

**CHAPTER 10****INDUSTRIAL CHEMISTRY****Industrial Chemistry**

Industrial Chemistry deals with the study of chemical processes, procedures and techniques used in the industries for the preparation of industrial products like soap, glass, cement, fertilizers, plastics, rubber etc. Chemical procedures are applied for the preparation of industrial products, so industrial Chemistry is also called applied Chemistry. In industrial chemistry, the chemical processing of raw materials to useable and profitable products is carried out. Industrial Chemistry is the study of fundamental chemical processes used in industry for transferring raw material to useful commercial products for society. Certain of these marketable products will be consumer goods and enter directly into economic life of the country.

**Chemical processing:** The industrial processing of the chemical raw materials leading to the products of enhanced industrial value is called chemical processing. Generally this involves the chemical conversion like oxidation, hydration, reduction, smelting, leaching and dehydration etc. like in the preparation of sulphuric acid from sulphur involves oxidation and hydration processes. In all the chemical processing, physical operations are also involved such as heat transfer and temperature control etc. which are important to good quality products in good yield.

**Economy of Pakistan**

Chemical industries play an important role in the economic development of a country. Pakistan trades in chemicals with other countries to earn foreign exchange in the field of certain chemical industries like fertilizers, plastics, rubber, medicine, dyes, pigments, soaps and detergents etc. the increase in imports is from 760 million US \$ in 2002-2003 to 5160 million US \$ in 2008-2009. The increment in export was shown from 118 million US \$ in 2002-2003 to 411 million US \$ in 2008-2009.

Fertilizers and pesticides supplied by the chemical industry to the farmers are used for increasing the crop yield. Fibers and dyes supplied by the chemical industry are used in textile industry. The synthetic sweeteners and synthetic flavours are used by food manufacturing companies. The provision of essential chemicals to the pharmaceutical and health care industry is also a major role of chemical industry. The manufacturing of plastics, rubbers, soaps, detergents, paper, glass, cement, fertilizers etc. which are the daily life products are manufactured in chemical industries.

Chemical industry contributes directly and indirectly to almost every sector of economy.

### Safety Consideration in the Process of Industry

Before launching any chemical industry, the following safety considerations must be kept in view.

1. To keep away the factory from corrosion, proper material of construction must be selected by the designing chemical engineers.
2. To avoid harmful impurities in the raw materials, to secure the requisite yield and purity of products, careful process control by periodic analysis is required as well as modern instrumentation and automatic control.
3. To transmit goods in a clean and economical manner from the manufacturer to the customer, suitable containers must be provided.
4. To ensure the safety of workmen and the plant all procedures must be carried on in a non-hazardous manner.
5. Securing the processes from excessive competition and to ensuring an adequate return for large sums spent on the research and plants.
6. To guarantee progress to continue profits and to replace obsolescent processes and equipments much attention and money must be spent upon continuing research and development.
7. To prevent the contamination of water and air, factories must avoid discharge of toxic material into the air and water of their localities.

### Dyes

A natural or synthetic substance used to add colour to or change the colour of a substance is called dye. It is a substance which adds value to products for their cost. In most of the cases the color of a product is the reason for its sale. The purpose of a dye is to help the purchaser to sell his product. A dye must be coloured but it must also be able to impart colour to something else on a reasonably permanent base.



### Chemical Composition of a Dye

A dye consists of the following two components.

1. **Chromogen:** Chromogen is a combination of two words chromo means colour and gen means producer, so chromogen is colour producing substance.

Chromogen is a colour producing structure; it is an aromatic body containing a colour giving group called chromophore. Chromogen is an electron acceptor substance.

**Chromophore:** Chrome mean colour and phore mean carrier so chromophore is a colour carrier substance. Any structural feature present in a molecule that is responsible for the absorption of electromagnetic radiations and which impart colour to a compound is called chromophore. Chromophores cause colour by altering absorption bands in the visible spectrum.

**2. Auxochrome:** The auxochrome is a part to regulate the solubility and dyeing properties. It is an electron donor part. An Auxochrome is the part of dye which does not produce any colour but when attached with chromophore it enhances its colour producing ability. Without both parts the material is simply a coloured body.

Auxochromes are groups which are when attached to a chromophore, these cause the absorption of a chromophore to shift to longer wavelength.

The auxochrome part of the dye causes it to adhere to the material which it colours.

**Red shift or bathochromic effect:** Shift of the absorption to longer wavelength is called red shift or bathochromic effect.

**Blue shift or hypsochromic effect:** Shift of the absorption to shorter wavelength is called blue shift or hypsochromic effect.

**Mordant:** It is a substance used to set dyes on fabrics or tissues by forming a coordination complex with the dye which then attaches to the fiber. Examples of mordants are tannic acid, alum, urine, chrome alum, sodium chloride etc.

Dyes are usually classified on the basis of chromophore groups. Some common chromophore groups are given below.

S.No.	Chromophores	Structure
1.	Nitroso group	$-\text{NO}$ (or $=\text{N}-\text{OH}$ )
2.	Nitro group	$-\text{NO}_2$ (or $\text{NOOH}$ )
3.	Azo group	$-\text{N}=\text{N}-$
4.	Ethylene group	$-\text{C}=\text{C}-$
5.	Carbonyl group	$\begin{array}{c} \text{O} \\    \\ -\text{C}- \end{array}$
6.	Carbon-nitrogen group	$\begin{array}{c} \text{N} \\    \\ -\text{C}\equiv\text{N}, -\text{C}- \end{array}$
7.	Carbon-sulphur groups	$\text{CH}_3-\text{SH}$

Examples of auxochrome are:  $-\text{NH}_2$ ,  $-\text{OH}$ ,  $-\text{NR}_2$ ,  $-\text{COOH}$  and  $-\text{SO}_3\text{H}$ .  $-\text{NH}_2$

and  $-NR_2$  cause solubility in acids while  $-OH$ ,  $-COOH$  and  $-SO_3H$  cause solubility in basic solutions.

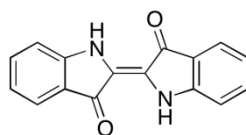
### Classification of Dyes

- 1. Acid dyes:** These are used for dyeing of protein fibers such as wool, silk, nylon and also leather and paper. These contain one or more sulphuric acid substituents or other acidic groups. Example is acid yellow 36 (Metanil yellow).
- 2. Basic dyes:** These are used to dye wool or cotton with a mordant but are usually used for duplicator inks, carbon paper and type writer ribbons. In solvents other than water these form writing and printing inks. Basic dyes are mostly amino compounds soluble in acids and made insoluble by the solution being made basic. Basic dyes were the first synthetic dyes. Mauve was the first basic dye. Examples are basic brown 1 (bismark brown) and basic violet 3 (crystal violet).
- 3. Azo dyes:** These are brilliant and long lasting dyes and are used primarily for printing on cotton. These ice colours are made right on the fiber by coupling diazotized materials while in contact with the fibers.
- 4. Direct dyes:** These are used to dye cotton directly without the addition of a mordant. These are also used to dye union goods (mixed cotton and wool or silk). These are generally azo dyes and their solubility in the dyes bath is often reduced by adding salt. Examples are direct orange 26 and direct black 22.
- 5. Disperse dyes:** Some fibers such as plastics, cellulose acetate, polyesters and nylon fibers are difficult to dye so disperse dyes are applied as very finely divided materials which are absorbed on to these fibers with which these then form a solid solution. The dye dissolves into the fiber at or near the glass transition temperature of the polymer. Examples are disperse red 4, disperse red 77, disperse orange 25 and disperse blue 27.
- 6. Fiber reactive dyes:** These dyes react with the substrate usually cellulose to form a covalent link or bond between the dye and the fiber. Cotton, rayon and some nylons are dyed by these dyes. Example is vinyl sulfone (sulfatoethyl sulfone).
- 7. Mordant dyes (and lakes):** Some dyes combine with metallic salts to form highly insoluble coloured materials called lakes. Lakes are usually used as pigments. If a cloth made of cotton, wool or other protein fiber is impregnated with an Al, Cr or Fe salt and then contacted with a lake forming dye, the metallic precipitate forms in the fiber and the color become far more resistant to light and washing. The azo and anthraquinone nuclei having attached the groups like  $-OH$  and  $-COOH$  can act as mordant dyes.
- 8. Sulphur dyes (sulphide dyes):** These dyes have been used for a long time. These are large low costing group of dyes which produce dull shades on cotton. The chromophore is complex and not well defined. Sulphur dyes are usually colourless

