Contents

Syllabus

B. Sc. (Part III) Chemistry II
INDUSTRIAL CHEMISTRY (SC-132)

UNIT–I : INTRODUCTION TO UNIT OPERATIONS AND UNIT PROCESS

Introduction, Conveying, Crystallization, Distillation, Drying, Evaporation, Filtration, Leaching, Liquid-liquid extraction, Membrane separation, Particle size reduction and enlargements, Solid-solid separation.

Alkylation, amination by ammonolysis, amination by reduction, Calcination, Carbonylation, Double decomposition, Esterification, Halogenation, Hydrogenation, Hydroformylation, Hydrolysis, Nitration, Oxidation, Polymerization, Sulphonation.

UNIT–II : PETROCHEMICALS AND POLYMERS

Introduction to petrochemicals, Manufacture of petrochemicals, Major petrochemical industries in India.

Introduction to polymers, Nomenclature and classification, Methods of preparation, Classification of polymerization reactions, Polymerization techniques, Utilization of commercial polymers, Thermoplastic and thermosetting polymers, Rubber, Inorganic Polymers, Scenario of polymer industries in India.

UNIT–III : DYES AND DRUGS

Dyes : Introduction, Colour and chemical constitution, Classifications of dyes, Picric acid, Methyl orange, Congo red, Para red, Auramine G, Malachite green, Para aniline, Rosaniline, Crystal violt, Phenolphthalein, Fluorescein, Eosin, Mercurochrome, Indophenols, Quinoline, Indigo, Alizarin, Manufacture of dyes (Rhodamine B).

Drugs : Introduction, Sulphonamides, Sulphamethizole, Sulphacetamide, Sulphaguanidine, Sulphanilamide, Sulphapyridine, Sulphathiazole, Sulphamerazine, Phenacetin, Acetanilide, Aspirine, Salol, Salicylamide, Dapsone, Paracetamol, Antipyrine, Chloroquin, Paludrine, Antibiotics with penicillin, Chloromycetin and streptomycin as examples, Manufacture of drugs by taking example of aspirins.

UNIT–IV : INORGANIC CHEMICALS AND INDUSTRIAL GASES

Alumina, Aluminum sulphate, Fluorocarbons, Bromine, Sodium, dichromate, Sodium Silicate, sodium, dichromate thiosulphate nitrate, Sodium sulphide, Sodium bisulphite, Sodium bisulphate, Copper sulphate, Potassium permanganate, Potassium bromide, Potassium nitrate, Potassium dichromate, Urea, Ammonium sulphate Ammonium nitrate, Bromine and fluorocarbon industries in India.

Introduction to industrial gases, Nitrogen, Oxygen, Hydrogen, Carbon dioxide, Industrial gases industries in India.

UNIT–V : PIGMENTS, CEMENT AND LIME

Pigments : Introduction, White pigments, Black pigments, Blue pigments, Red pigments, Green pigments, Brown pigments, Toners and lakes, Metallic powders as pigments, Scenario of dyes and pigment industries in India.

Cement and lime : Introduction, Cement, Lime, Cement and lime Industries in India.

UNIT 1

INTRODUCTION TO UNIT OPERATIONS AND UNIT PROCESSES

STRUCTURE

- Introduction
- Conveying
- Crystallisation
- Distillation
- *Drying*
- Evaporation
- Filtration
- Leaching
- Liquid-Liquid extraction
- Membrane Separation
- Particle Size Reduction and Enlargement
- Solid-Solid Separation
- Alkylation
- Amination by ammonolysis
- Animation by Reduction
- Calcination
- Carbonylation
- Double Decomposition
- Esterfication
- Halogenation
- Hydrogenation
- *Hydroformylation*
- Hydrolysis
- Nitration
- Oxidation
- Polymerisation
- Sulphonation
- Student Activity
- Summary
- Test Yourself.

LEARNING OBJECTIVES

After studying this chapter, you will learn about the various processes used in unit operations, e.g., filtration, distillation, crystallisation etc. You will also learn about hydrolysis, nitration, polymerisation etc, processes also.

1.1. INTRODUCTION

The knowledge of **unit operations** in chemical industries is of great importance for students studying chemical engineering and industrial chemistry as well. Chemical engineering emerged as a separate branch of engineering in about 1910 when it was seen that mechanical engineering as well as chemistry do not provide proper approach for the designing of a chemical plant. The researchers at the Massachusetts Institute of Technology (MIT) characterised the physical operations required for the manufacture of chemicals as unit operations. These unit operations are now used with sound mathematical procedures for designing a chemical plant.

Some of these unit operations involve particulate solids and many of them are aimed at achieving a separation of the components of a mixture. The separation of solids from a suspension by filtration, the separation of liquids by distillation and the removal of water by evaporation and drying are typical unit operations.

Principally, the problem of designing a distillation unit is principally the same in the case of fermentation industry, petroleum industry or the chemical industry. The problem deals with the construction where the difference occurs. The concentration of solutions by evaporation is again a typical operation which is basically similar in the handling of sugar, salt or fruit juices, though there are differences in the most suitable arrangements.

The planning of a process plant involves the determination of the most economic method and the most economical operations used in the process. This accounts for designing a process so as to provide the best combination of capital cost and operating cost. Without adequate knowledge of the physical principles involved in various operations, it is very difficult to select the most suitable one for a given process. This view of the design may be considered by taking one or two simple examples of separation processes. The particles in a solid-solid system may be separated, firstly according to the size and secondly, according to the materials. In general, sieving is the most satisfactory method of separating relatively coarse materials according to the size, but this method is not practicable for very fine particles. In the first of these processes, the size of the particles is used as the basis for the separation and the second process depends upon variation with size of the behaviour of particles in a fluid. A mixed material can be separated into its components by using settling method because the shape and density of particles affect their behavior in fluids. The other methods of separation depend on difference in surface properties (froth flotation), magnetic properties (magnetic separation) and difference in solubility in a solvent (leaching). In case of separation of miscible liquids, following three methods are usually used :

(1) Distillation depending on difference in volatility.

(2) Liquid- liquid extraction depending on difference in solubility in liquid solvent.

(3) Freezing depending on difference in melting point.

The selection of most appropriate operation has become complicated because of the factors such as concentration of liquid solution at which crystals begin to form. For example, in the separation of a mixture of ortho, para and meta-mononitrotoluenes, it is necessary to take the decision as to whether the separation be performed by distillation followed by crystallization or in the reverse order. Another example is of concentration of a solution of a solid. In this case it is necessary to decide whether to stop the evaporation process when a certain concentration of solid has been reached and then to proceed with filtration followed by drying or whether to continue concentration by evaporation to such an extent that the filtration stage can be avoided before moving on to drying.

There are two important factors in the smooth functioning of a chemical industry, *viz*, safety considerations and protection of environment. Safety considerations must be taken into account in the selection of the unit operations and general maintenance of the plant. A chemical plant should be so designed as to minimise risk of all the hazards being released. The control systems, the efficiency of which plays a major role in safe operation of a chemical plant, must be designed at an early stage of construction of the plant. Regarding the protection of the environment, the chemical engineers and chemists working in the chemical plants have three important responsibilities These are as follows :

(i) To utilise natural resources including raw materials and energy sources.

(ii) To ensure that the effluents (solids, liquids and gases) of the plant do not give rise to unacceptable environments effects.

(iii) To adopt effluent control system at the time of designing a plant.

A series of unit operations have been developed by chemical engineers with combination of science and engineering. A brief outline of various unit operations with schematic representation and their applications are summarised below.

1.2. CONVEYING

The unit operation **conveying** deals with the transportation of solids and fluids. The selection of equipment (conveyor) for conveying depends upon the shape and size of the material, and whether the material is to be transported on an incline, horizontally or vertically.

The conveyors used for transportation of material may be classified as follows :

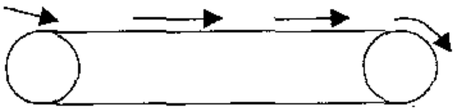


Fig. 1. Belt conveyor

[I] Belt Conveyor

Belt conveyor is a very simple equipment. It consists of an endless belt, a drive, a support and a tightener. In addition to these, the feeding and discharge devices are esential. The belt is made up of fabrics or rubber. The belt conveyors are used to move large quantity of solid material from storage to the reaction section over a long distance. The schematic representation of belt conveyor is shown in fig. (1).

[II] Chain Conveyors

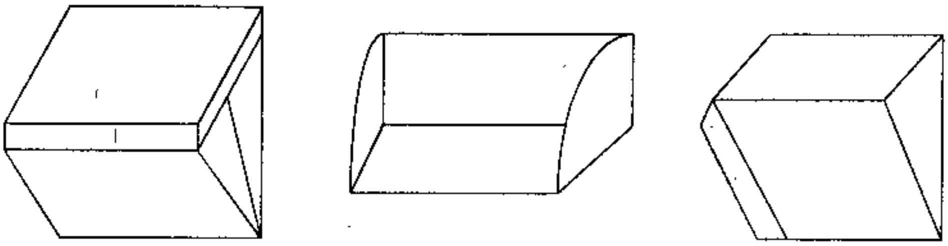
(1) Scraper or flight conveyors : These are the simplest and cheapest type of conveyors. The merits are their adaptability to a wide variety of conditions, suitability for steeper inclines, and their ability to handle large pieces. However, heavy power consumption and heavy repair chargers are some of the demerits of scraper conveyors. Chain conveyor is preferred to belt conveyor when the distance between storage section and processing section is short.

(2) Apron conveyors : Apron conveyors are used usually for heavy loads and short distances. The simplest apron conveyor consists of two chains made up of malleable detachable links with attachments. Wooden bars are used to fasten these attachments between the chains and the whole conveyor drags on the support.

(2) Bucket conveyors : The deep apron conveyors have been developed gradually into bucket conveyers. The simple bucket conveyors consist of deep steel stampings with overlapping edges carried on long-pitch straight-side steel chain. If the buckets are sufficiently deep, there is no distinction in construction of the horizontal conveyor and a steeply inclined bucket elevator. Bucket conveyors are useful for handling coal in powerhouses.

(4) Bucket elevators : The belt, scraper or apron conveyors are used for lifting and transportation of material, provided that the lift is short in comparison with the horizontal run so that the angle of the conveyor with the horizontal is not great. The belt conveyors and scraper conveyors are rarely run at angles greater than 15 to 20° and 30°, respectively. When the lift is more fast than this and when a straight vertical lift is needed, then in such cases an elevator is used. The usual type of elevator consists of a series of buckets carried either on chains or on a belt.

Buckets are of different types. The **Minneapolis type bucket** (fig. 2 (a)) is used for grains and pulverized material. **Flatter bucket** (fig. 2 (b)) is used for sticky materials and **stamped steel bucket** (fig. 2 (c)) is useful for heavy materials such as coal or crushed stone.



(a) Minneapolis type bucket (b) Flatter bucket (c) Stamped steel bucket

Fig. 2.

[III] Screw Conveyors

Screw conveyor is an important type of conveyor which is used for transportation of the material in form of finely divided solids or pasty solids. It consists of a spiral blade revolving around an axis (fig 3).

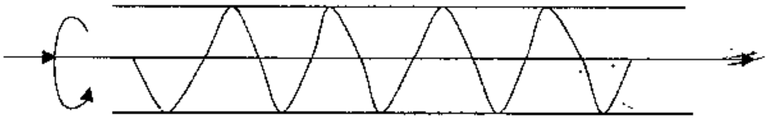


Fig. 3. Screw conveyor

[IV] Pneumatic Conveyors

The pneumatic conveyor is generally used for conveying light and bulky material. In this system, the material is transferred into suspension in a stream of air. A variety of systems are available and all of them consist of:

(i) A pump or fan for producing the stream of air

(ii) A cyclone for separating the layer particles

(iii) A bag filter for removing dust.

In a simple type of pneumatic conveyor, a pump of cycloidal type produces a moderate vacuum and its suction is connected to the conveying system. The material is sucked up through a nozzle, which may be fixed or movable. The stream with the solid in suspension goes to a cyclone separator and then to the pump. When the material carries dust, then a bag filter is placed between the separator and pump.

Generally, cement and coal industries require this type of pneumatic conveying. Schematic representation of pneumatic conveyor is shown in figure (4).

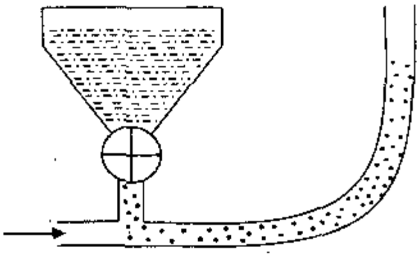


Fig. 4. Pneumatic conveyor

1.3. CRYSTALLISATION

Crystallisation process is one of the unit operations used for the production of materials on a large scale, *e.g.*, sodium chloride, aluminium sulphate and sucrose, etc. A number of organic liquids are purified by crystallisation rather than distillation. It is because the enthalpies of crystallisation are generally much lower than enthalpies of vaporisation (Table 1).

Table 1: Physical constants and enthalpies of substances

Compound	Melting point (K)	Enthalpy of *crystallisation (kJ/kg)*	Boiling *point (K)*	Enthalpy of *evaporation (kJ/kg)*
o-Cresol	304	115	464	410
m-Cresol	285	117	476	423
p-Cresol	306	110	475	435
o-Xylene	246	128	414	347
m-Xylene	225	109	412	343
p-Xylene	286	161	411	340
o-Nitrotoluene	269	120	495	344
m-Nitrotoluene	289	109	506	364
p-Nitrotoluene	325	113	511	366
Water	273	334	373	2260

After crystallisation, solvent separation and washing and drying stages are required. Crystallisation operation is of importance in processes like :

(i) Desalination of sea water

(ii) Freeze-concentration of fruit juices

(iii) Recovery of metal salts from electroplating processes

(iv) The production of materials for electronic industries and in biotechnological operations.

