CHAPTER 22
INDUSTRIAL CHEMISTRY

DYES

Chromogen: colour producing structure

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

Chromophore:

Nitroso group	$-NO$
Nitro group	$-NO_2$
Azo group	$-N=N-$
Ethylene group	$-C=C-$
Carbonyl group	$-\overset{O}{\overset{\|\|}{C}}-$
Carbon-nitrogen group	$-C\equiv N$, $-\overset{N}{\overset{\|\|}{C}}-$
Carbon-sulphur group	CH_3-SH

AUXOCHROME

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

* Causing Solubility In Acids:

NH_2, NR_2

* Causing Solubility In Basic Solution:

OH, $COOH$, SO_3H

CLASSIFICATION OF DYES

1. ACID DYES

→ for dyeing protein fibers such as wood, 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.

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, polyesterr, nylon fibers.

→ These dyes dissolve into the fiber at or near the glass transtion 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 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

9. SOLVENT DYES

→ Sometimes called spirit-soluble dyes

→ usually azo, triarylmethane or anthraquinones

→ used to color oil, waxes, varnishes, shoepolishes, 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

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% 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

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

1. ADDITION POLYMERS

→ self-combination of many monomer units
→ molecular weight is multiple of monomer
→ Emperical 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 $HgCl_2$ or CuCl

$$H-C\equiv C-H + HCl \xrightarrow[CuCl]{HgCl_2} H_2C=CH-Cl \text{ (Vinyl Chloride)}$$

→ 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 as sodium lauryl sulphate.
→ Autoclave operates at approximately 50°C for 72 hours (3 days) to give a yield of 90% of polymer with particle size of 0.1 - 1 μm.
→ 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 by products 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

→ Dyes must be water-insoluble
→ Water-soluble dyes can be used but they are usually first combined with metal oxides such as aluminium hydroxide $[Al(OH)_3]$

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 stearalkonium hectorite) to maintain the sparkling particles in suspension within the bottle.

→ Ultraviolet stabilizers (eg 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.

NAIL POLISH REMOVER

→ Most common type : Acetone $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

→ 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

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 H_2O_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.

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°C – 180°C)

→ Solidify on cooling to form strong bonds b·w materials.

→ Exampler: ethylene vinyl acetate, glue-gun

REACTIVE ADHESIVES

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) Polyol – Polyurethane resins

c) Acrylic Polymers – Polyurethane resins

→ Individual components donot 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.