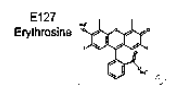
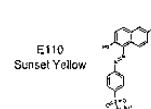
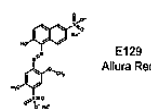
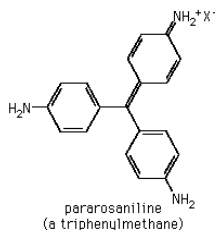
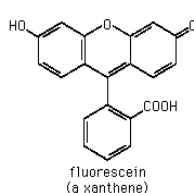
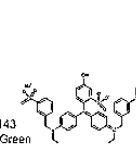
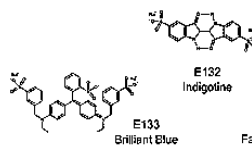
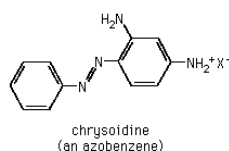
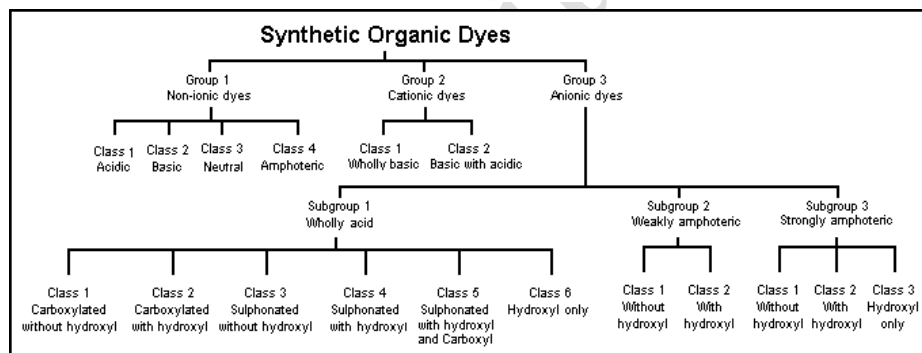
when in the reduced form in a sodium sulfide bath but again colour on oxidation.

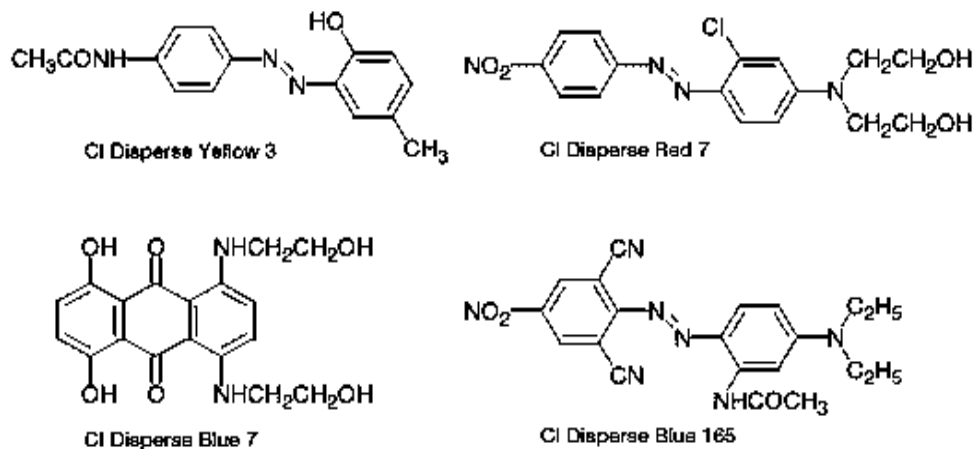
**9. Solvent dyes:** These are also called spirit soluble dyes and are usually azo triarylmethane or anthraquinones. These are used to colour oils, waxes, varnishes, shoe polishes and gasolines.

**10. Vat dyes:** These are water insoluble organic pigments that become water soluble when mixed with powerful reducing agents in the dyeing process. The reducing operation formerly was carried in wooden vats and hence the name vat-dyes is given to it. These have highly complex chemical structures and mostly are derivatives of anthraquinone or indanthrone. Vat dyes are quiet expensive and are most often used on cotton fabrics that are to be subjected to serve conditions of washing and bleaching such as men's shirts. Some vats are supplied as pastes for printing. The best known dye of this class is indigo which is one of the most popular colour in the world.



Indigo





My ph.D research was on the photocatalytic degradation of toxic dyes by bimetallic oxides nanoparticles. The toxic, carcinogenic and mutagenic complex dyes were excellently degraded by the prepared multiwalled carbon nanotubes supported bimetallic oxides nanoparticles. The research provides a road-map to minimize water pollution caused by the toxic dyes.

## Pesticides

**Pest:** Any organism, plant or animal which is harmful to man and plants of desire is called pest. It attacks on plant or animal for food and shelter. It causes food deficiency and many diseases in plants and animals.

**Pesticide:** The substance used to control or kill the pests is called pesticide. It minimizes or fully controls the harmful effects of pests. The use of chemical pesticides has been a major feature of modern agriculture. Our modern system of agriculture depends on the use of fertilizers and pesticides. Fertilizers stimulate plant growth and pesticides control various insects and pests that eat and destroy the crops in the fields or the harvest in the storage sheds. Uptill now more than 10,000 chemicals are used as pesticides.



**Benefits of pesticides:** Pesticides control the crop diseases and hence make the crops healthy and increase crop yield.

**History of pesticides:** The time from which pesticides are used is unmemorable. The first commercial pesticide was Paris Green (Copper aceto arsenate), prepared in 1868. It was used upto the 20<sup>th</sup> century. Then lead arsenate,  $Pb_3(AsO_4)_2$  was used against pests. But both lead and arsenic are damaging a wide variety of living systems. Then nicotine sulphate a traditional insecticide was used which is extremely poisonous to most pests and man. Due to the toxicity and poisoning nature these pesticides were not really satisfactory.

**Properties of an ideal pesticide:** Such pesticide must be preferred and used which must have the following properties.

- i. It must destroy specific pests without injuring the beneficial insects.
- ii. It must not harm the wild life and men.
- iii. It must be specific in its action/function.
- iv. It must decompose easily.
- v. It must be easy in use and easy in handling.
- vi. It must be chief, easily available and not expensive.
- vii. It must not cause soil and water pollution.

Modern insecticides were introduced in 1943. In 1939 P.Muller prepared DDT (dichlorodiphenyltrichloroethane) which has a remarkable effectiveness against mosquitoes which can malaria and lice. DDT has high specificity and acts directly on insects and not on mammals. Muller was awarded Nobel Prize in 1948. Besides its effectiveness DDT also kills good insects like bees. Also it does not break down easily. It is very stable and has a half life of 10 – 15 years. Its persistence is more troublesome by its tendency to become concentrated in all forms of animal life. This phenomenon is called biological magnification.

Now a days many compounds like organophosphates, carbamates and several chlorinated hydrocarbons are used as pesticides.

## Classification of Pesticides

### 1. Classification based on chemical nature

- i. **Inorganic:** These include Arsenic, Mercury and Thallium poisons. Borax, boric acid, copper sulphate, sodium arsenate, cyanides of sodium, fluorides of potassium and chlorides of mercury etc. are the examples.
- ii. **Organic:** DDT, DDD, DDE, TCDD, 2,4-D, 2,4,5-T, methoxychlore, pentachlorophenole, baygon, parathion, malathion, carbaryl, sevin, aldrin, dieldrin and lindane etc.

### 2. Classification based on mode of action

- i. **Physical poisons:** Kerosene oil
- ii. **Protoplasmic poisons:** Borates, fluorides etc.
- iii. **Respiratory poisons:** HCN, H<sub>2</sub>S, CO etc.