[I] Crystal Forms

We know that there are six classes of crystals as follows:

(1) **Cubic** : Three equal axes at 90° to each other.

(2) **Tetragonal**: *Three axes (one longer than the other two) at 90° to each other.*

(3) **Orthorhombic**: Three axes (all of different lengths) at 90° to each other.

(4) **Hexagonal**: Three equal axes in one plane at 60° to each other, one at 90° to this plane but not necessarily of the same length as others.

(5) **Monoclinic**: Two axes at 90° in one plane, and the third axis at some odd angle to this plane

(6) **Triclinic**: Three axes at odd angles to each other.

[II] Classification of Crystallisers

Crystalliser is an equipment employed for crystallisation operation. Solution crystallisers are classified according to the method by which supersaturation is performed, *e.g.*, by cooling, evaporation, vacuum, reduction and salting out.

(1) Cooling crystallisers : (a) Non-agitated vessels : The simplest type of cooling crystalliser is an unstirred tank wherein a hot feedstock solution is delivered to an open vessel for cooling. Metallic rods are sometimes suspended in the solution for the growth of crystals on them thereby reducing the amount of product that settles at the bottom of the unit. The crystallized product is collected manually. Large interlocked crystals are generally formed because of slow cooling.

(b) Agitated vessels : When an agitator is installed in an open-tank crystallizer, smaller and uniform crystals are obtained. The mother liquor retained after filtration is less in quantity and, therefore, efficient washing is possible to get the final product in pure form.

Agitated cooling crystalliser with internal circulation through a draught tube is shown in fig. (5). The agitator located in the lower region of a draught tube circulates the crystal slurry through the growth zone of the crystalliser.

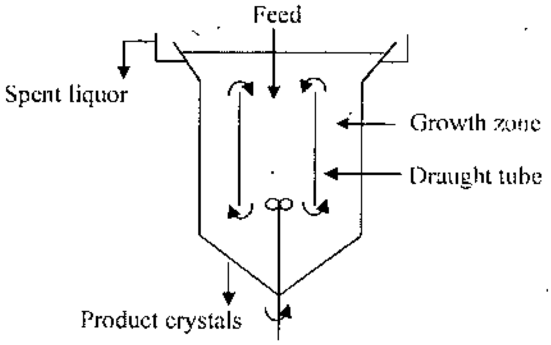


Fig. 5. Agitated cooling crystalliser with internal circulation through a draught tube

The agitated cooling crystalliser with external circulation through a heat exchanger is shown in the following fig. (6). It provides good mixing inside the unit and high rate of heat transfer between liquor and cooling.

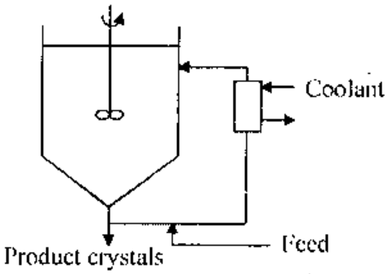


Fig. 6. Agitated cooling crystalliser with external circulation through a heat exchanger

(2) Evaporating crystallisers : When lowering of temperature does not decrease the solubility of a solute in a solvent, then super saturation of solution can be obtained by evaporating some of the solvent. Solar energy is used for this purpose throughout the world. Multiple effected evaporators–crystallisers are used in sugar industries, whereas steam-heated evaporators are used in the production of common salt from brine. The evaporating crystallisers, operated under reduced pressure for the removal of solvent, are called **reduced-pressure evaporating crystallisers**. They minimise the heat consumption and also lower the operating temperature of the solution.

(3) Vacuum (adiabatic cooling) crystallisers : In this type of crystalliser, supersaturation of the solution is obtained by simultaneous evaporation and adiabatic cooling of the feedstock. A hot saturated solution is delivered into an insulated vessel maintained under reduced pressure. If the temperature of the feed liquor is higher than the boiling point of the solution under reduced pressure existing in the vessel, the liquor cools adiabatically and the heat of crystallisation liberated by the solution evaporates the solvent to concentrate the solution.

(4) Continuous crystallisers : The continuous crystallisers are of three types :

(a) ***Forced-circulation crystalliser*** : A Swenson forced-circulation crystalliser, which operates at reduced pressure, is shown in fig. (7). The high rate of recirculation through the external heat exchanger provides good heat transfer. The crystal magma is circulated from the bottom of the evaporator body into the heat exchanger and reintroduced into the evaporator below the liquor level to create swirling action. The feedstock enters on the pump inlet side of the circulation system and the product crystal magma is removed below the conical section.

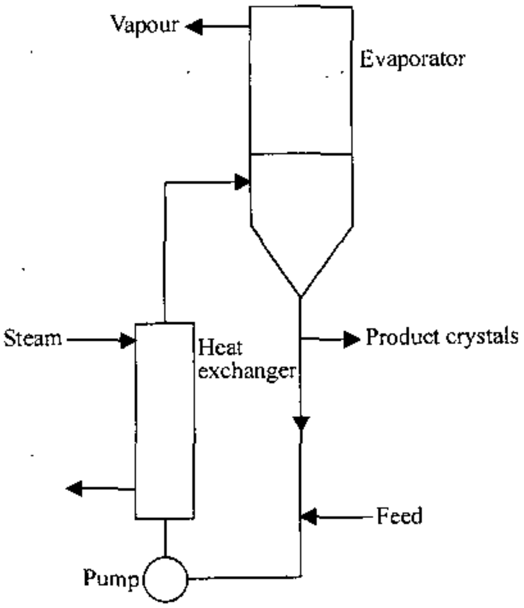


Fig. 7. Swenson forced -circulation crystalliser

(b) ***Fluidized crystallisers :*** An Oslo fluidized crystalliser is depicted in figure (8). A hot concentrated feed solution is fed into the vessel at a point directly above the inlet to the circulation pipe. The saturated solution from the upper regions of the crystalliser together with the small portion of feedstock is circulated through heat exchanger and cooled by circulating the water. Thus, solution becomes supersaturated.The product crystal magma is removed from the lower region of the vessel.

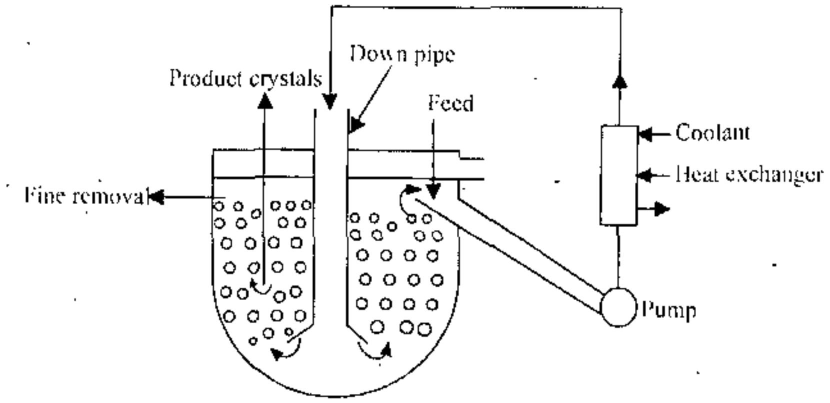


Fig. 8. Oslo fluidized bed crystalliser

(c) ***Draught tube agitated vacuum crystallisers :*** A Swenson draught-tube-baffled (DBT) vacuum crystalliser is depicted in fig. (9). A hot concentrated feed-stock enters at the base of draught pipe and a steady movement of magma and feedstock to the surface of the liquor produces a gentle boiling action over the whole cross-sectional area of the crystalliser. The internal baffle forms an annular space free of agitation and provides a settling zone for regulating the magma density. An elutriating leg is provided below the crystallisation zone to effect product classification.

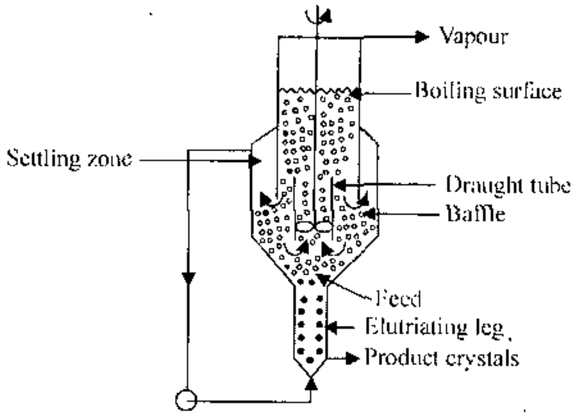


Fig. 9. Swenson draught-tube-baffled (DBT) crystalliser.

1.4. DISTILLATION

Distillation is one of the major operations in the processing industries used for the separation of liquid mixtures into their different components. It is the key operation in any oil refinery. In engineering terms, distillation columns are to be designed with a bigger range in capacity than any other type of processing equipments. For example, single columns are 0.3 to 10 m in diameter and 03–75 m in height. A distillation unit, along with the control systems, is often operated in association with several other separate units. The vertical cylindrical column provides a large number of separate stages of vaporisation and condensation.

The separation of toluene from a mixture with benzene requires only a single unit, [Fig. 10 (a)]. On the other hand, purification of crude styrene formed by the dehydrogenation of ethylbenzene requires a complex arrangement. Fig. 10 (b) shows several columns and it is essential to recycle some of the streams into the reactor.

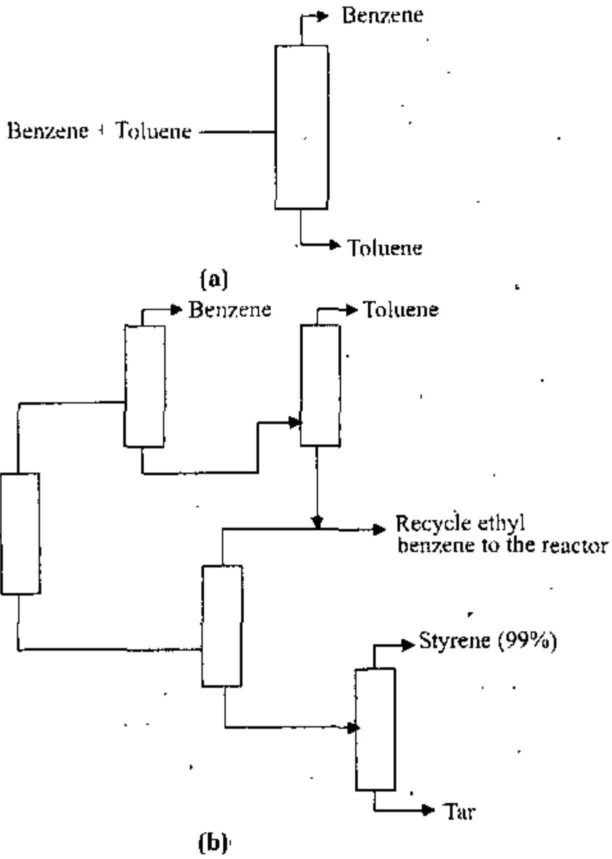


Fig. 10. Separation of toluene from benzene in a given mixture.

[I] Batch Distillation

In batch distillation, more volatile component is evaporated from the still, which becomes richer in less volatile component. Distillation is continued till the residue of still contains a material with low content of volatile material or until the distillate is no longer sufficiently pure with respect to the volatile content. Batch distillation unit is shown in figure (11).

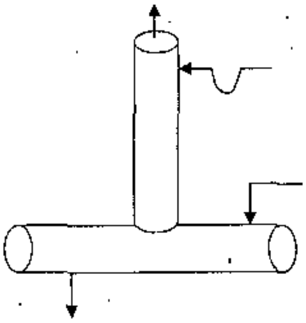


Fig. 11. Batch distillation

[II] Continuous Fractionators

Continuous fractionators [Fig. (12)] are used for continuous separation of complex mixtures of petroleum fractions in the petroleum industry. The column consists of a cylindrical structure divided into sections by a series of perforated trays. The fractionators are connected with pumps, reboilers, condensers and automatic controllers.

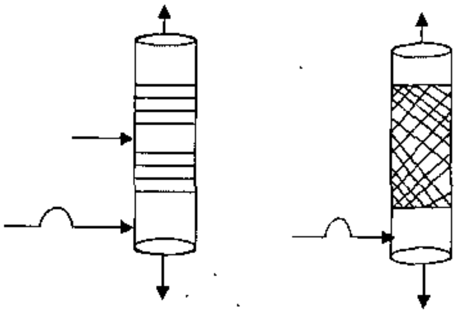


Fig. 12. Continuous fractionators

[III] Steam Distillation

Steam distillation operation is generally used for the separation of :

(i) High boiling point compounds from non-volatile impurities (for example, the separation of high boiling point but heat sensitive essential oils from water soluble impurities).

(ii) Removal of high boiling point impurities from higher boiling point compounds (for example, removal of high boiling point impurities from still higher-boiling edible vegetable oils).

In steam distillation, steam is passed directly into the liquid in the still (the solubility of the steam in the liquid must be very low). Two cases must be considered. In one case, the steam provides sufficient heat to vapourise the material concerned without itself condensing. In another case, some of the steam may condense to form a liquid water phase. According to ideal gas laws, the composition of the vapour produced in either case may be obtained from the following equation,

$$\left(\frac{m_A}{M_A}\right)\Big/\left(\frac{m_B}{M_B}\right)=\frac{P_A}{P_B}=\frac{P_A}{P-P_A}$$

where the subscript A corresponds to component being recovered, and the subscript B corresponds to steam, m = mass, M = molecular weight, P_A and P_B are the partial pressures of components A and B, P = total pressure.

If there is no liquid phase present, then according to the phase rule, the degree of freedom will be two, both total pressure and operating temperature can be fixed independently, and $p_B = P - p_A$ (which must not exceed the vapour pressure of pure water, if no liquid phase is to appear).

