preservatives  
→ Usually perfumes are added to combat unpleasant fatty odour of oil  
→ mainly composed of a mixture of non-volatile oil and solid wax.

→ To reduce stickiness, usually esters of fatty acids are added

→ The colours and dyes of lipsticks include many water-soluble (and fat-soluble) products such as

erythrosine (reddish pink synthetic dye)

amaranth (dark red to purple azodyes)

eosin (brilliant blue)

tetra bromo fluorescein

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→ Dyes must be water-insoluble

→ Water-soluble dyes can be used but they are usually first combined with metal oxides such as aluminium hydroxide  
[Al(OH)<sub>3</sub>]



to form an insoluble precipitate that is then suspended in the oil base of lipstick.

## NAIL POLISH / NAIL VARNISH

- Mostly made up of nitrocellulose dissolved in a solvent (e.g butyl acetate or ethyl acetate).
- Basic Components: Film forming agents, resins and plasticizers, solvents and colouring agents.
- Adhesive polymers are added to make sure that nitrocellulose adheres to nail surface.
- Plasticizers (e.g camphor) or chemicals that link b.w polymer chains, spacing them to make the film sufficiently flexible after drying.
- Pigments and sparkling particles (e.g mica)
- Thickening agents (e.g stearylalkonium hectorite) to maintain the sparkling particles in suspension within the bottle.
- Ultraviolet stabilizers (e.g benzophenone-1) resist color changes when exposed to sunlight.
- Nail polish ingredients often include toluene, formaline etc which are toxic.
- Water based nail polish is based on acrylic polymer emulsion (e.g styrene-acrylate copolymer) and pigments similar to those used in water colour paints.

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# NAIL POLISH REMOVER

- Most common type: Acetone  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$
- can also be used to remove artificial nails, that are usually made of acrylic.
- Principal Ingredients: Acetone, Ethyl acetate or butyl acetate and alcohol
- Non-Acetone Nail Polish Remover usually contain ethyl acetate which is less aggressive.
- highly inflammable
- contain conditioning ingredients like castor oil, ethyl palmitate or lanolin to counter the dehydration and brittleness effects

# HAIR DYES

Four Types

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## 1. PERMANENT HAIR DYES

- usually oxidation dyes are used
- Ingredients:
  1. Oxidizing Agent (usually hydrogen peroxide)
  2. Coupling Agents or couples (meta-substitutive derivatives of aniline)
  3. Primary Intermediate (aromatic para-compounds such as 1,4-diaminobenzene, 4-aminophenol; 2,5-diaminotoluene)
- The process is essentially performed under basic conditions, for which ammonia is usually used
- The combination of  $\text{H}_2\text{O}_2$  and primary intermediate causes the natural hair to be lightened which provides a blank canvas for the dye
- Ammonia opens the hair shaft so the dye can actually bond with the hair and ammonia speeds up reaction of dye with hair

- The couplers define the color of hair dye.
- Various combinations of primary intermediates and couplers provide different shades of hair colours.

## 2. SEMI-PERMANENT HAIR DYES

- smaller molecules than temporary hair dyes
- survive washing with typically 4-5 shampoos.
- contain no or very low levels of developers, peroxide or ammonia
- may contain toxic compound p-phenylenediamine

## 3. DEMI-PERMANENT HAIR DYES

- permanent hair colours that contain alkaline agent other than ammonia (e.g. ethanolamine, sodium carbonate)
- concentration of  $H_2O_2$  in developer may be lower than the one used in permanent hair dyes
- No lightening of hair colour during dyeing.

## 4. TEMPORARY HAIR DYES

- Dye molecules are large and cannot penetrate cuticle layer.
- Available as: Resins, shampoos, gels, sprays, foams
- Colour particles remain adsorbed to hair shaft
- easily removed in single shampooing

# ADHESIVES

- Materials; usually in liquid or semi-liquid states that adhere or bond items together.
- Adhesives cure (harden) by either evaporating a solvent or by chemical reactions that occur b.w two or more constituents.

Types of Adhesives:

- 1) Non-Reacting Adhesives
- 2) Reactive Adhesives.

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## NON-REACTIVE ADHESIVES

### 1. DRYING ADHESIVES

Two types of adhesives that harden by drying:

#### i) SOLVENT BASED ADHESIVES

- mixture of ingredients (typically polymers) dissolved in a solvent
- White glue, contact adhesives, rubber cements

#### ii) POLYMER DISPERSION ADHESIVES

- also called emulsion adhesives
- milky white dispersions often based on polyvinyl acetate (PVAc)
- used in wood working and packing industries
- used in fabrics and fabric based components
- used in loudspeaker cones

### 2. PRESSURE SENSITIVE ADHESIVES (PSA)

- Adhesive form a bond with adhesive by applying light pressure.
- Major raw materials for PSAs are acrylate based polymers
- Molecular interactions such as Van der Waals forces are involved

### 3. CONTACT ADHESIVES

- used in strong bonds with high 'shear-resistance' like laminates, such as bonding formica to a wooden counter and in footwear, as in attaching outsoles to uppers.
- Examples: natural rubber, polychloroprene (Neoprene)
- Contact Adhesives must be applied to both surfaces and allowed for sometime to dry before the surfaces are pushed together.

### 4. HOT ADHESIVES

- Also called hot melt adhesives or thermoplastics
- Applied in molten form ( $65^{\circ}\text{C} - 180^{\circ}\text{C}$ )
- Solidify on cooling to form strong bonds b.w materials.
- Exemplar: ethylene vinyl acetate, glue-gun

## REACTIVE ADHESIVES [Koracademy.com](http://Koracademy.com)

chemically react with material, when harden.

They may be multiparts adhesives or one part adhesives

### 1. MULTIPARTS ADHESIVES

- harden by mixing two or more components which chemically react
- This reaction causes polymers to cross link into acrylics, urethanes and epoxies.
- Some of the combinations of multiparts adhesives include:
  - a) Polyester resin - Polyurethane resin
  - b) Polyols - Polyurethane resins
  - c) Acrylic Polymers - Polyurethane resins
- Individual components do not act as adhesives

## 2. ONE PART ADHESIVES

- harden via a chemical reaction with an external energy source such as radiation, heat or moisture.
- Light curing adhesives are generally acrylic based.
- Heat curing adhesives include epoxies, urethanes and polyimides.
- Moisture curing adhesives include cyanoacrylates and urethanes.

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