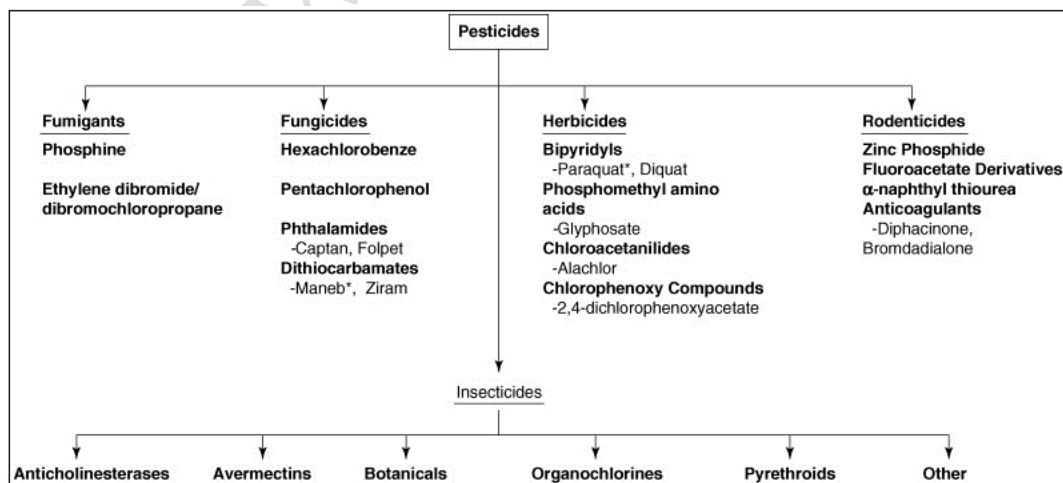
### 3. Classification based on LD<sub>50</sub> Value

**LD<sub>50</sub> value:** Lethal dosage is the unit of toxicity of a pesticide. It is the amount of toxicant required to kill 50% of the test organisms. On the basis of LD<sub>50</sub> the pesticides may be of the following types.

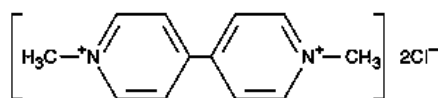
- i. **Extremely toxic:** LD<sub>50</sub> value 1mg/kg or less.
- ii. **Highly toxic:** LD<sub>50</sub> value 1- 50 mg/kg.
- iii. **Moderately toxic:** LD<sub>50</sub> value 50 - 500 mg/kg.
- iv. **Slightly poisonous:** LD<sub>50</sub> value 0.5 - 5g/kg.
- v. **Practically non-poisonous:** LD<sub>50</sub> value 5 - 15g/kg.

### 4. Classification based on the target organism

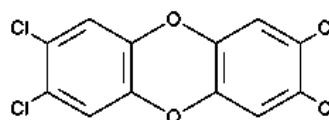
- |                  |                   |
|------------------|-------------------|
| (i) Insecticides | (ii) Fungicides   |
| (iii) Algaecides | (iv) Rodenticides |
| (v) Avcides      | (vi) piscicides   |



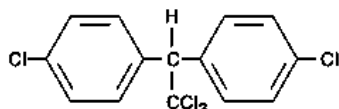




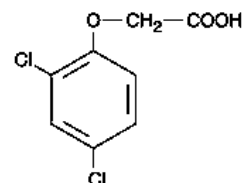
Paraquat dichloride



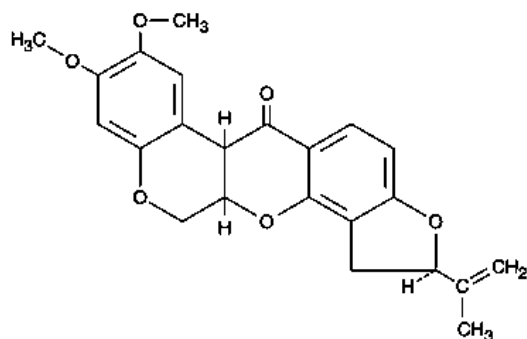
2,3,7,8-Tetrachlorodibenzodioxin (TCDD)



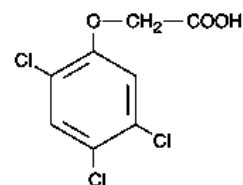
Dichlorodiphenyltrichloroethane (DDT)



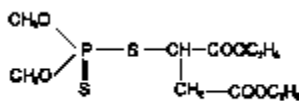
2,4-Dichlorophenoxyacetic acid (2,4-D)



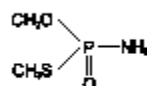
Rotenone



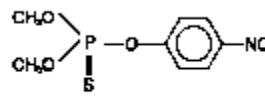
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)



Malathion

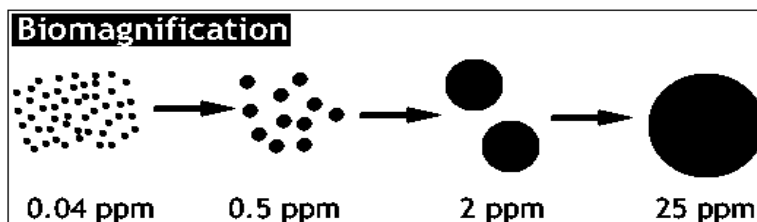


Melbamidophos



Parathion-methyl

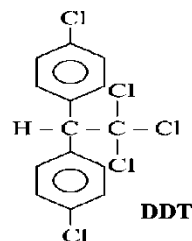
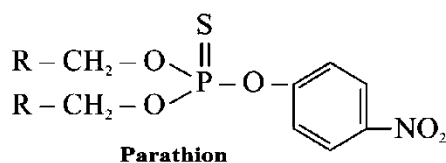
**Bio magnification or bio amplification:** Increase in the amount of a pesticide from organism to organism is called bio magnification or bio amplification. If an organism has a small amount of pesticide in its body, it is not harmful to that organism but when this organism is eaten by another organism which has already some amount of pesticide, the amount of pesticide in his/her body increases and cause hazards. Man is at the top of the consumer list in the ecosystem so food reaching to man would be rich in pesticides and would cause harms and hazards in man.



An area may be sprayed with DDT so that the concentration of the DDT in the water of the area might be much less than 1ppm. But the food chain that proceeds from insects through fish to fish eating birds can concentrate the DDT until it is at the 100 to 1000ppm level. Even man is not immune from this DDT accumulation and our fatty tissues now contain something over 10ppm of DDT more than would be tolerated in the foods we eat.

DDT is non-polar and insoluble in water. DDT when shaken with water an oily layer is formed, almost all the DDT would be found in the oil layer. In nature this distribution occurs and DDT accumulates in animals and in particular in their fatty tissues. Although DDT can be used in very small amount to control insects, it accumulates in the fatty tissues of each successive member of the food chain. Due to the undesirable effects of DDT it has been banned in USA and all over the world.

**Alternates of DDT:** There are still some chlorinated pesticides that are used for more specific targets than DDT. These are mirex, chlordane, heptachlor, aldrin and dieldrin. The important non-chlorinated pesticides are parathion and malathion. These compounds break down fairly readily to products that appear to cause no biological damage. These are however toxic to man and other animals as well as to insects. Thus it avoids long term damage but unless handled carefully it can make for that by short term effects. There is no ideal pesticide available. All the chemical poisons will give us benefit in one way but damage at other.



## Toxicity of Pesticides

Pesticides are toxic to pests, toxic to animals and human. Its effects may be acute or chronic. It has its toxic effects on humans, plants, pests, wildlife, aquatic life and microorganisms.

## Petrochemicals

Chemicals obtained from petroleum and used as starting materials in the preparation of many organic compounds are called petrochemicals. These are pure identifiable substances derived from petroleum and used in chemical trade. The petrochemicals may be used as such or may be converted into more desirable products. Most organic chemical substances could be considered petrochemicals.

The first organic chemical made on large scale from a petroleum base was

isopropyl alcohol produced by standard oil of New Jersey in 1920. In 1925 the standard oil of New Jersey was making 75 tons per year of isopropanol. Currently over 80% of all organic chemicals and 98% aromatic chemicals are petrochemicals.

### Separation of Chemicals from Petroleum

While separating individual species from petroleum, the process involve well refined engineering methods. The most important of these methods are distillation and selective absorption. Once separated from petroleum, most materials then undergo chemical conversion into more desirable products. alkylation involving propenes and butenes yield C<sub>6</sub> to C<sub>8</sub> hydrocarbons for high octane gasoline. Propylene becomes polypropylene, polyamides, polyamines, propylene glycol and other compounds.