If a liquid water phase is present, the degree of freedom will be one. So by selecting the temperature or pressure the system is fixed with water and the other component each exerting a partial pressure equal to its vapour pressure at the boiling point of the mixture. The distillation temperature will be less than that of boiling water at the total pressure. A high boiling point organic compound may be steam distilled below 373 K at atmospheric pressure.

1.5. DRYING

In the manufacturing processes, drying of materials is the *operation performed quickly prior to packing*. The drying operation deals with the removal of water or other solvents and it often follows operations like evaporation, filtration or crystallisation. Drying is an important operation in manufacturing processes for the following reasons :

(i) To reduce the expenditure on transportation of the finished products.

(ii) To make the material suitable for handling, detergents, dyestuffs and fertilisers should be dried perfectly.

(iii) To maintain definite properties *e.g.,* free flowing nature of the salts can be maintained by proper drying.

(iv) To remove moisture from the finished product (for example: drying of gaseous fuel or benzene prior to chlorination is very essential).

In case of crystalline products, the crystals should not break during drying operation. In case of pharmaceuticals care should be taken to avoid contamination during this operation. It is also essential to prevent shrinkage (in case of paper), cracking (in case of wood), and loss of flavour (in case of fruits) during drying operation. Generally, all drying operations involve the removal of water by vaporization, which requires an additional heat (partial drying of material by squeezing in a press or the removal of water by adsorption are some exceptional cases).

[I] Drying Equipments

Classification of dryers is a difficult task because of the availability of wide range of dryer designs. However, the classification is based on the following factors :

(i) Temperature and pressure conditions in the dryer

(ii) Heating method

(iii) Means by which moist material is transported through the dryer

(iv) Any kind of mechanical aid provided at drying

(v) Method of air circulation

(vi) Heating medium

(vii) Nature of wet feed and the method of introducing it into the dryer

Tunnel drier, rotary drier and spray drier are some of the important driers.

(1) **Tunnel drier** : In tunnel drier [Fig. (13)] a series of trays or trolleys are moved through a long tunnel (which may or may not be heated) and drying takes place in a current of warm air. Tunnel drier is for drying paraffin wax, gelatin, soap, and pottery wares etc.

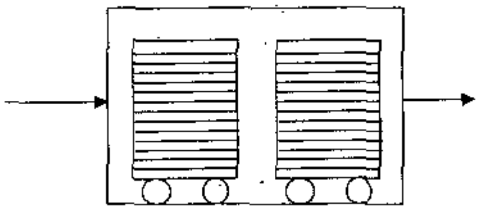


Fig. 13. Tunnel drier

(2) **Rotary drier** : A rotary drier is used for continuous drying of materials on a large scale (one tonne per hour or more). It consists of a long cylindrical shell mounted on rollers and driven at a low speed (up to 0.4 Hz is suitable). The shell is supported at a small angle to the horizontal so that material fed in at the higher end may travel through the dryer under gravity, and hot air (or gases used as the drying medium) is fed in either at the upper end of the drier to give co-current flow or at the discharge end of the machine

to give counter current flow. Heating is provided by one of the following methods:

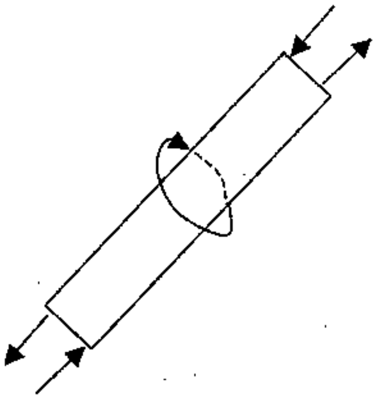


Fig. 14. Rotary drier

- **(i)** Direct heating (hot gases or air passes through the material in the drier).
- **(ii)** Indirect heating (material in an inner shell is heated externally by hot gases)

Rotary driers [Fig. (14)] are used for drying free flowing solids and also for calcining cement and lime.

(3) Spray drier : Water may be evaporated from a solution or a suspension of solid particles by spraying the mixture into a vessel through which a current of hot gases is passed. Thus, a large interfacial area is produced and, therefore, a high rate of evaporation is obtained. The drop temperature remains below the wet bulb temperature of drying gas until drying is complete. This process is convenient for drying substances (milk, coffee and plasma), which may deteriorate if their temperature rises high up.

In spray drying, it is essential to automise and redistribute under controlled conditions a wide variety of liquids such as solutions, emulsions, slurries and gels. Most of the automisers commonly used are designed for simple liquids. An automiser is a device which causes liquid to be disintegrated into drops lying within a specified size range and which controls their spatial distribution. When automisers are used for slurries and pastes, then there is a great deterioration in performance and sometimes automisers may be eroded rapidly.

The performance of spray dryer depends upon the drop size produced by the automiser and the way in which gaseous medium mixes with the drops. The schematic representation of spray dryer is shown in figure (15).

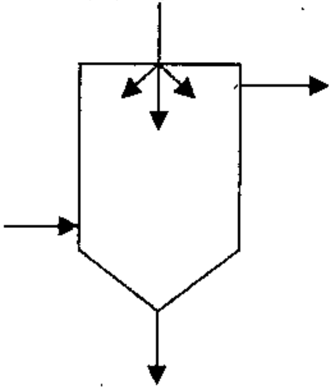


Fig. 15. Spray drier

1.6. EVAPORATION

The unit operation of evaporation is widely used for the concentration of aqueous solutions. It involves the removal of water from the solution by boiling in a suitable vessel called evaporator and withdrawing the vapour. If the solution contains dissolved solids, then the resulting liquor may become saturated so that crystal formation takes place. The liquors to be evaporated are classified as follows :

(i) Liquors which can be heated to high temperature without decomposition and those which can be heated only to about 330 K.

(ii) Liquors which form solids on concentration and those which do not form solids

(iii) Liquors which boil at nearly the same temperature as water and those which possess a much higher boiling point.

Evaporation is carried out by heating the solution to vaporise the solvent. The heat is supplied for providing the latent heat of vaporisation, and by adopting methods for the recovery of heat from the vapour (it is possible to achieve great economy in heat utilisation). The normal heating medium is low pressure exhaust steam from turbines. Special heat transfer fluids or flue gases are also useful. The designing of evaporation units (evaporators) *requires the data of heat transfer to the boiling liquids.*

[I] Types of Evaporators

Different types of evaporators, *e.g.*, single effect evaporator and multiple effect evaporator are used for evaporation operation.

(a) Single-effect evaporator : Single effect evaporators are used in industries when

(i) A cheap supply of steam is available

(ii) Expensive material of construction is used as in case with corrosive feedstock

(iii) The vapours are contaminated by impurities and therefore cannot be reused.

Single effect units are preferably operated in batch or semi-batch or continuous processes. In batch units the filling, evaporating and emptying are the consecutive steps. This type of operation is seldom used because it requir~~es a very~~ large vessel to hold the entire charge of the feed. Semi-batch is the usual mode of operation in which there is continuous addition of feed for maintaining a constant level until the entire charge attains the required product density. In continuous units there is a continuous feed and discharge and concentration of both feed and discharge remains constant. A schematic representation of single effect evaporator is shown in figure (16). The single effect evaporator us~~es more~~ than one kg of steam to evaporate one kg of water.

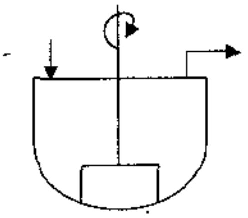


Fig. 16. Single effect evaporator

(b) Multiple effect evaporators : Multiple effect evaporators are employed for the evaporation of paper mill black liquor (paper industries), sugar syrup (sugar industries) and solutions of inorganic chemicals (inorganic chemical industries). These evaporators achieve maximum heat economy. A schematic representation of these evaporators is shown in figure (17).

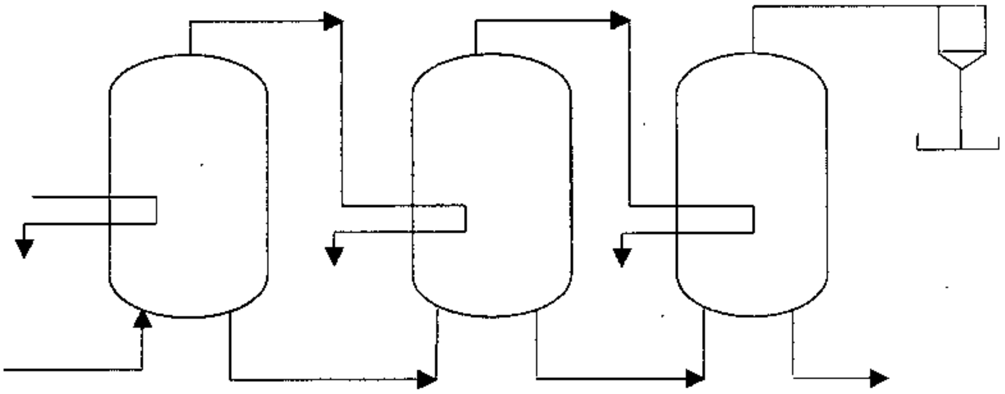


Fig. 17. Multiple effect evaporator

1.7. FILTRATION

The unit operation **filtration** deals with the separation of solids from a suspension in a liquid. This process is done with the help of porous medium or screen which retains the solid and allows the liquid to pass. In laboratory, filtration is often carried by using a Buchner funnel or a conical funnel fitted with a filter paper. In chemical industries filtration is performed in large quantities. A typical filtration operation is shown in figure (18).

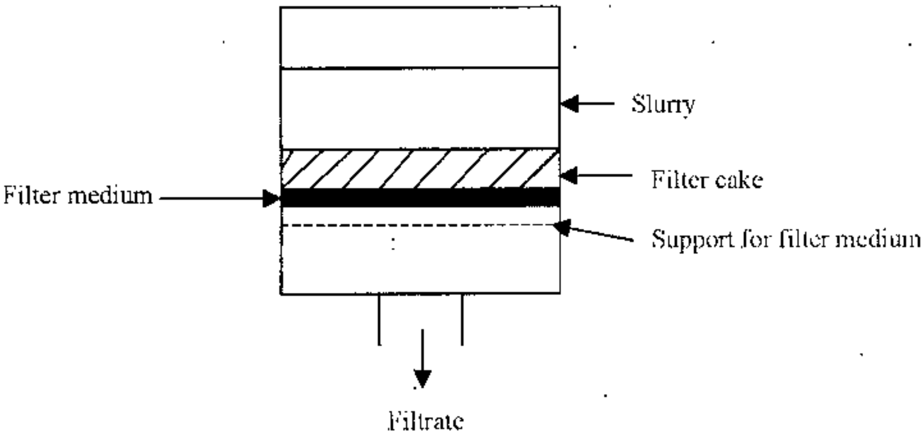


Fig. 18. A typical filtration operation

In case of solids, their physical size and properties are of prime importance. For the selection of equipment for filtration and operating conditions, following factors are to be considered:

(1) The properties of the fluid (viscosity, density and corrosive properties).
(2) The concentration of solids in suspension
(3) The quantity of material
(4) Whether it is necessary to wash the filtered solid
(5) Whether any form of pretreatment is required

Filtration is a mechanical operation and demands less energy as compared to evaporation and drying operations. The rate of filtration depends upon the following factors:

(1) Area of the filtering surface

(2) Viscosity of the filtrate

(3) Resistance of the filtered cake

(4) Resistance of the filter medium

[I] Types of Filtration

There are two types of filtration:

(i) **Cake filtration:** The particles from the suspension are deposited on the surface of a porous septum, which should offer only a small resistance to flow. As the solid builds up on septum, the initial layer from effective filter medium prevents the particles from embedding themselves on the filter cloth and ensures the particle free filtration

(ii) **Deep-bed filtration:** In this filtration, the particles penetrate into the pores of the filter medium where the impact between the particles and the surface of the medium is responsible for their removal and retention. This type is generally used for the removal of fine particles from dilute suspensions where the recovery of particles is not important. Typical examples are air and water filtration

[II] Types of Filters

Following are some of the important types of filters used for filtration operation :

(1) Bed filters : The bed filters are based on the principle of deep bed filtration in which the particles penetrate into the interstices of the filter bed where they are trapped following the impingement on the surface of the material of the bed.

In case of purification of water supplies and waste-water treatment, the granular bed filters have replaced the sand filters. The granular material (grain size 0.6-12 mm in beds 0.6-1.8 m deep) is used for the formation of beds.

(2) Bag filters : In case of liquid filtration, bag filters are completely superseded by other types of filters. The long thin bags are attached to the horizontal feed tray and the liquid flows under gravitation force. The bag filters are used for the removal of dust particles from gases. A schematic representation of bag filters is shown in fig. (19).

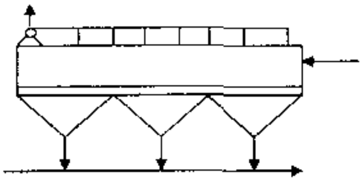


Fig. 19. Bag filter

(3) Filter press : There are two types of filter press: (a) plate and frame press and (b) recessed plate or chamber press.

(a) *The plate and frame press :* This type of press consists of plates and frames arranged alternately and supported on a pair of rails. The plates possess ribbed surface and the edges stand slightly proud. The hollow frame is separated from plate by using a hand screw or closed hydraulically using minimum pressure. This type of filter is used for making plates and fabric filter media of a variety of corrosion resistant materials. The schematic representation of the filter press is shown in fig. (20).

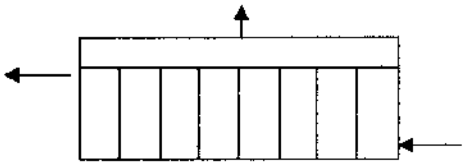


Fig. 20. The plate and frame press

(b) ***Recessed plate filter press :*** This type of press is similar to plate and frame filters except that the use of frame is obviated by recessing the ribbed surface of the plate in such a way that the individual filter chambers are formed between successive plates. The thickness of the cake formed in this press is double the depth of the recess on individual plate.

Merits of the filter press :

(i) The cost of maintenance is very low.

(ii) The joints are external and leakage is detected very easily.

(iii) High pressure operation is possible.

(iv) Filter press is used for a wide range of materials under varying operating conditions of cake thickness.

(v) Filter press provides a large filtering area.

(4) Rotary filters : A rotary filter is used for the separation of minerals from slurry, and pulp fibers from water. The schematic representation of rotary filter is shown in fig. (21).

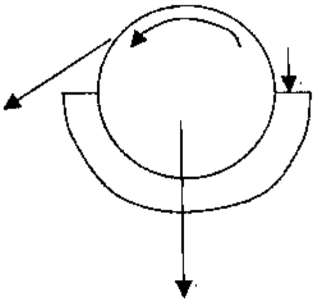


Fig. 21. Rotary filter

[III] Centrifuges

A centrifuge is a device, which uses centrifugal force for the separation of liquid from solid. Centrifugation is the development of the gravity filtration wherein the force acting on the liquid is enormously increased to more than gravitational force by applying centrifugal force. The force developed due to centrifugal action is represented by the following equation :

$$F_C = \frac{Wu^2}{g_c . r}$$

where

F_C = Force developed (lb)

W = Weight of rotating assembly plus load (lb)

u = Peripheral velocity of the basket (fps)

r = Radius of the basket (ft)

g_c = Dimensional constant, 32.2 (lb mass) (ft) / (lb force) (sec^2)

If N is the speed in rpm, then

$$u = 2\,\pi r N/60$$

Substituting the value of u and placing 32.2 for g_c gives

$$F = 0.000341\ W r N^2$$

The centrifugal separation is used extensively for the following purposes:

(i) For the separation of particles on the basis of their size or density.

(ii) For the separation of immiscible liquids having different densities.

(iii) For the filtration of suspension.

(iv) For the drying of solids preferably crystals.

(v) For breaking down of emulsion and colloidal suspension.

(vi) For the separation of gases.

(vii) For mass transfer processes.

A schematic representation of a centrifuge is shown in fig. (22).

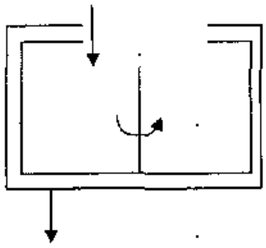


Fig. 22. A centrifuge

1.8. LEACHING

The unit operation **leaching** deals with the extraction of a soluble *constituent from a solid by using a solvent*. This operation is used for the production of concentrated solution of a solid material or for the removal of an insoluble solid (for example, a pigment) from a soluble material with which it is contaminated. The method used for extraction depends upon the proportion of soluble constituents present, its distribution throughout the solid and the nature of solid and the particle size.

When the solute is dispersed uniformly in the solid, then the dissolution of material near the surface will occur leaving behind a porous structure of the solid residue. The solvent has to penetrate this outer layer before it can reach further solute, and the process will become more difficult and there will be decrease in extraction rate. If the solute forms a very high proportion of the solid, the porous structure will be broken quickly to give a fine deposit of the insoluble residue, and the access of the solvent to the solute will not be retarded. Generally, the process can be considered under three parts as follows :

(1) Firstly, the change of phase of solute as it dissolves in the solvent.

(2) Secondly, its diffusion through the solvent in the pores of the solid to the outside of the particle.

(3) Thirdly, the transfer of solute from the solution in contact with the particles to the main bulk of the solution.

Any one of the above three processes is responsible for limiting the extraction rate.

[I] Factors Affecting the Rate of Extraction

There are four factors which influence the rate of extraction. These are (i) particle size, (ii) solvent, (iii) temperature and (iv) agitation of the fluid.

(i) **Particle size:** Particle size has a strong influence on the rate of extraction. The smaller the particle size, the greater will be the interfacial area between the solid and liquid. Therefore, the higher will be the rate of transfer of the material and the smaller will be the distance the solute must diffuse within the solid.

(ii) **Solvent:** The liquid chosen should be a good selective solvent and its viscosity should be sufficiently low to enable it to circulate freely.

(iii) **Temperature:** The solubility of the material to be extracted will increase with rise in temperature to give a higher rate of extraction. The diffusion coefficient will be expected to rise up with increase in temperature and therefore the extraction rate will be improved.

(iv) **Agitation of the fluid:** Agitation of solvent is of great importance because this increases the diffusion and hence the transfer of material from the surface of the particles to the bulk of solution. Also agitation of suspension of fine particles prevents sedimentation and therefore more effective use is made of interfacial surface.

1.9. LIQUID-LIQUID EXTRACTION

Liquid-liquid extraction is a unit operation which deals with the separation of components of a liquid mixture by treatment with a solvent in which one or more of the desired components are soluble. This operation is used in the processing of coal tar liquids, in the production of fuels in nuclear plants, and for the separation of hydrocarbons in petroleum industry. In this operation it is essential that the liquid-mixture feed and solvent are atleast partially, if not completely, immiscible. Following three stages are involved in liquid-liquid extraction.

(1) To bring the feed mixture and the solvent into intimate contact.

(2) To separate the resulting two phases.

(3) To remove and recover the solvent from each phase.

Extraction is complementary to distillation in many ways and is preferred in the following cases :

(i) When distillation requires large amount of heat

(ii) When azeotrope formation limits the degree of separation obtainable in distillation

(iii) When heating is to be avoided

(iv) When the components to be separated are different in nature

[I] Important Applications of Liquid-Liquid Extraction

(i) To separate aromatic compounds from kerosene based fuel oils for the improvement of their burning quality.

(ii) To separate aromatic compounds from paraffin and naphthenic compounds to improve the temperature viscosity characteristic of lubricating oils.

(iii) To obtain pure compounds such as benzene, toluene and xylene from catalytically produced reformates in the oil industry.

(iv) To extract phenols from coal tar liquors.

(v) In the production of acetic anhydride.

(vi) In metallurgical processes, for example, purification of uranium fuel and the recovery of spent fuel elements in the nuclear power industry by extraction methods.

(vii) In biotechnology. Many of the usual organic solvents degrade a sensitive product such as protein. This leads to the use of mild-aqueous based extractants. (water-polyethylene glycol-phosphate mixtures) which will partition and concentrate the product in one of the two aqueous layers formed.

[II] Extraction Processes

Liquid-liquid extraction operation may be performed either as a batch or as a continuous process.

(a) In a **single-stage batch process** [Fig. (23)], the solvent and solution are mixed together and then allowed to separate into two phases: one is the extract containing the required solute in the added solvent and the other is raffinate (the weaker solution with some associated solvent).

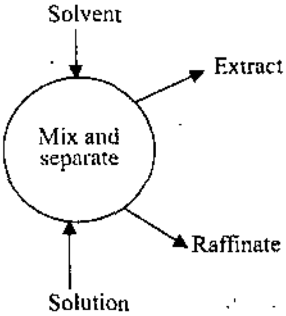


Fig. 23. Single-stage batch extraction

(b) A **continuous two-stage operation** is shown in fig. (24), where mixers and separators are shown as separate vessels.

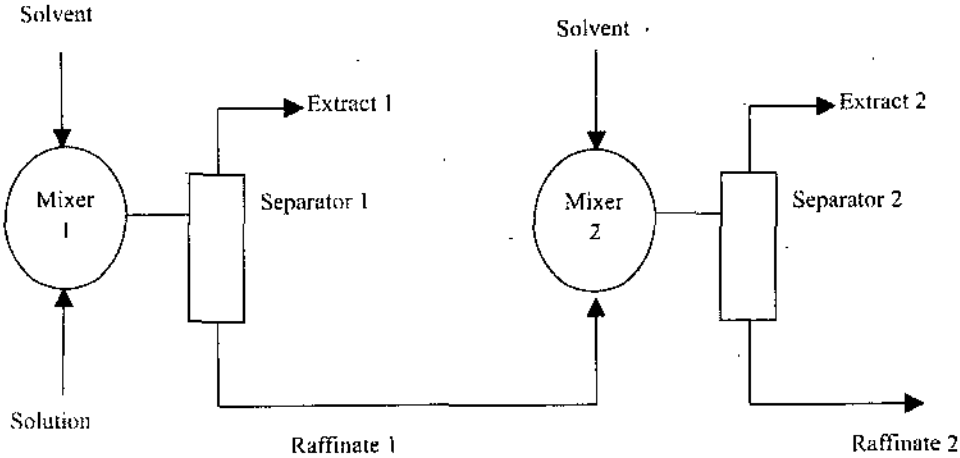


Fig. 24. Continuous two stage operation

The three main components of the equipment are,

(1) Mixer-settler.

(2) Column type of design with trays or packing as in distillation unit.

(3) A variety of units consisting rotating devices such as the Scheibel and the Podbielniak extractors.

In all the cases, the extraction units are followed by distillation in order to recover the solute and the solvent.

A system used for the separation of benzene, toluene and xylene groups from light feedstocks is shown in fig (25). The solvent used is *n*-methyl pyrolidone (NMP) with some glycol. The feed is delivered to a multistage extractor from which the raffinate (free from aromatics) is obtained at the top. The extract with solvent, aromatics and non-aromatics is distilled to provide extract recycle stream (top product) and the mixture of aromatics and solvent (bottom product). This stream is delivered to a stripper from which the glycol and aromatics are recovered.

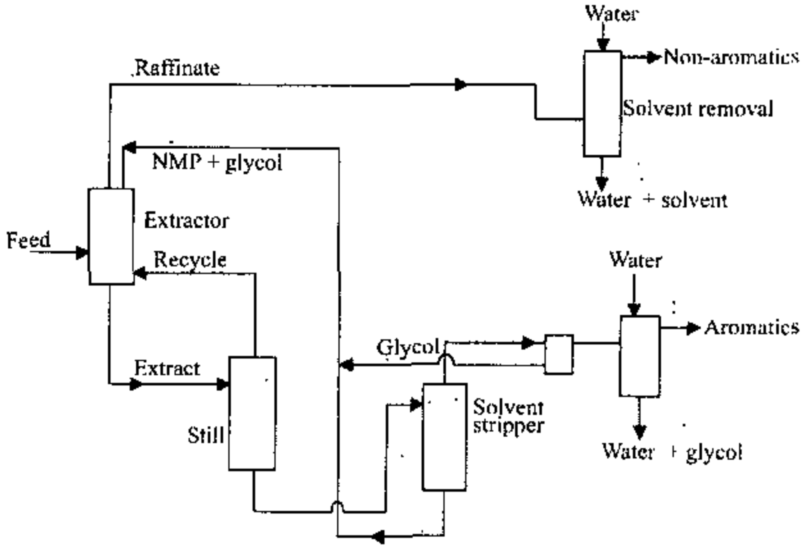


Fig. 25. Process for benzene, toluene and xylene recovery

Process for the concentration of acrylic acid by extraction with ethyl acetate is shown in fig. (26). The dilute acrylic acid solution (20%) is added to the top of the extraction column 1, and ethyl acetate solvent is added at the base. The acetate containing the dissolved acrylic acid and water received from the top of extraction column 1 is delivered to the top of distillation column 2. Here the acetate is removed as an azeotrope with water and the dry acrylic acid is recovered from the bottom.

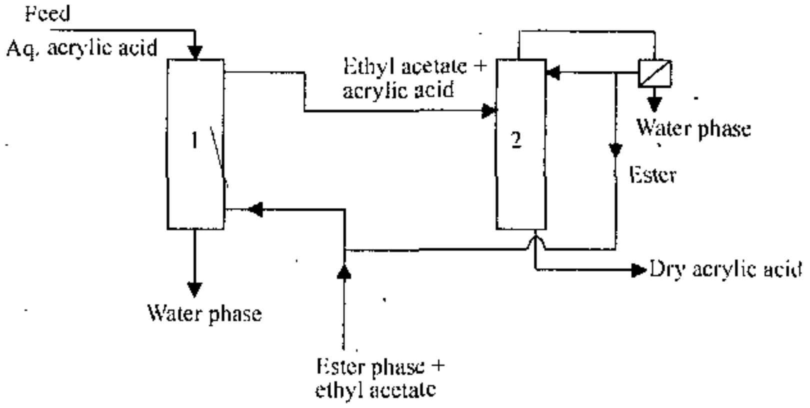


Fig. 26. Concentration of acrylic acid by extraction with ethyl acetate

1.10. MEMBRANE SEPARATION

In processing industries, sometimes it becomes very difficult and expensive to separate certain types of materials. For example,

(i) Finely dispersed solids, which possess density very close to that of the liquid phase or possess high viscosity or are gelatinous.

(ii) Low molecular weight compounds, non-volatile organics or pharmaceuticals or dissolved salts.

(iii) Biological materials, which are sensitive to their physical and chemical environment.

A new technology has been used for process separation using synthetic membranes. The membrane separation is widely used for conventionally difficult separations. They need relatively low capital and operation cost. Some of the important membrane separation processes frequently used in industries are described as follows.

[I] Dialysis

This process is used for the separation of materials in solution having large difference in their molecular weight, for example, separation of caustic from sugar or cellulose. A schematic representation *is shown in figure (27).*

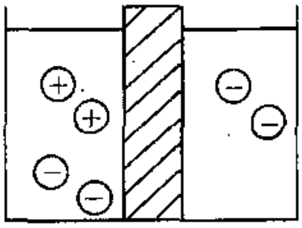


Fig. 27. Dialysis

[II] Gaseous Diffusion

The gaseous diffusion process is useful in nuclear plants preferably for the separation of $^{235}UF_6$ and $^{238}UF_6$ *i.e.* separation of light components from *heavy components.* A schematic representation is shown in fig. (28).