The most basic raw materials supplied by petroleum refineries or natural gas companies are LPG, natural gas from cracking operations, liquid distillate, distillate from special cracking processes and selected or isomerized cyclic fractions for aromatics. Most of these substances are of high value for using as fuel. Some of the petrochemicals are given in the table below.

Raw Materials by Distillation	Precursors (basic Chemicals) by conversion.	Intermediates by conversion	Finished Products By conversion
Paraffins And Cyclics	Olefins, diolefins, Acetylene, aromatics	Various inorganics and organics,	Inorganic And organics
Natural gas Sulfides Hydrogen Methane	H <sub>2</sub> S	S, H <sub>2</sub> S synthesis gas	Carbon black H <sub>2</sub> SO <sub>4</sub> ,  NH <sub>3</sub>
Refinery gases	Acetylene	Acetic acid	Methanol Formaldehyde
Ethane	Isobutene	Acetic anhydride	Acetates
Propane	Ethylene	Isoprene	Fibers
N-butane	Propylene	Ethylene oxide etc.	Rubber
Hexane	n-butaness		Rubber & fiber
Heptanes		Butadiene	Rubber

Refinery naphtha's		Adipic acid Ethyl benzene Styrene	Fibers Styrene Rubber
Naphthalene		Cumene	Phenol, acetone
Benzene	Cyclohexadiene	Alkyl benzene	Nylons
Toluene	Toluene	Phenol	Plastics
Xylene	Toluene	Benzoic acid	Phenol
Methyl naphthalenes	O - , m -, p -, xylene, toluene naphthalene	Pthalic Anhydride	Plastics

The lower members of the paraffin and olefin series have been the preferred and most economical sources of organic raw materials for conversion.

The major petrochemicals obtained from methane are given below.

Basic	Uses, (Percent)
Ammonia	Fertilizers (80%), plastics and fibers (10%), explosives (5%).
Carbon black	Tyres (65%), other rubber (25%), colorant and fillers (10%).
Methanol	Polymers (50%), solvents (10%), derivatives (HCHO, CH <sub>3</sub> COOH) (40%).
<b>Chloromethane</b>	
Methyl chloride (CH <sub>3</sub> Cl)	Silicones (57%), tetramethyl lead (19%).
Methylene chloride (CH <sub>2</sub> Cl <sub>2</sub> )	Paint remover (30%), aerosol propellant (20%), degreaser (10%).
Chloroform (CHCl <sub>3</sub> )	Fluorocarbons (90%).
Carbon tetrachloride (CCl <sub>4</sub> )	Fluorocarbons (95%), degreasing, fumigant etc. (5%).
Acetylene	VCM (37%), 1,4-butanediol (25%), Vinyl acetate (14%), Vinyl fluoride and acetylene black (5%).
Hydrogen Cyanide	MMA (58%), cyanuric chloride (17%), chelating agents (13%), NaCN (9%).

Petrochemicals obtained from ethylene are given below.

Basic Derivatives	Uses, (Percent)
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Ethyl Benzene	Styrene (99%), solvent (1%).
Ethyl chloride	TEL (90%) ethyl cellulose of pharmaceuticals (5%).
Ethylene dichloride	VCM (84%), solvent (7%).
Ethylene glycol	Antifreez (38%), polyester fibers and films (49%).
Ethylene oxide	Glycol (60%), ethoxylates (10%), glycol ethers (10%).
Perchloro ethylene	Textile cleaning (40%), metal cleaning (21%), chemical intermediates (6%).
<b>Polyethylene</b>	
Low	Film, sheet, molding and extrusion plastics.
High density	Film sheet molding and extrusion plastics.
Styrene	Polystyrene (52%), ABS (9%), SBR (7%), polyester resins (6%), SB latex (6%).
1, 1, 1 trichloroethane	Cold cleaning (40%), Vapour degreasing (22%), Adhesives (12%), aerosols (10%), electronics (6%).

### Fractional Distillation of Petroleum

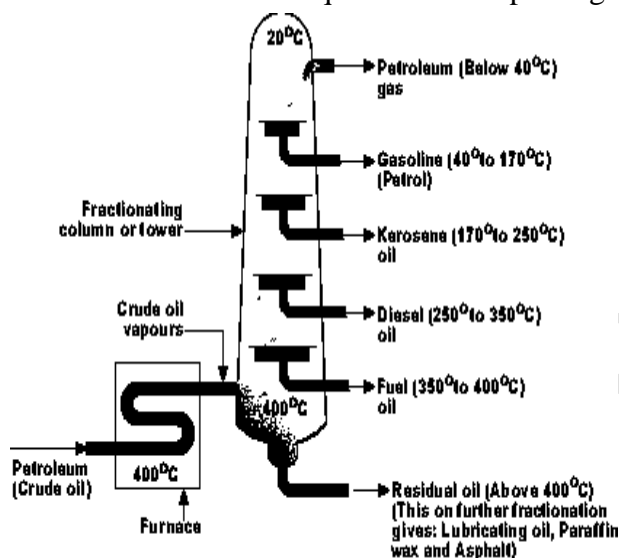
Petroleum in the unrefined form is called crude oil. It is a naturally occurring thick viscous brown or greenish black liquid which is obtained from earth crust. It consists of mostly hydrocarbons along with some other elements, mainly sulphur, nitrogen and oxygen. Crude oil is first treated to remove sulphur compounds that may be present. The removal of sulphur from petroleum is called *sweetening of crude oil*. The cleaned hydrocarbon material is then distilled, and fractions with various boiling ranges are obtained. The principal goal of refinery operations is the production of gasoline.

**Distillation:** It is a separation, purification and isolation process. Distillation is the process of evaporation followed by condensation. The components of a liquid mixture can be separated from one another by distillation if the boiling points of the components are different. Distillation may be fractional distillation, steam distillation and vacuum distillation.

**Fractional distillation:** Fractional distillation is a process in which the liquid mixture is separated into different components on the basis of differences in their boiling points.

Fractional distillation of petroleum is carried out in distillation tower or fractionating column. The distillation tower consists of various portions which are provided with bubble caps. Petroleum is first heated in a furnace to 400°C and the

vapours are introduced into the distillation column or fractionating column. The vapours are condensed by the bubble cap phenomenon and various fractions at different temperatures are obtained in the liquid form except the gaseous fraction.



Fractional distillation of petroleum.

Main fractions obtained during fractional distillation are:

- 1. Refinery gas:** It is a mixture of hydrocarbons containing methane, ethane propane, and butane, i.e.,  $C_1$  to  $C_4$  atoms per molecule. It is obtained at a temperature below  $20^\circ\text{C}$ . This fraction is used as “fuel” in homes and industries and for making other organic compounds.
- 2. Petroleum ether:** It is obtained in the boiling range of  $20^\circ - 60^\circ\text{C}$ . It consists of pentane and hexane ( $C_5 - C_6$ ) and is used as organic solvent.
- 3. Light naphtha:** It is obtained in the boiling range of  $60 - 100^\circ\text{C}$ . It contains hexane and heptane ( $C_6 - C_7$ ) and is used as organic solvent.
- 4. Gasoline (Petrole):** This is the most important fraction containing hydrocarbons from  $C_7$  to  $C_{10}$ . It is obtained in the boiling range of  $80^\circ - 180^\circ\text{C}$  and is used as motor fuel.
- 5. Kerosene (Paraffin oil):** It is obtained in the boiling range of  $160^\circ - 300^\circ\text{C}$ . It contains hydrocarbons from  $C_{11}$  to  $C_{15}$ . It is used as jet fuel, and for oil fired domestic heating. It can also be used for cracking to produce gasoline (motor fuel).
- 6. Heavy oil (Diesel oil or fuel oil or gas oil):** This fraction is obtained in the boiling range of  $300^\circ\text{C}$  to  $400^\circ\text{C}$  and contains hydrocarbon from  $C_{15}$  to  $C_{18}$ . It is used as industrial fuel and as fuel for diesel engines.
- 7. Lubricating oil:** It is a mixture of non-volatile liquids which is obtained at a temperature above  $400^\circ\text{C}$ . It contains hydrocarbons from  $C_{18} - C_{20}$ . It is used for lubricating heavy machinery.