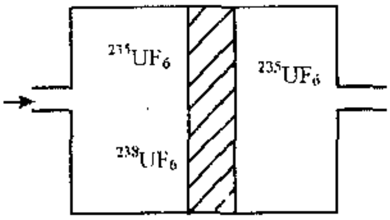


Fig. 28. Gaseous diffusion

1.11. PARTICLE SIZE REDUCTION AND ENLARGEMENT

In order to obtain a material in the required size range, it is necessary to reduce or enlarge the size of the particles of the material. Suppose, the starting material is very coarse and the final product needs to be in the form of a fine powder, then it is necessary to reduce the particle size in stages. Selection of the appropriate machine required to reduce the size in each stage depends upon the initial size of the feed and the product as well as their other physical properties like compressive strength, brittleness and stickiness. For example, a large jaw crusher may be required in first stage and a sand grinder in the final stage.

On the other hand, material of very fine powder gives rise to hazardous dust clouds during transportation and it is also very difficult to handle it. Therefore it is essential to increase the particle size of the material. The size enlargement operations include granulation for the preparation of fertilizers and compaction by using compressive force to form tablets in medicines and pharmaceuticals. Some of the operations required for reduction and enlargement cf the particle size are discussed as follows.

[I] Crushing

Crushing is used to reduce the particle size of the solid from 5 mesh to 20 mesh. A schematic representation is shown in fig. (29).

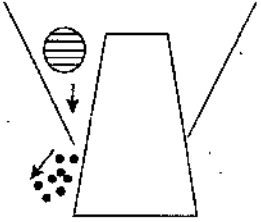


Fig. 29. Crushing unit

[II] Grinding.

Grinding is required to reduce the size of the solid balls or rods or pebbles from 4 mesh to 100 mesh. A schematic representation is depicted in fig. 30.

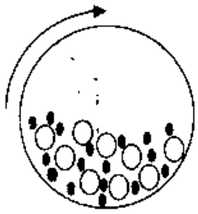


Fig. 30. Grinding unit

[III] Pelletizing

Pelletizing is used to enlarge the particle size of the material, for example, preparation of tablets from the powdered material of medicines and catalysts. A schematic representation is depicted in the following figure 31.

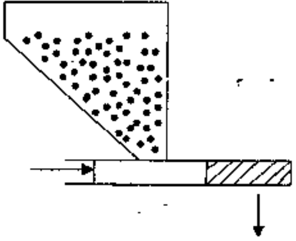


Fig. 31. Pelletizing unit

1.12. SOLID-SOLID SEPARATION

For the separation of solids from solids, operations like screening, elutriation, froth floatation, jigging and magnetic separation etc are required, which are discussed as follows,

[I] Screening

Screening is used for the separation of solids of varying sizes. Plastic or wire or fabric screens are used for this purpose. A schematic representation is shown in fig. (32).

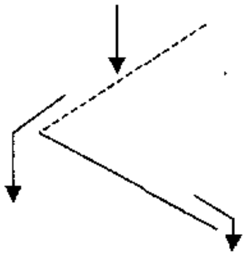


Fig. 32. Screening unit

[II] Elutriation

Elutriation is used for the removal of fine particles from large solid particles by the passage of gas to fluidise and transportation of fine particles. A schematic representation of this operation is shown in fig. (33).

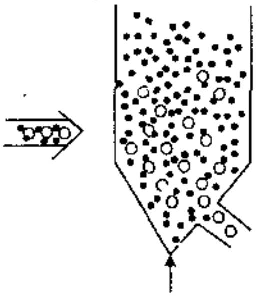


Fig. 33. Elutriation unit

[III] Froth Floatation Process

Froth floatation process is used in metallurgical industries for the concentration and purification of ore. This process is generally used for purifying the sulphide oves. Finely ground and crushed ore (~ 50 mesh) is suspended in water in the presence of floating agent such as R COONa and then it is blown with air. The desired product collects in froth and the impurities settle as gangue. A schematic representation of the froth flotation operation is shown in fig. (34).

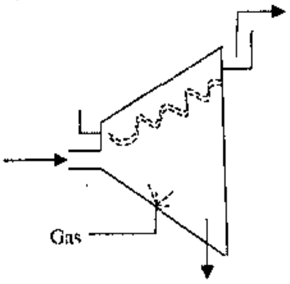
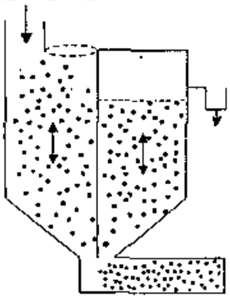


Fig. 34. Froth floatation unit

[IV] Jigging

Jigging is used for the separation of heavy minerals from lighter gangue. For example, separation of coal from heavier contaminants. Figure (35) shows schematic representation of jigging operation.



Fig, 35, Jigging unit

[V] Magnetic Separation

Magnetic separation is used to concentrate magnetic iron ore in iron industries. It is also used to remove tramp iron from feed before grinding and pulverising steps. A schematic representation of magnetic separation is shown in fig. (36).

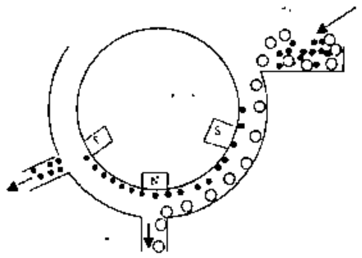


Fig. 36. Magnetic separation.

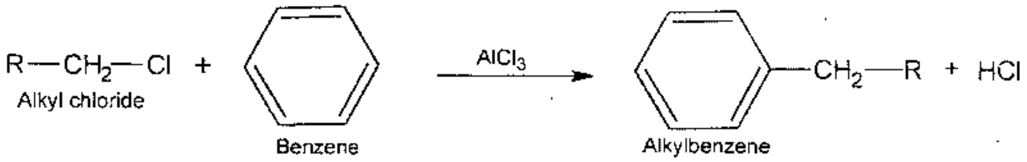
1.13. INTRODUCTION TO UNIT PROCESSES

The unit processes in organic synthesis deal with the reactions that occur in the manufacture or production of organic chemicals in chemical industries. Unit processes and unit operations are closely related with each other in manufacturing processes of organic and inorganic chemicals. The production in chemical industries is the function of chemical changes and physical changes occurring in the process. Chemical changes deal with unit process, whereas physical changes deal with unit operation. Some of the important unit processes are discussed in the following articles.

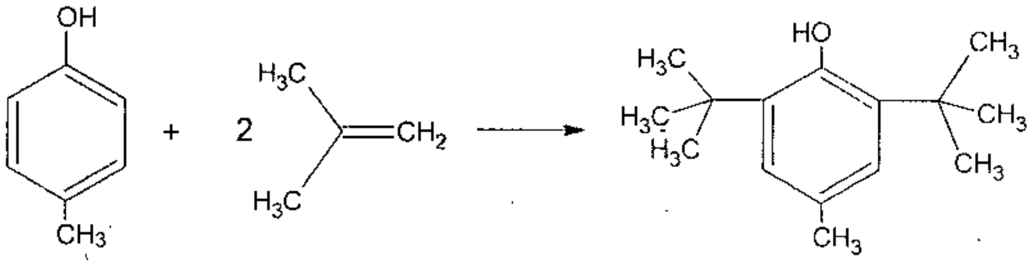
1.14. ALKYLATION

Alkylation is defined as the *introduction of an alkyl radical by substitution or addition into an organic compound*. This unit process is used in the production of anesthetics, antipyretics, alkaloids, antiseptics, detergents, dyes, explosives, flavours, hypnotics, intermediates, lubricants, medicines, perfumes, photographic chemicals, plasticizers, resins, synthetic rubber, solvents and synthetic gasolines etc.

Aluminium chloride acts as a catalyst in many alkylation reactions. Paraffins, benzene, toluene and xylene are alkylated in the presence of aluminium chloride **(Friedel-Crafts reaction)**.



Phenols and cresols are alkylated with tertiary olefins using sulphuric acid as catalyst. The preparation of 2,6- di-tert-butyl-4-methylphenol (I) is shown below.



(I)

Friedel-Craft type catalyst is also effective for such type of alkylation.

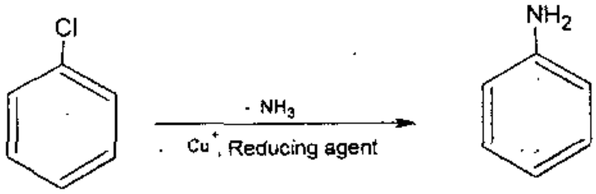
1.5. AMINATION BY AMMONOLYSIS

Amination is the process for the formation of amines by the action of ammonia. These reactions are classified as follows :

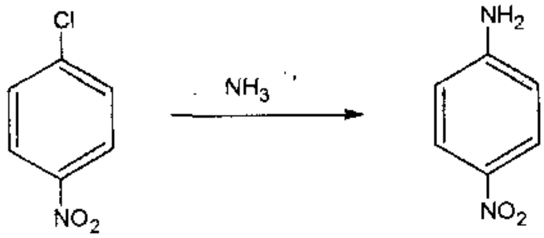
[I] Conversion of Halogeno Compounds into Amines

Alkyl halides are susceptible for the replacement of halogen by —NH_2 group by the action of ammonia but aromatic compounds require drastic conditions for the replacement of halogen by —NH_2 group. Some reactions are mentioned here. Copper, its oxide and salts are preferred when catalyst is needed for the reaction. Copper in reduced form is essential for the production of aniline because it is susceptible to oxidation. Cupric salts and oxidants, such as chlorates and nitrobenzene, are essential for the preparation of aminoanthraquinone from chloroanthraquinone.

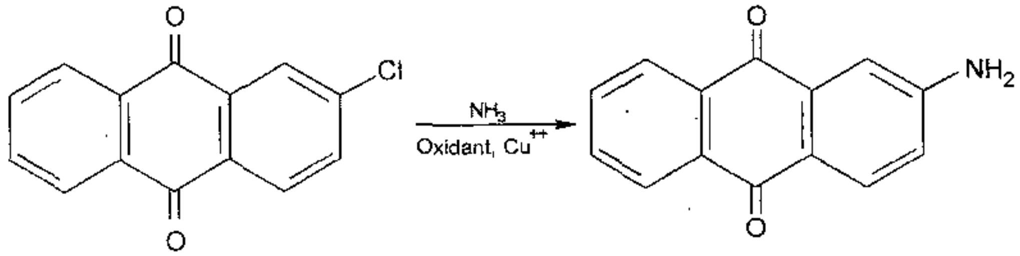
(i) Chlorobenzene to aniline



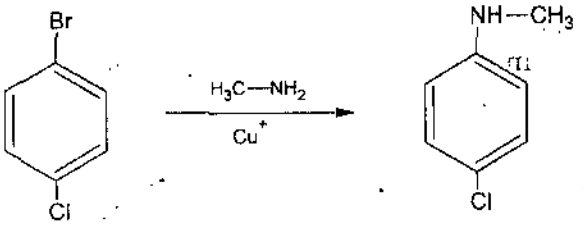
(ii) *p*-Nitrochlorobenzene to *p*-nitroaniline



(iii) 2-Chloroanthraquinone to 2-aminoanthraquinone



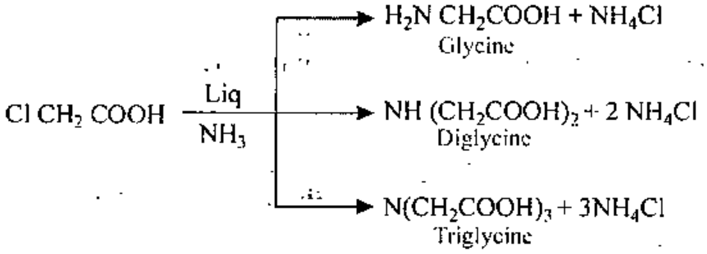
(iv) 4-Chlorobromobenzene to 4-chloro (*N*-methyl) aniline



(v) Ethylene dichloride to ethylenediamine

$$ClH_2C—CH_2Cl \xrightarrow{NH_3} H_2NCH_2CH_2NH_2$$

(vi) Chloroacetic acid to glycines



[II] Replacement of —SO_3H Group

The replacement of —SO_3H group by –NH_2 group is useful for obtaining anthraquinone series. Amination occurs at 165°C with concentrated aqueous ammonia.

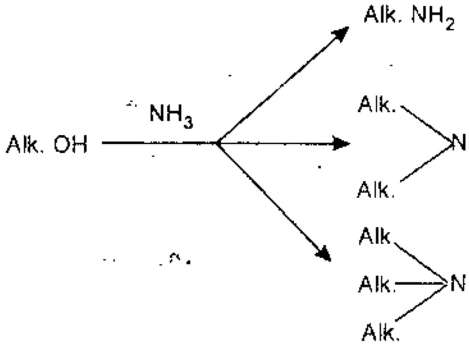
$$C_{14}H_7O_2\,.\,SO_3H + NH_3 \longrightarrow C_{14}H_7O_2.NH_2 + H_2SO_4$$

[III] Conversion of Alcohols to Amines

Alkylamines are obtained by the following three methods:

(1) Ammonolysis of alcohols over alumina catalysis.
(2) Hydroammonolysis of alcohols over hydrogenation catalysts.
(3) Hydroammonolysis of aldehydes, ketones and carboxylic acids.

Low molecular weight alkylamines (alkamines) can be prepared by passing alcohol and ammonia over a dehydrating catalyst at 350-500°C under 10-150 atm pressure. Aluminium or phosphorus compounds are used for this purpose.



Lower aliphatic alcohol on treatment with ammonia in the presence of nickel catalyst (hydrogenation catalysts) yields nitrile, which, on hydrogenation, gives corresponding amine:

$$\text{Alk.}CH_2OH + NH_3 \xrightarrow[\text{catalyst}]{\text{Ni}} \text{Alk.}\,CN \xrightarrow[\text{Ni catalyst}]{H_2} \text{Alk.}\,CH_2NH_2$$

[IV] Hydroammonolysis of Carbonyl Compounds

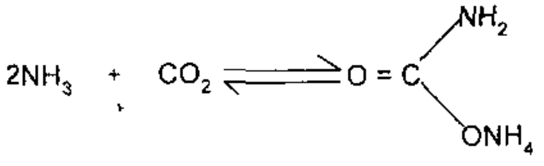
Aldehydes, ketones and carboxylic acid are converted into amines by action of ammonia in the presence of hydrogen and hydrogenation catalyst. For example, acrolein on hydroammonolysis gives *n*-propylamine and crotonaldehyde gives *n*-butylamine.

$$\underset{\text{Acrolein}}{CH_3CHCHO} \xrightarrow[\text{Hydrogenation catalyst}]{NH_3\ +\ H_2} \underset{n\text{-Propylamine}}{CH_3CH_2CH_2NH_2}$$

$$\underset{\text{Crotonaldehyde}}{CH_3CH{=}CHCHO} \xrightarrow[\text{Hydrogenation catalyst}]{NH_3\ +\ H_2} \underset{n\text{-Butylamine}}{CH_3CH_2CH_2CH_2NH_2}$$

[V] Addition Reactions

Addition of ammonia to carbon dioxide gives ammonium carbamate. At high, temperature, ammonium carbamate forms urea



Ammonium carbamate

Ammonium dithiocarbamate is formed by the addition of ammonia to carbondisulphide.

$$2NH_3 + CS_2 \longrightarrow H_2N\,CS\,SNH_4$$

Ammonium dithiocarbamato

[VI] Reaction of Ammonia with Hydrocarbons

Ammonia reacts with hydrocarbons, in the presence of a catalyst and at higher temperature, to give nitriles or cyanides.

$$C_6H_5CH_3 + NH_3 \xrightarrow[\text{Catalyst}]{524\text{–}552°C} C_6H_5CN + 3H_2$$

$$C_6H_5CH = CH_2 + NH_3 \xrightarrow[\text{Catalyst}]{480\text{–}600°C} C_6H_5CN + CH_4 + H_2$$

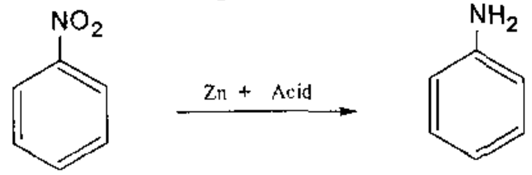
$$C_6H_5C_2H_5 + NH_3 \xrightarrow[\text{Catalyst}]{480\text{–}600°C} C_6H_5CN + CH_4 + 2H_2$$

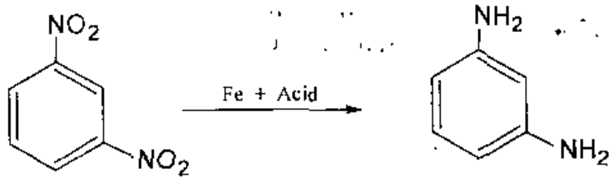
1.16. AMINATION BY REDUCTION

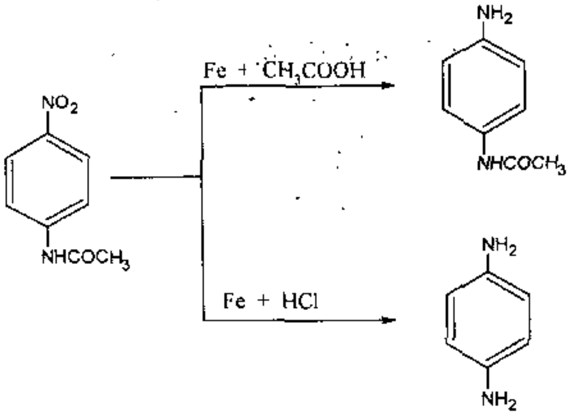
Amination by reduction deals with the synthesis of amines. A number of reduction methods are used for the synthesis of amines as shown below :

[I] Reduction by Metal and Acid

Zinc, tin and iron are used as metals and HCl, H_2SO_4, CH_3COOH and HCOOH etc are used as acids, *e.g.*,







[II] Catalytic Reduction

This process involves the use of hydrogen and a catalyst (nickel, copper, platinum, palladium or molybdenum sulphide). It is used to form aliphatic and aromatic amines.

$$RNO_2 + 3H_2 \longrightarrow RNH_2 + 2H_2O$$

$$RCN + 2H_2 \longrightarrow RCH_2NH_2$$

$$RCONH_2 + 2H_2 \longrightarrow RCH_2NH_2 + H_2O$$

$$RCSNH_2 + 2H_2 \longrightarrow RCH_2NH_2 + H_2S$$

[III] Sulphide Reduction

Sulphide reduction has wide applications with respect to partial reduction and application in anthraquinone series. Sodium sulphide, sodium hydrosulphide, sodium polysulphide etc are employed. The alkali metal sulphides are used for preparation of nitroamines from dinitro compounds, for reduction of nitrophenols and for reduction of nitroanthraquinones. The activity of alkali sulphides in the reduction of nitro compounds is due to the ease with which they take up oxygen. The reactions are shown as follows :

$$4RNO_2 + 6Na_2S + 7H_2O \longrightarrow 4RNH_2 + 3Na_2S_2O_3 + 6NaOH$$

$$RNO_2 + Na_2S_2 + H_2O \longrightarrow RNH_2 + Na_2S_2O_3$$

$$4RNO_2 + 6NaHS + H_2O \longrightarrow 4RNH_2 + 3Na_2S_2O_3$$

[IV] Electrolytic Reduction

Aliphatic and aromatic nitro compounds are reduced to amines under different conditions

$$RNO_2 + 6H^+ + 6e^- \longrightarrow RNH_2 + 2H_2O$$

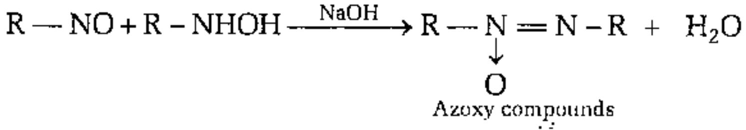
Most of the catholytes are aqueous or aqueous alcoholic solutions of minerals. In most of the cases promotors (stannous chloride, cupric chloride, titanium chloride) are used. Copper, nickel and mercury cathodes are employed.

[V] Metal and Alkali Reduction

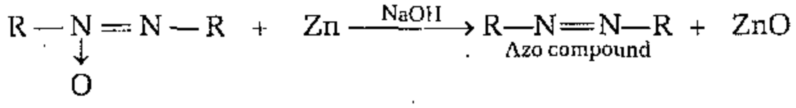
This process is used for the synthesis of azoxy, azo and hydrazo compounds. Nitrobenzene and its homologues can be reduced step-by-step in the presence of zinc or iron in alkaline solution to give hydrazo compound.

$$R - NO_2 + Zn \xrightarrow{NaOH} \underset{\text{Nitroso derivative}}{R - NO} + ZnO$$

$$R - NO + \underset{\text{nitroso derivative}}{Zn} + H_2O \xrightarrow{NaOH} \underset{\substack{\text{Hydroxylamine}\\ \text{derivative}}}{R - NHOH} + ZnO$$



$$R - NO + R - NHOH \xrightarrow{NaOH} \underset{\text{Azoxy compounds}}{R - \underset{\underset{O}{\downarrow}}{N} = N - R} + H_2O$$



$$R-\underset{O}{\underset{\downarrow}{N}}=N-R \;+\; Zn \xrightarrow{NaOH} \underset{\text{Azo compound}}{R-N=N-R} \;+\; ZnO$$

$$R-N=N-R \;+\; Zn \;+\; H_2O \xrightarrow{NaOH} \underset{\text{Hydrazo compound}}{R-NH=NH-R} \;+\; ZnO$$

[VI] Sodium Hydrosulphite Reduction

Sodium hydrosulphite (hyposulphite), $Na_2S_2O_4$, in alkaline solution is used to reduce very insoluble nitro compounds which cannot be reduced by economical process.

$$RNO_2 + 3Na_2S_2O_4 + 6NaOH \longrightarrow RNH_2 + 6Na_2SO_3 + 2H_2O$$

[VII] Sulphite Reduction

Aromatic nitro compounds can be reduced by sodium sulphite and bisulphite to give mixture of amine and aminoaryl sulphonic acid.

$$RNO_2 + 3Na_2SO_3 + H_2O \longrightarrow RNH_2 + 3Na_2SO_4$$

$$2RNO_2 + 6NaHSO_3 + 2H_2O \longrightarrow 2RNH_2 + 3Na_2SO_4 + 3H_2SO_4$$

$$R(H)NO_2 + 2Na_2SO_3 + NaHSO_3 \longrightarrow R(SO_3Na)NH_2 + 2Na_2SO_4$$

$$2R(H)NO_2 + 6NaHSO_3 \longrightarrow 2R(SO_3H)NH_2 + 3Na_2SO_4 + H_2SO_4$$

1.17. CALCINATION

Calcination is a process which is used in the manufacture of cement and magnesium compounds.

$$CaCO_3 \xrightarrow[600\text{–}900°C]{Heat} CaO + CO_2\uparrow$$

$$2CaMg(CO_3)_2 \xrightarrow{Heat} 2CaO + 2MgO + 4CO_2\uparrow$$

$$4Mg(OH)_2 \xrightarrow[700°C]{Heat} 4MgO + 4H_2O\uparrow$$

1.18. CARBONYLATION

Monsanto acetic acid process is the best example of carbonylation (insertion of CO) process. More than one million pounds of acetic acid is being produced annually by this process using methanol and carbon monoxide. The reaction proceeds in the presence of reactive catalyst $[Rh(CO)_2I_2]$

$$CH_3OH + CO \xrightarrow{[Rh(CO)_2I_2]^-} \underset{\text{Acetic acid}}{CH_3COOH}$$

Acetic anhydride is also produced by carbonylation process. Reaction between methyl acetate and carbon-monoxide is depicted below which proceeds in the presence of reactive catalyst $[Rh(CO_2)I_2]^-$

$$CH_3COOCH_3 + CO \xrightarrow{[Rh(CO)_2I_2]^-} \underset{\text{Acetic anhydride}}{(CH_3CO)_2O}$$

1.19. DOUBLE DECOMPOSITION

Double decomposition process is used in the manufacture of inorganic chemicals. For example, potassium nitrate is made by double decomposition between sodium nitrate and potassium chloride. A hot concentrated solution of $NaNO_3$ and solid KCl are dumped into the reaction kettle. On heating, KCl crystals are converted to NaCl crystals and hot KNO_3 solution collects at the bottom of the kettle. This process gives a good yield of KNO_3.

$$NaNO_3\,(aq.) + KCl\,(s) \longrightarrow NaCl\,(s) + KNO_3\,(aq.)$$

Calcium sulphate is obtained by the double decomposition of calcium hydroxide and sulphuric acid

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\,H_2O$$

1.20. ESTERIFICATION

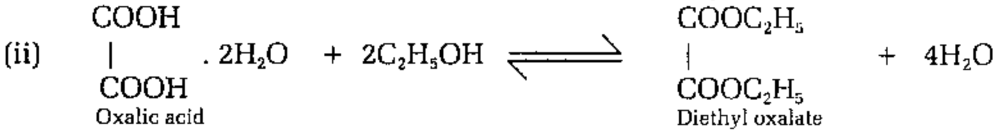
Esterification is one of the unit processes by which esters are formed. An ester is defined as *a compound formed by substitution of an organic radical for an ionizable hydrogen of an acid.* This process is used in he manufacture of esters, *viz.*, ethyl acetate, butyl acetate, cellulose acetate, vinyl acetate as well as in the manufacture of alkyd resins, plasticizers and polyester resins etc.

[I] Esterification by Organic Acids

Esters like ethyl acetate, diethyl oxalate and butyl acetate are produced by direct esterification of carboxylic acid using H_2SO_4 as catalyst.