**8. Residue:** The residue (solid mass) is a mixture of higher hydrocarbons. It is further fractionated into paraffin wax and pitch.

**9. Paraffin wax:** It is used for making greases, vaseline, waxed paper, ointments and candles.

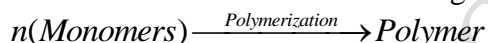
**10. Coal tar/asphalt/pitch:** The final residue (with more than  $C_{30}$ ) is a black coal tar and is called asphalt or pitch or bitumen. It is used for metalling/surfacing of roads.

## Synthetic Polymers (PVC and Nylon)

**Polymers:** High molecular mass molecules (macromolecules) formed as a result of a process known as polymerization.

**Polymerization:** The process of formation of polymers is called polymerization.

**Monomers:** Small molecules which polymerizes and form polymer by the process of polymerization are called monomers. These are the building blocks of polymers.



The well known example of polymers is polyethylene which is composed of large number of monomers ethylenes.

Berzelius, Baekeland, Hermann Staudinger, W.H. Carothers, Ziegler-Natta, Paul Flory and Bruce Merrifield contributed in the process of polymerization.

### Types of polymers

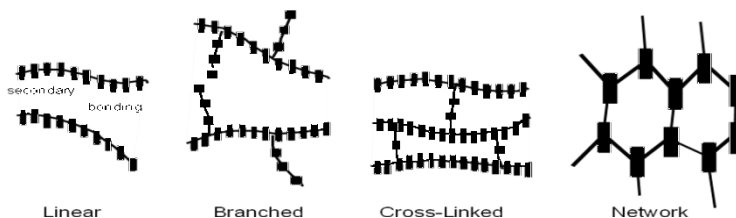
**1. Polymers may be natural and artificial.** Diamond, graphite, proteins etc. are the examples of natural polymers. Polyethylene, polystyrene, polyesters and polyamides are the examples of artificial polymers.

**2. Polymers may be organic and inorganic.** Proteins, carbohydrates, nylon etc. are the examples of organic polymers. Diamond, silicates etc. are the examples of inorganic polymers.

**3. Polymers may be homopolymer, copolymer and terpolymer.** Homopolymers are made of same type of monomers. Copolymers are made of two different types of monomers while terpolymers are made of three different types of monomers.

### Shape of Polymers

Polymers shape may be linear, branched, cross linked and networked.



**Degree of polymerization:** The number of monomers in a polymer is called its degree of polymerization. It specifies length of the polymer chain. For PVC the D.P = 1000

Molecular weight of the polymer = D.P × M. Mass of the monomer.

## Types of Polymerization

Carothers classified the process of polymerization into addition and condensation polymerization.

### Addition Polymerization

In addition polymerization the monomers combine to form polymer without the elimination of small molecule as by product. It is also called chain growth polymerization. Examples of addition polymers are, polyethylene, polystyrene, polypropylene, polyvinyl chloride, polyvinyl acetate, polyvinyl nitrile, polyvinyl acetate and Teflon etc.

### Condensation Polymerization

In condensation polymerization the monomers combine to form polymer with the elimination of small molecule as by product. It is also called step growth polymerization. In this polymerization the monomers are different and each monomer is bifunctional. Examples of condensation polymers are, polyesters, polyamides, epoxy resins etc.

### Mechanism of Addition Polymerization

Addition polymerization may proceed through the following mechanisms.

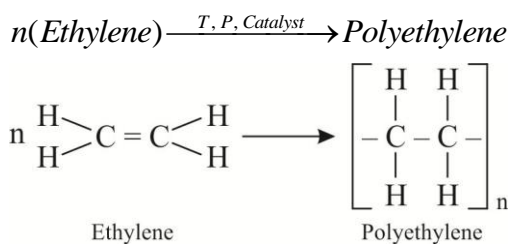
- (1) Free radical mechanism
- (2) Ionic mechanism.

Ionic mechanism may further be cationic and anionic mechanism.

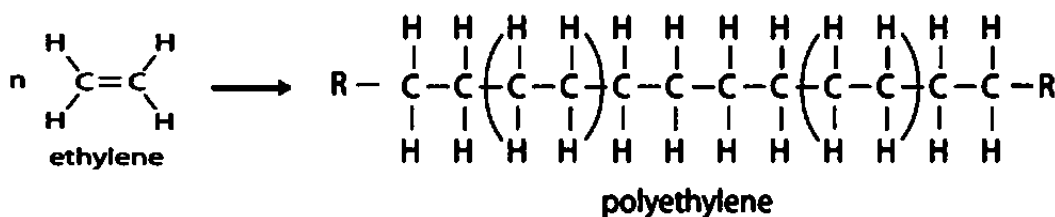
### Addition Polymers

In these polymers, the monomers combine together and form a long chain polymer. The molecular weight of the polymer is multiple of the molecular weight of the monomer. Empirical formula of the polymer is the same as that of the monomer.

**1. Polyethylene:** It is the polymer of ethylene monomers. Many ethylene molecules combine at high pressure, high temperature and in the presence of catalyst to form a transparent solid polymer called polyethylene. Its molecular mass is from 2000 to 20000 depending on the temperature and pressure.

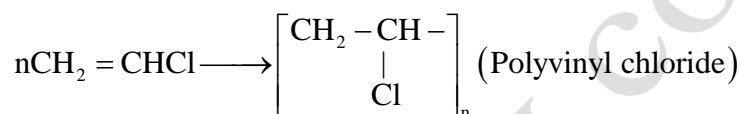
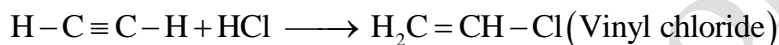






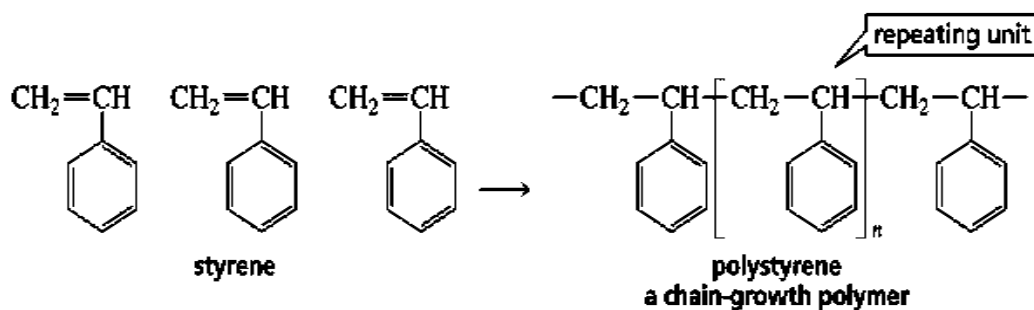
## 2. Polyvinyl chloride (PVC)

Acetylene reacts with HCl and form vinyl chloride in the presence of  $\text{HgCl}_2$  or  $\text{CuCl}$ . Many vinyl chlorides polymerize and form a polymer called polyvinyl chloride.



## 3. Polystyrene

It is a polymer made from styrene monomers.



## Industrial Preparation of PVC

The largest branch of the vinyl family is polyvinyl chloride (PVC). The popularity of PVC is due to its

- i. Excellent physical properties.
- ii. Ability to be compounded for a wide range of applications.
- iii. Ease of processing.
- iv. Relatively low cost.