(i) $$\underset{\text{Acetic acid}}{CH_3COOH} + C_2H_5OH \rightleftharpoons \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

(ii)



$$\underset{\text{Oxalic acid}}{\begin{array}{l}COOH\\ |\\ COOH\end{array}} .2H_2O + 2C_2H_5OH \rightleftharpoons \underset{\text{Diethyl oxalate}}{\begin{array}{l}COOC_2H_5\\ |\\ COOC_2H_5\end{array}} + 4H_2O$$

(iii) $$CH_3COOH + n\text{-}C_4H_9OH \longrightarrow \underset{n\text{-Butyl acetate}}{CH_3COO\,C_4H_9} + H_2O$$

[II] Esterification by Acid Anhydrides

Esterification of an alcohol by an anhydride is faster than that by the corresponding acid. The reactions taking place are irreversible because products formed do not interact to give starting material. For example,

$$(CH_3CO)_2O + C_2H_5OH \longrightarrow CH_3COO\,C_2H_5 + CH_3COOH$$

$$(CH_3CO)_2O + (CH_3)_3C\,OH \longrightarrow CH_3COO\,C\,(CH_3)_3 + CH_3COOH$$

$$(CH_3CO)_2O + C_6H_5\,ONa \longrightarrow CH_3COO\,C_6\,H_5 + CH_3COONa$$

[III] Esterification by Acid Chloride

Acid chlorides are widely employed in esterification reactions. Use of acid chlorides is better than acid anhydrides because acid chlorides are easily prepared and the inorganic by-products formed in esterification processes are readily removed from the esters produced. Some esterification reactions are depicted below :

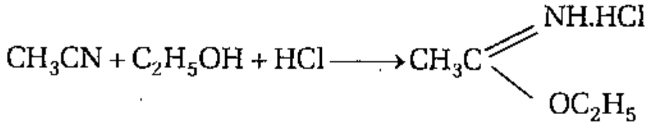
$$C_2H_5OH + ClCOCl \longrightarrow C_2H_5OCOCl + HCl$$

$$C_2H_5OH + C_2H_5OCOCl \longrightarrow (C_2H_5O)_2\,CO + HCl$$

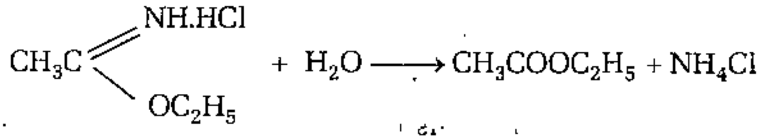
$$C_6H_5ONa + CH_3COCl \longrightarrow C_6H_5OCOCH_3 + NaCl$$

[IV] Esterification by Nitriles (Esters from Nitriles)

This process requires higher temperature and more time for completion. In this process nitrile is dissolved in appropriate alcohol and the solution is then saturated with hydrogen chloride. The amino ether hydrochloride formed is then treated with water to get ester. In this process, sulphuric acid acts as a catalyst.



$$CH_3CN + C_2H_5OH + HCl \longrightarrow CH_3C\begin{cases}=NH.HCl\\ -OC_2H_5\end{cases}$$



$$CH_3C\begin{cases}=NH.HCl\\ -OC_2H_5\end{cases} + H_2O \longrightarrow CH_3COOC_2H_5 + NH_4Cl$$

[V] Esterification by Metal Salts and Alkyl Halides (Esters from Metal Salts and Alkyl Halides)

Metal salt of acid on treatment with an alkyl halide gives corresponding alkyl ester.

$$CH_3COONa + BrC_2H_5 \longrightarrow CH_3COOC_2H_5 + NaBr$$

$$CH_3COONa + ClCH_2C_6H_5 \longrightarrow CH_3COOCH_2C_6H_5 + NaCl$$

[VI] Esterification by Acetylene (Esters from Acetylene)

In the presence of a suitable catalyst, acetylene and acetic acid react to from a vinyl ester or an ester of ethylidene glycol.

$$HC \equiv CH + CH_3COOH \xrightarrow{Hg(OAc)_2} CH_3COOCH = CH_2$$

$$HC \equiv CH + 2CH_3COOH \xrightarrow{Hg(OAc)_2} CH_3CH(OCOCH_3)_2$$

[VII] Esters of Inorganic Acids

Esters of inorganic acids are formed by direct esterification of alcohol by nitric acid.

$$C_2H_5OH + HNO_3 \longrightarrow C_2H_5ONO_2 + H_2O$$

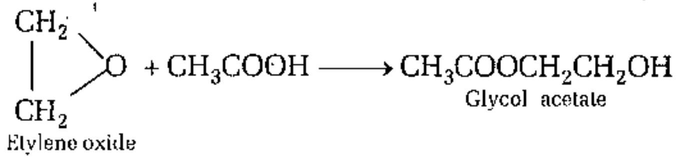
$$\underset{\text{Glycerol}}{C_3H_5(OH)_3} + 3\,NHO_3 \longrightarrow \underset{\text{Glyceryl trinitrate}}{C_3H_5(ONO_2)_3} + 3H_2O$$

$$\underset{\text{Cellulose unit}}{[C_6H_7O_2(OH)_3]} + 3\,NHO_3 \longrightarrow \underset{\text{Nitrocellulose unit}}{[C_6H_7O_2(ONO_2)_3]} + 3H_2O$$

Esters of inorganic acids (nitric, sulphuric, and phosphoric acid) are of commercial importance.

[VIII] Esterification by Ethylene Oxide

Glycol acetate is formed by reaction of acetic acid and ethylene oxide in the presence of sulphuric acid as a catalyst. Ethylene oxide is passed through heated acetic acid solution containing sulphuric acid.



$$(CH_2)_2O + CH_3COOH \longrightarrow \underset{\text{Glycol acetate}}{CH_3COOCH_2CH_2OH}$$

[IX] Esterification by Ketene

Esters are produced by reacting ketene with alcohols in the presence of a suitable catalyst, without formation of any by-product.

$$H_2C=CO + C_2H_5OH \longrightarrow CH_3COOC_2H_5$$

1.21. HALOGENATION

Halogenation (chlorination/bromination/fluorination/iodination) process is defined as the *process of introduction of one or more halogen atoms into an organic compound.* Halogenation involves addition, substitution and replacement reactions. These reactions may require halogenating agent and a suitable catalyst. Most of the catalysts are halogen carriers. Active carbon, clays also catalyse halogenation process.

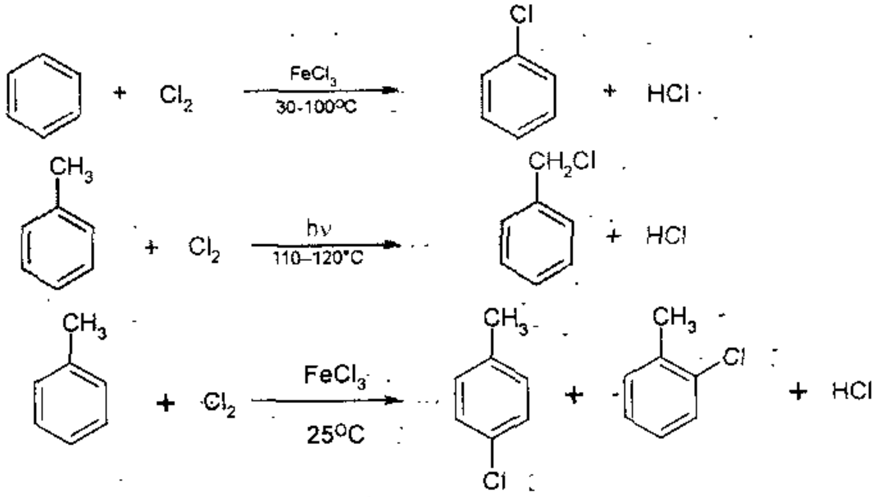
[I] Chlorination

Various methods, used for the preparation of chlorine compounds, are summarized as follows :

(1) Action of Cl_2

$$H_2C{=}CH_2 + Cl_2 \xrightarrow{FeCl_3} ClCH_2CH_2Cl$$

$$CH_4 + Cl_2 \xrightarrow{400\text{-}500^\circ C} CH_3Cl + CH_2Cl_2 + HCl$$



(2) By the action of HCl as chlorinating agent

$$HC{\equiv}CH + HCl \xrightarrow{HgCl_2} H_2C{=}CHCl$$ (Addition reaction)

$$2\,C_6H_6 + 2\,HCl + O_2 \xrightarrow{CuCl_2} 2\,C_6H_5Cl + 2\,H_2O$$

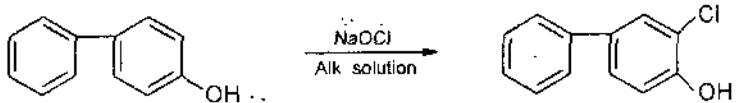
(Substitution reaction)

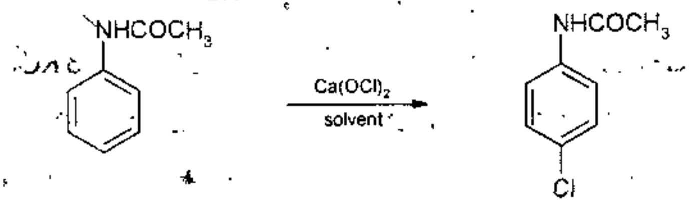
$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$$

(Replacement reaction)

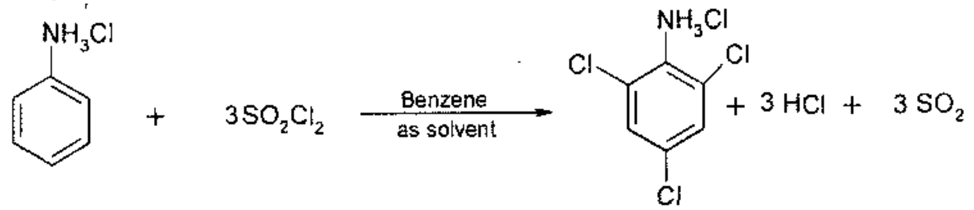
(3) By the action of phosgene as chlorinating agent

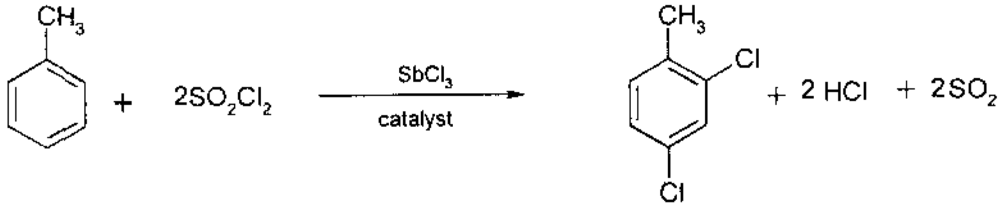
(4) By the action of sodium hypochlorite as chlorinating agent





(5) By the action of sulphuryl chloride as chlorinating agent





(6) Sandmeyer and Gattermann reactions

$$RN_2Cl + Cu_2Cl_2 \xrightarrow{HCl} RCl + N_2 + Cu_2Cl_2 \text{ (Sandmeyer reaction)}$$

$$RN_2Cl \xrightarrow[Cu]{HCl} RCl + N_2 \text{ (Gattermann reaction)}$$

(7) By the action of phosphorus chloride as chlorinating agent

$$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$$

$$3RCOONa + PCl_5 \longrightarrow 3RCOCl + NaPO_3 + 2NaCl$$

(8) By the action of thionyl chloride as chlorinating agent

$$ROH + SOCl_2 \longrightarrow RCl + SO_2 + HCl$$

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

[II] Bromination

Bromine, bromides and alkaline hypobromites are used in bromination reactions.

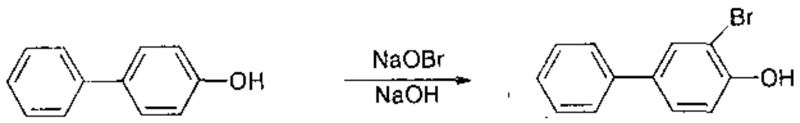
Addition reaction,

$$H_2C{=}CH_2 + Br_2 \longrightarrow BrCH_2CH_2Br$$

Replacement reaction,

$$C_2H_5OH + KBr + H_2SO_4 \longrightarrow C_2H_5Br + KHSO_4 + H_2O$$

Substitution reaction,



[III] Iodination

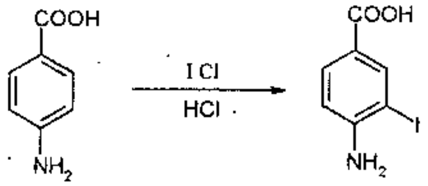
Hydriodic acid (HI) and alkali hypoiodite (KOI) are used for iodination reactions as agents.

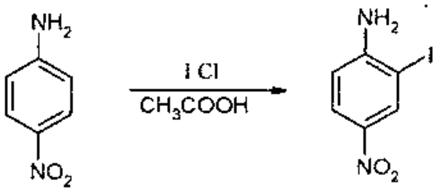
$$H_2C{=}CH_2 + HI \longrightarrow CH_3CH_2I$$

$$CH_3COCH_3 + 3\,KOI \xrightarrow{\text{Alkali}} CH_3\,CO\,Cl_3 + 3\,KOH$$

$$CH_3\,CO\,Cl_3 + KOH \longrightarrow CH_3COOK + CHI_3$$

Iodine monochloride is used as a catalyst for iodination of amino compounds.



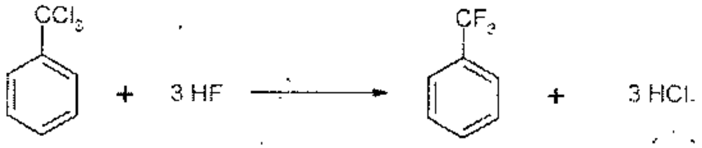


[IV] Fluorination

Fluorination is carried out by using fluorinating agent such as hydrogen fluoride (HF) and metal fluorides (cobalt trifluoride, antimony pentafluroide, silver difluroide, lead tetrafluoride and manganic trifluoride etc) to obtain fluoro compounds. Some typical fluorination reactions are represented as follows :

$$HC{\equiv}CH + HF \xrightarrow[\Delta]{\text{Catalyst}} CHF{=}CH_2$$

$$HC{\equiv}CH + 2HF \xrightarrow[\Delta]{\text{Catalyst}} CHF_2CH_3$$



$$CF_2 = CClF + 2CoF_3 \xrightarrow{100\text{–}300°C} CF_3CClF_2 + 2CoF_2$$

$$\left(CH_2CH_2\right)_n + 2n\,CoF_3 \xrightarrow{275\text{-}350°C} \left(CF_2CF_2\right)_n + 2n\,CoF_2 + 4n\,HF$$

Aromatic fluorides are obtained by action of hydrogen fluoride on aromatic diazo compounds.

$$RN{=}NCl + HF \longrightarrow RF + HCl + N_2$$

Alkali hydrogen sulphates and acid chloride on treatment with NaF and KF produce organic fluorides as follows :

$$RHSO_4 + NaF \longrightarrow RF + NaHSO_4$$

$$RCOCl + KF \longrightarrow RCOF + KCl$$

1.22 HYDROGENATION

The unit process of **hydrogenation** consists of the reaction of compounds with molecular hydrogen in the presence of catalysts. The reactions in which addition of hydrogen to molecule takes place or the reactions in which cleavage of molecule by hydrogen (destructive hydrogenation) takes place are included in hydrogenation reactions. Hydrogenation process also includes isomerisation and cyclisation reactions, which occur in the presence of molecular hydrogen and catalyst.