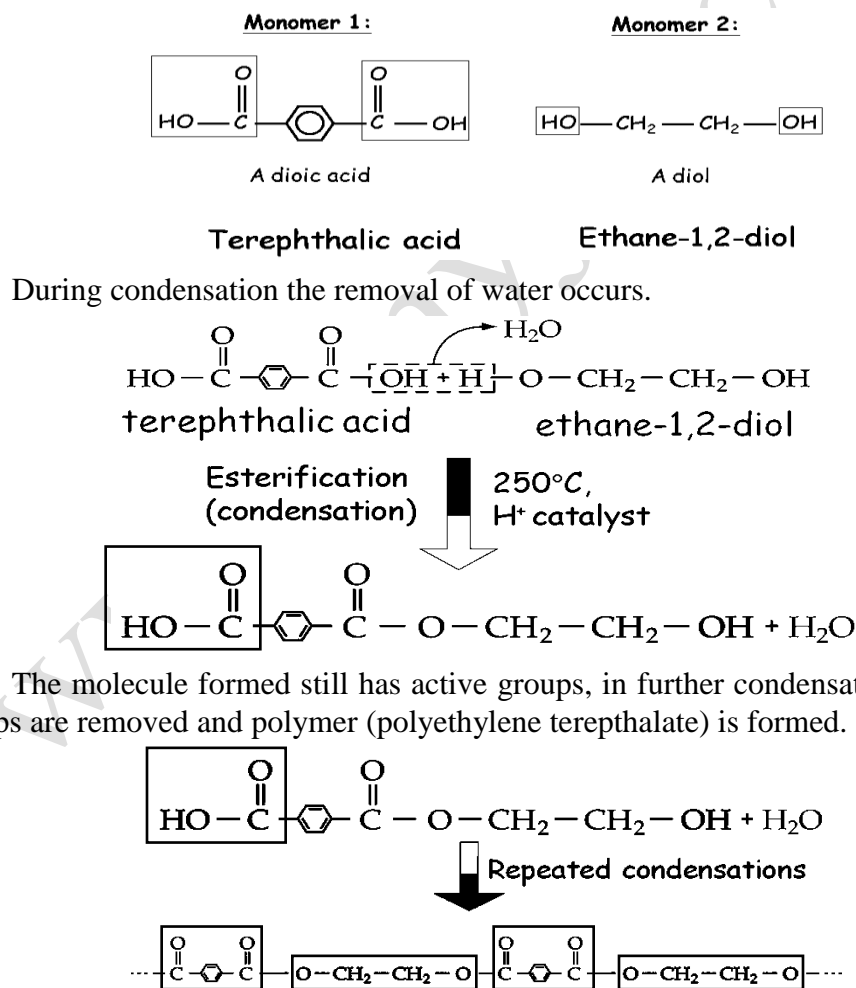
**Procedure:** The liquid monomer is formed into tiny globules by vigorous stirring in water containing a suspending agent. A typical recipe lists 100 parts of water, 100 parts of liquid vinyl chloride, 1 part of a persulphate catalyst and 1.5 parts of an emulsifier such as sodium lauryl sulphate. The autoclave operates at approximately  $50^\circ\text{C}$  for 72 hours to give a yield of 90 percent of polymer with a particle size of 0.1

to 1.0 $\mu$ m. To achieve the desired properties, plasticizers, stabilizers, lubricants and fillers are added.

## Condensation Polymers

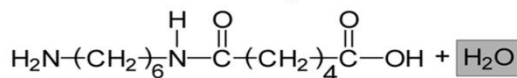
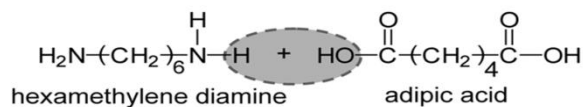
As discussed earlier, in condensation polymerization along with polymer a small molecule like water, ammonia, HCl, methanol or acetone as by product is also formed. Such reactions in which a byproduct along with a main product is formed by the combination of two molecules are called condensation reactions. In condensation polymerization both the monomers are bifunctional (having two functional groups). Examples of condensation polymers are, polyesters, polyamides, epoxy resins etc.

**1. Polyesters :** This polymer has many ester functional groups so called polyester. It is a copolymer as it is made of two different monomers, each monomer is bifunctional. One monomer is aromatic dicarboxylic acid (terephthalic acid) and other monomer is a dihydric alcohol (ethane diol)

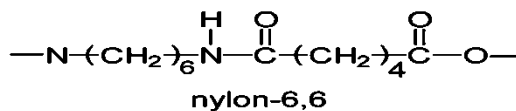
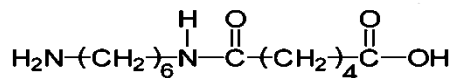


**2. Polyamides (nylon):** This polymer has many amide functional groups that's

why called polyamide. It is a copolymer, made of two different bifunctional monomers. One of the monomer is an aliphatic dicarboxylic acid (adipic acid) and other monomer is a diamine (hexamethylene diamine). Elimination of water molecule as byproduct occurs.

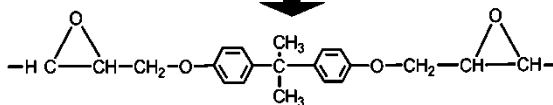
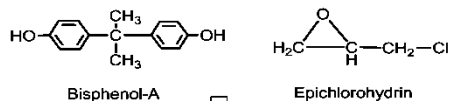


This molecule still has some active groups, which are when removed by repeated condensation we will get the polymer nylon.



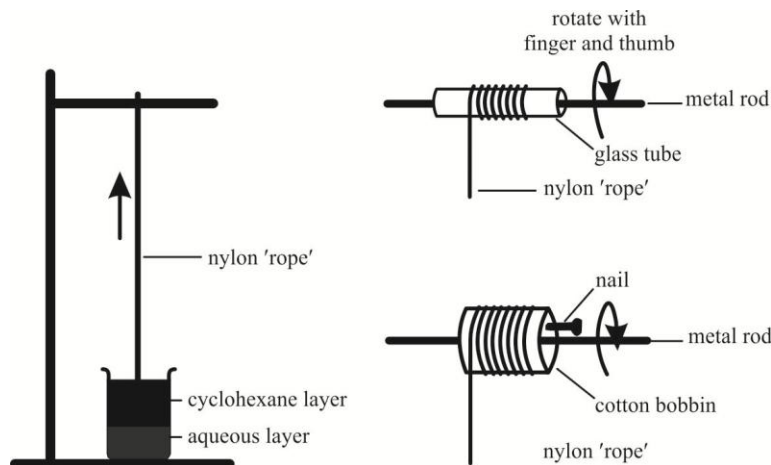
The polymer name nylon 6,6 is due to the fact that both the monomers has six carbon atoms each. If one monomer has six carbons and other have ten then the polymer will be called nylon 6,10.

**3. Epoxy resins:** These polymers are also copolymers, made of different monomers by condensation. One monomer is Bisphenol-A and other is epichlorohydrin.



**Preparation of Nylon (6, 10) (the nylon rope trick)**

**Procedure:** 50 cm<sup>3</sup> of a 2% (by volume) solution of decanedioyl dichloride (sebacoyl chloride) in CCl<sub>4</sub> is measured into a 100 cm<sup>3</sup> tall form beaker. 25 cm<sup>3</sup> of an aqueous solution containing 2.2g of 1,6-diamino hexane (hexamethylene diamine) is added carefully to the beaker so that the aqueous solutions floats on top of the CCl<sub>4</sub> solution, without mixing. A thread of the nylon is drawn from the interface between the two liquids, using a pair of forceps and wound around thick glass rod as shown in the figure below.



### Uses of PVC

PVC or poly vinyl chloride is widely used in

- i. Imitation leathers.
- ii. Floor coverings.
- iii. Corrugated roofing materials.
- iv. Drainage pipes.
- v. Electrical pipes.
- vi. Gramophone records.

### Uses of Nylon

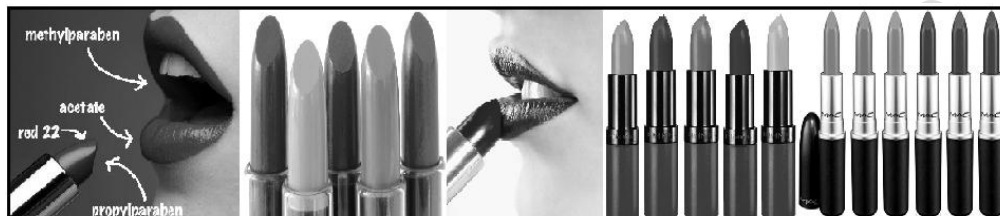
Nylon is well known as synthetic fiber in

- i. Carpets.
- ii. Fabrics.
- iii. Ropes.
- iv. Stockings and other clothing.
- v. Because of its mechanical strength, nylon is also used in moulded machine parts such as gears and bearings.

### Cosmetics

The substances which are applied on skin, nails and hairs for protection and beauty purposes are called cosmetics. Examples of cosmetics are lipsticks, nail polishes and hair dyes.

- Lipsticks:** These are oily, waxy, pigmentary, preservative, antioxidant and perfumery liquid mixtures which are applied on lips to protect its soft tissues and give the lips brilliant colour appearance. These were introduced in their modern form after World War I.



**Properties:** Lipsticks must have the following properties.

- Neutral in taste.
- Lack of toxicity.
- Lacking of irritancy.
- Stable at fluctuating temperatures.
- Stable to moisture.
- Stable to air flow.
- Antioxidant.
- Water insoluble.

**Composition:** The chemical composition of lipsticks varies greatly. The main constituents of lipsticks are given below.

- Mixture of oils: May be castor oil, vegetable oil, lanolin oil, mineral or wool fat etc. Oils make the lipsticks soft and easily applicable.
- Waxes: Usually bees wax or carnauba is used.
- Pigments: Used for colors.
- Antioxidants: To avoid oxidation.
- Preservatives: To ensure preservation.
- Perfumes: To give it specific smell and odour.
- Esters of fatty acids: To reduce the stickiness of lipsticks 2-propyl myristate is added.

**Colours:** Lipsticks are available in variety of colours. The colours are due to the presence of dyes in it. The dyes are water soluble and fat soluble products. Various dyes give it specific colour.

*Erythrosine* give it reddish pink colour.

*Amaranth* give it dark red colour.

**Tetrabromoflourescein** give it brilliant blue colour.

These dyes must be water insoluble, otherwise the colour would quickly fade or be removed in a short time by the consumer through the movement of the saliva-soaked tongue across the lips. Water soluble dyes such as green or blue food dyes can be used to provide lipstick colouration, but these are usually first combined with metal oxides such as aluminium hydroxide to form an insoluble precipitate that is then suspended in the oil base of the lipstick.

## 2. Nail vanish and remover

- i. **Nail varnish:** A lacquer applied to human nails to decorate and protect the nail plate is called nail polish or nail varnish.



**Purposes of using nail polish:** Following are the major purposes of using nail polish or varnish.

- |                                  |                                 |
|----------------------------------|---------------------------------|
| (i) To cause nails growth.       | (ii) To make nails stronger.    |
| (iii) To prevent nails breaking. | (iv) To prevent nails cracking. |
| (v) To prevent nails slitting.   | (vi) To prevent nails biting.   |

**Colours:** Nails varnishes are available in variety of colours like; red, pink and brown. Besides solid colours, nail polish has also developed an array of other designs and colours such as; nail polish stamps, crackled, magnetic nail polish strips and stickers.

**Composition:** Following are the main components of nail varnish.

- i. Film forming agents
- ii. Resins
- iii. Plasticizers: Camphor is added to make it flexible after drying.
- iv. Solvent
- v. Colouring agents: Pigments and sparkling particles like mica are used to impart desired colours and reflecting properties.
- vi. Adhesive polymers: Tosylamide-formaldehyde resin is added to make sure that the nitrocellulose adheres to the nail surface.
- vii. Thickening agents: Stearalkoniumhectorite are added to keep the sparkling particles in suspension within the bottle.
- viii. Ultraviolet stabilizers: Benzophenone-I is added to resist colour changes when exposed to sunlight.

**Disadvantages:** Nail polish ingredients often include toluene, formalin, xylene and petroleum based products have been linked to cancer. Formalin may cause allergic reactions and is unsafe for use by asthmatic people. It is a carcinogen.

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. This is marketed as environmentally conscious products, since nail polish is considered a hazardous waste by some regulatory authorities. When applied, the solvent (water) does not completely evaporate as in the case of the traditional nail polish; part of water is absorbed through the fingernail.

### ii. **Nail polish remover**

Nail polish is removed with nail polish remover or nail pads which is an organic solvent, but may also include oils, scents and colouring. The most common

type of nail polish remover contains acetone  $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_3$ . It is powerful and effective but is harsh on skin and nails which can even make them more brittle. Acetone is a volatile organic compound which can also be used to remove artificial nails, that are usually made of acrylic. There are many different types of nail polish removers in the market and different brands may have different chemical compositions. However, the principal ingredients in most of them are acetone, ethyl acetate or butyl acetate and alcohol. The “non-acetone nail polish remover” usually contains ethyl acetate which is less aggressive solvent and can therefore, be used to remove nail polish from artificial nails.

These chemicals used are known to dehydrate the skin, cause irritation to eyes and make nails dry and brittle. These also have a distinct chemical smell and are highly inflammable. To counter the dehydration and brittleness effects, many removers also contain conditioning ingredients like castor oil, ethyl palmitate or lanolin.

### **Applications**

With liquid removers, the remover is taken on a cotton ball or tissue and wiped over the nail to strip away the finger nail polish on it. Depending upon the type of finger nail polish, the number of applied coats and the type of remover, one application may suffice for removal or several applications may be necessary.

To understand how nail polish remover works, it is necessary to know that a finger nail polish remover and a finger nail polish both contain similar organic solvents; the nail polish also contains drying agents, thickeners, hardening agents and colouring agents. The organic solvent in a nail polish keeps them in a liquid state, while the solvent present in remover, dissolve the hardened polish and transforms it back into its original liquid form. When the nail polish remover is applied to the nail polish that is to be removed, the solvent molecules of the remover interrupt loosen and break the polymer chains of the polish. This dissolved the hardened polish and

transforms it back into its original liquid form. It can then be wiped off from the nail.

### 3. Hair dyes

These are dyes used for hair colouring. These are used to change the hair colour to more fashionable and desirable and to restore the original hair color by hair dressing and sun bleaching processes.



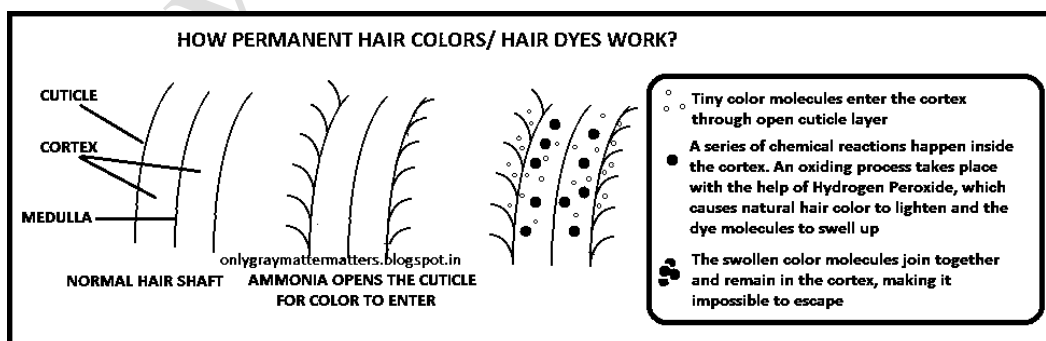
### Types of Hair Dyes

**i. Permanent hair dyes:** These are also called oxidation dyes. These consist of the following components.

- i. Oxidizing agent: Hydrogen peroxide.
- ii. Coupling agents: Metaderivatives of aniline.
- iii. Primary intermediates: Aromatic para-compounds such as 1,4-diaminobenzene or 4-aminophenol or 2,5-diaminotoluene.
- iv. Basic medium is needed, which is provided by ammonia.

The combination of  $H_2O_2$  and the primary intermediate causes the natural hair to be lightened (removal of blackness) which provides a blank canvas (channel) for the dye. Ammonia opens the hair shaft so that the dye can actually bond with the hair and ammonia speeds up the reaction of the dye with the hair.

The couplers (meta-substituted derivatives of aniline) are the chemical compounds that define the colour of the hair dye. Various combinations of primary intermediates and couplers provide different shades of hair colours.



**ii. Semi-permanent hair dyes**

These dyes molecules partially penetrate to the hair shaft. That's why these



colours can survive washing with typically 4-5 shampoos. Semi-permanent hair dyes contain no or very low levels of developers, peroxide or ammonia and are thus, safer for damaged or fragile hair. However, these may still contain the toxic compound p-phenylenediamine or other such ingredient.

The final colour of each strand of hair depends on its original colour and porosity, so there will be large variations in shade across the whole head. This gives a more natural result than that of a solid permanent colour. Semi-permanent colour can lighten the hair.

### **iii. Demi-permanent hair dyes**

These are in fact, permanent hair colours that contain an alkaline agent other than ammonia (e.g; ethanolamine, sodium carbonate) and the concentration of  $H_2O_2$  in the developer may be lower than used in a permanent hair colour. Since the alkaline agents employed in these colours are less effective in removing the natural pigment of hair than ammonia, these products provide no lightening of hair colour during dyeing.

As a result, these cannot colour hair to a lighter shade than it was before dyeing and are less damaging to hair than permanent counterpart.

### **iv. Temporary hair dyes**

Temporary hair dyes are most oftenly used to colour hairs for special occasions such as weddings, costume parties, dramas, films etc. These are available in various forms, such as resins, shampoos, gels, sprays and foams. A temporary hair colour is typically brighter and more vibrant than semi-permanent and permanent hair colour. The dye molecules in temporary hair colour are large and cannot penetrate the cuticle layer. The colour particles remain absorbed (closely adherent) to the hair shaft and are easily removed with a single shampooing.

## **Adhesives**

Adhesives are the materials, usually in liquid or semi-liquid states, that adhere or bond items together. These may be either of natural or synthetic sources. Although a large number of materials can be bonded by means of adhesives. These are especially useful for bonding thin materials. Adhesives cure or harden by either evaporating a solvent or by chemical reactions that occur between two or more constituents of the adhesive.



### Importance

With the passage of time and during their development, adhesives have gained an important position in an increasing number of production processes. There is hardly any product in our surroundings that does not contain at least one adhesive in it. For example the label on a beverage bottle, protective coating on automobiles, profiles on window frames, bonding formica to wooden counters or attaching out soles to uppers in foot wear.

**Types of adhesives:** On the basis of their mode of adhesion, adhesives are of two main types, non-reactive and reactive.

#### 1. Non-reactive adhesives

These adhesives may be either of natural or of synthetic origin. Drying adhesives, pressure sensitive adhesives, contact adhesives and hot adhesives are some examples of this class.

**A. Drying adhesives:** These adhesives harden by drying and are of the following two types.

##### i. Solvent based adhesives

These are a mixture of ingredients (typically polymers) dissolved in a solvent. White glue, contact adhesives and rubber cements are the members of the drying adhesive family.

##### ii. Polymer dispersion adhesives

These are also known as emulsion adhesives and are milky white dispersions often based on polyvinyl acetate (PVAc). These are extensively used in the wood working and packing industries; also used in fabrics and fabric based components and in the engineered products such as loudspeaker cones.

#### B. Pressure sensitive adhesives (PSA)

These adhesives form a bond by the application of light pressure to adhere the adhesive with the adherent. Once the adhesive and the adherent are in close proximity, molecular interactions, such as “Van der Waals forces” become involved in the bond, contributing significantly to its ultimate strength. Major raw materials for PSA’s are acrylate based polymers.

#### C. Contact adhesives

These are 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 of contact adhesives are natural rubber and polychloroprene (Neoprene). It must be remembered that contact adhesives must be applied to both surfaces and allowed for some time to dry before the two surfaces are pushed together. Once the surfaces are pushed together, the bond forms very quickly.

#### **D. Hot adhesives**

These are also known as hot melt adhesives or thermoplastics and are applied in molten form ( $65^{\circ}\text{C} - 180^{\circ}\text{C}$  range) which solidifies on cooling to form strong bonds between a wide range of materials. Hot adhesives containing “ethylene vinyl acetate”, are particularly popular for crafts because of their ease of use and the wide range of common materials they can join.

A glue-gun is one method of applying hot adhesive. The glue-gun melts the solid adhesive, then allows the liquid to pass through its barrel onto the material where it solidifies. Glue-gun is shown in the figure above. Thermoplastic glue may have been invented around 1940 by “Proctor & Gamble” as a solution to water based adhesives commonly used in packing at that time failing in humid climates, causing packages to open.

#### **2. Reactive adhesives**

These adhesives chemically react with the material, when harden. These may be;

- (i) Multiparts Adhesives                      (ii) One Part Adhesives

##### **i. Multiparts adhesives**

These adhesives harden by mixing two or more components which chemically react. This reaction causes polymers to cross link into acrylics, urethanes and epoxides. Commercially, there are several combinations of multi-component adhesives that are used in the industry. Some of these combinations are:

- (a) Polyester resin-Polyurethane resin.  
(b) Polyols-Polyurethane resins.  
(c) Acrylic Polymers-Polyurethane resins.

The individual components of these adhesives do act as adhesive by nature. These components however react with each other after being mixed and show full adhesion only on curing.

##### **ii. One part adhesives**

These adhesives harden via a chemical reaction with an external energy source such as radiation, heat or moisture.

- i. Light curing adhesives are generally acrylic based, and due to their rapid action, these are significantly used in electronics, telecommunications, medical, aerospace, glass and in optics.
- ii. Heat curing adhesives include epoxies, urethanes and polyimides.

- iii. Moisture curing adhesives cure when these react with moisture present on the substrate surface or in the air. This type of adhesives includes cyanoacrylates and urethanes.

## EXERCISE

### Q.1. Choose the correct one.

- (i) "Mauve" is an example of \_\_\_\_\_ dye.  
 (a) Acidic (b)✓ Basic  
 (c) Direct (d) Azo
- (ii) Which is true for DDT? It is  
 (a) Not a pollutant (b) An antibiotic  
 (c) An antiseptic (d)✓ A non-degradable pollutant

**Note:** DDT is an antiseptic and it is a non-degradable pollutant. It is antiseptic it is known to all but it is famous for its non degradability.

- (iii) Which one of the following is not petrochemicals?  
 (a) Napthalene (b) Mineral oils  
 (c) Wax (d)✓ Table salt
- (iv) What is called "black gold"?  
 (a) Petroleum (b)✓ Coal  
 (c) Coal Tar (d) Natural gas
- (v) Petrochemicals are used in the manufacture of  
 (a) Polythene (b) Detergents  
 (c) Fibers (d)✓ All of these
- (vi) Which one of the following is synthetic polymer?  
 (a) Cellulose (b) Protein  
 (c)✓ Rubber (d) Polythene

**Note:** Rubber and polythene both are synthetic polymers.

- (vii) Which one of the following is a condensation polymer?  
 (a) PVC (b) Polythene  
 (c)✓ Nylon (d) None of these

## SHORT QUESTIONS

### Q.2. Short Questions:

- 
- (i) Differentiate between reactive and non-reactive adhesives.
- 

**Ans.** Given in the theory.

---

- (ii) How nail-polish remover removes the nail-polish?
-

Ans. Given in the theory.

**(iii) Why temporary hair dyes are removed with single shampooing?**

Ans. Given in the theory.

**(iv) What are the uses of PVC and nylon?**

Ans. Given in the theory.

**(v) Write down the four applications of pesticides.**

- Ans. 1. Use for the killing of pests.  
2. Use to control plant disease.  
3. To increase the crop yield.  
4. To remove undesirable plants from the crops.

**(vi) How DDT reaches to animals fatty tissues?**

Ans. Given in the theory.

**(vii) Differentiate between addition and condensation polymers.**

Ans. Given in the theory.

## LONG QUESTIONS

### Q.3. Long Questions:

- Q.1. (a) Define Dyes. What is its chemical composition?**  
**(b) How dyes are classified.**

Ans. Given in the theory.

**Q.2. Explain the fractional distillation of petroleum.**

Ans. Given in the theory.

**Q.3. What is meant by hair dyes. Classify it into different groups?**

Ans. Given in the theory.

**Q.4. What are adhesives. Discuss its importance in our daily life?**

Ans. Given in the theory.

**Q.5. Explain the types of adhesive.**

---

**Ans.** Given in the theory.

---

**Q.6. Write a note on following:**

- |                           |                                     |
|---------------------------|-------------------------------------|
| (a) <b>Petrochemicals</b> | (b) <b>Synthetic polymers</b>       |
| (c) <b>Lipsticks</b>      | (d) <b>Nail polish and removers</b> |
- 

**Ans.** Given in the theory.

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