[I] Catalytic Hydrogenation

Catalytic hydrogenation is applied to the materials of different molecular weights and structures (rubber, vitamins, proteins, steroids, nylons etc). Catalysts like nickel or chromium are used in hydrogenation process.

Hydrogenation of alkene, in the presence of Wilkinson catalysts Rh Cl $(PPh_3)_3$, is one of the best examples of homogenous catalysis.

$$CH_2{=}CH_2 + H_2 \xrightarrow{Rh\,Cl\,(PPh_3)_3} CH_3{-}CH_3$$

[II] Coal Hydrogenation

Coal hydrogenation process is used to produce motor fuels but it is not economical. However, credit goes to this process for various by-products like phenols, cresols, xylenes, toluenes, naphthalenes and liquefied hydrocarbon gases.

[III] Petroleum Hydrogenation

In petroleum processing, mild hydrogenation is used particularly in product finishing of naphtha, kerosene, diesel, heating oil and lubricating oils.

[IV] Fat Hydrogenation

Fat hydrogenation process represents the addition of hydrogen to fatty acids, especially edible oils (cottonseed and soybean etc).

Two types of fat (edible and non-edible) are obtained due to hardening of whale oil, fish oil and vegetable oils (linseed, soyabean and cottonseed oil), by the addition of hydrogen under pressure. Edible fats are used in baking industries whereas non-edible fats are used in soap industry. Non-edible fats also find use in leather dressing, making of candles and manufacture of paints and pharmaceutical ointments.

1.23. HYDROFORMYLATION

Hydrofarmylation is a process in which addition of hydrogen and formyl group takes place across carbon-carbon double bond to give aldehyde or aldehyde derivatives. $Co_2\,(CO)_8$ or $Rh(CO)_3\,(PPh_3)_2$ is used as a catalyst. More than five million tons of aldehyde and aldehyde derivatives are produced annually by this process.

$$2RCH{=}CH_2 + CO + H_2 \longrightarrow RCH_2\,CH_2\,CHO$$

1.24. HYDROLYSIS

Hydrolysis involves the reactions in which water undergoes double decomposition with another reacting compound. Both organic and inorganic compounds undergo hydrolysis.

$$KCN + H_2O \longrightarrow KOH + KCN$$

$$C_5H_{11}Cl + H_2O \longrightarrow C_5H_{11}OH + HCl$$

Following are the important types of hydrolysis :

(i) Hydrolysis with water.

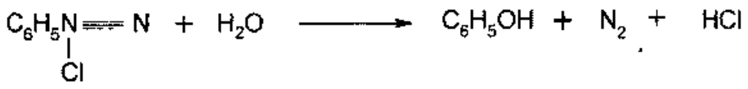
(ii) Hydrolysis with aqueous acid.

(iii) Hydrolysis with aqueous alkali.

(iv) Hydrolysis with enzymes as catalysts.

[I] Hydrolysis with Water

Acid anhydrides, lactones, lactides and ethylene oxide are easily hydrolyzed by water. Diazonium salt on heating with water undergoes hydrolysis quickly.



$$C_6H_5\underset{\substack{| \\ Cl}}{N}\equiv N + H_2O \longrightarrow C_6H_5OH + N_2 + HCl$$

Phenol can be prepared from aniline by this route but it is not economical.

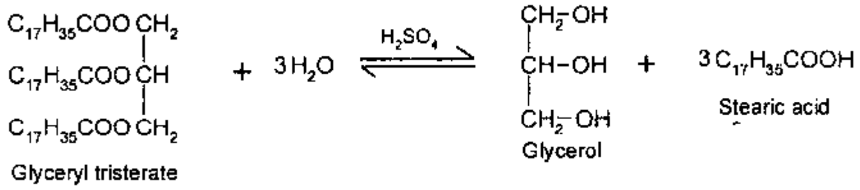
Benzene sulphonic acid undergoes hydrolysis by water (steam) to give benzene and sulphuric acid.

$$C_6H_5SO_3H + \underset{\text{Steam}}{H_2O} \longrightarrow C_6H_6 + H_2SO$$

[II] Acid Hydrolysis

For acid hydrolysis, hydrochloric acid and sulphuric acid are generally used. Esters, and amides undergo acid hydrolysis rapidly.

$$CH_3COOC_2H_5 + H_2O \overset{HCl}{\rightleftharpoons} CH_3COOH + C_2H_5OH$$



[III] Alkali Hydrolysis

Some of the alkali hydrolysis reactions are represented as follows.

$$C_6H_5Cl + NaOH\,(aq.) \longrightarrow C_6H_5OH + NaCl + H_2O$$

$$2CH_3Cl + Ca(OH)_2 \xrightarrow{\text{Steam}} 2CH_3OH + CaCl_3$$

When vapours of chlorinated hydrocarbon are mixed with steam over lime, alcohol is obtained.

[IV] Enzymatic Hydrolysis

Manufacture of industrial alcohol from molasses in the presence of enzyme *invertase* and hydrolysis of starch into maltose and glucose by enzyme *amylase* are the well-known examples of enzymatic hydrolysis.

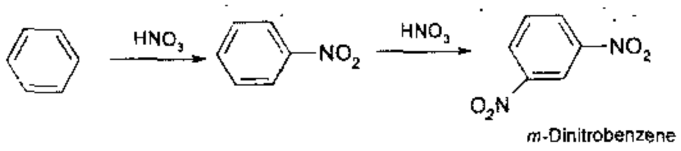
1.25. NITRATION

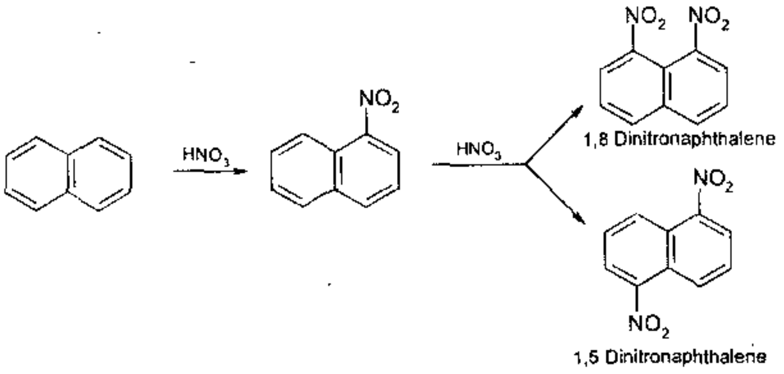
Nitration process involves *introduction of one or more nitro groups (–NO₂) into the reacting molecule*. Nitro group may attach to carbon to give nitroaromatic or nitroparaffinic compound, or to oxygen to form a nitrate ester, or to nitrogen to from a nitramine. The entering NO_2 group may replace a number of different monovalent atoms or groups of atoms.

Nitration process is useful for the synthesis of organic chemicals, dyestuffs, pharmaceuticals and explosives. Amines are prepared generally by the reduction of corresponding nitro compounds. A number of nitrating agents are used to perform nitration, for example, nitric acid (aqueous, fuming or concentrated), mixture of nitric acid with sulphuric acid (or acetic acid/phosphoric acid/acetic anhydride/chloroform), nitrogen pentoxide (N_2O_5) and nitrogen tetroxide (N_2O_4).

[I] Aromatic Nitration

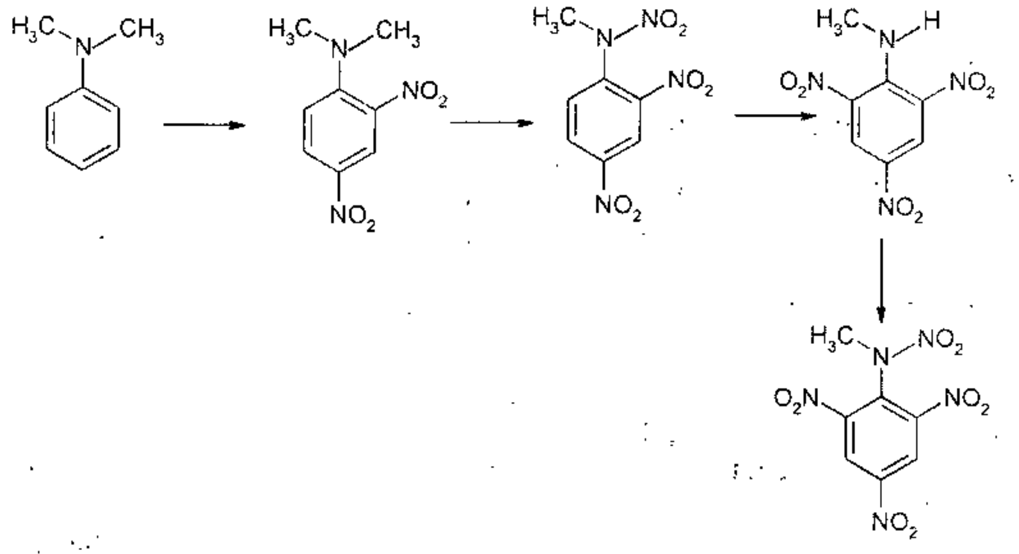
Benzene and naphthalene undergo nitration by nitric acid to given corresponding nitro compounds.





[II] N-Nitroso Compounds

Nitramines are included in N-nitroso compounds. Nitramines are used as explosives and propellents. Tetryl (2, 4, 6 trinitro-N-nitro-N-methylaniline) and RDX (trimethylenetrinitramine) are used as explosives. Tetryl is prepared by nitration and nitrolysis of dimethylaniline with mixed acid.


Tetryl

[III] Nitration of Acetylene

Nitration of acetylene in the presence of nitric acid gives tetranitromethane [$(NO_2)_4C$], which is used to increase the cetane number of diesel and is also used as military explosive.

$$HC{\equiv}CH + 6HNO_3 \longrightarrow (NO_2)_4C + CO_2 + 4H_2O + 2NO_2$$

[IV] Nitrate Esters

Nitrate esters are synthesized by the action of nitric acid on alcohol.

$$ROH + HNO_3 \longrightarrow \underset{\text{Nitrate ester}}{RONO_2} + H_2O$$

The nitrates of polyhydroxy compounds (glycerol) are used as explosives and propellants. Mixture of nitric acid and sulphuric acid is used for nitration reactions.

1.26. OXIDATION

Oxidation is one of the important unit processes used in the preparation of organic and inorganic chemicals. The different types of oxidation reactions are discussed below. Oxidising agents such as permanganates, dichromates, chlorates, hypochlorous acid and salts, peroxides, nitric acid and fuming sulphuric acid etc are used for oxidation reactions. The different types of oxidative reactions are described as follows.

[I] Dehydrogenation

Dehydrogenation is a process which is used for the conversion of primary alcohol into an aldehyde and a secondary alcohol into ketone.

$$C_2H_5OH + 1/2\,O_2 \longrightarrow CH_3CHO + H_2O$$

$$CH_3CHOHCH_3 + 1/2\,O_2 \longrightarrow CH_3COCH_3 + H_2O$$

[II] Dehydrogenation and Introduction of Oxygen

Aldehydes are prepared from hydrocarbons and benzoic acid is prepared from benzyl alcohol by this process :

$$CH_4 + O_2 \longrightarrow HCHO + H_2O$$

$$C_6H_5CH_2OH + O_2 \longrightarrow C_6H_5COOH + H_2O$$

[III] Introduction of Oxygen

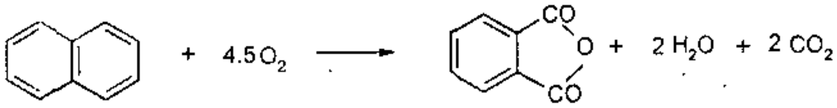
Acetic acid is formed by oxidation of acetaldehyde and an alcohol is formed by oxidation of a hydrocarbon as represented below :

$$CH_3CH + 1/2\,O_2 \longrightarrow CH_3COOH$$

$$(C_6H_5)_3CH + 1/2\,O_2 \longrightarrow (C_6H_5)_3COH$$

[IV] Dehydrogenation, Introduction of Oxygen and Carbon Linkage Destruction

The best example of this process is the oxidation of naphthalene to form phthalic anhydride :



[V] Oxidation of Olefins

Oleic acid undergoes oxidation in the presence of alkaline $KMnO_4$ to give dihydroxystearic acid.

$$CH_3(CH_2)_7\,CH{=}CH\,(CH_2)_7\,COOH \xrightarrow[\text{alkali}]{KMnO_4} CH_3(CH_2)_7\,CHOH\,CHOH\,(CH_2)_7\,COOH$$

[VI] Dehydrogenation and Molecular Condensation

Diphenyl is obtained from benzene by this process

$$2\,C_6H_6 + \frac{1}{2}O_2 \longrightarrow \underset{\text{Diphenyl}}{C_6H_5 - C_6H_5} + H_2O$$

[VII] Peroxidation

Peroxidation reactions occur under certain conditions. For example, isopropylbenzene reacts with air to give isopropylbenzene peroxide. Ultraviolet radiation catalyzes the reaction.

$$\text{Isopropylbenzene} \xrightarrow[\text{UV}]{\text{Air}} \text{Isopropylbenzene peroxide}$$

1.27. POLYMERISATION

When two compounds have same empirical formula but they differ in molecular weight, then the more complicated compound is called a **polymer** of the simple one (**monomer**). Polymerisation is defined as an *intermolecular combination that is functionally capable of proceeding indefinitely*, The terms polymer and polymerisation are used mainly in connection with high molecular weight compounds.

Polymerisation process is of two types as mentioned below :

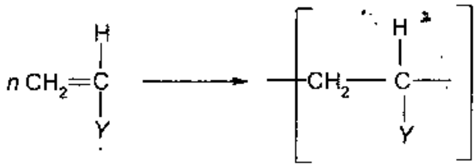
(i) Addition polymerisation

(ii) Condensation polymerisation.

[I] Addition Polymerisation

Addition polymerisation occurs among molecules that contain double or triple bonds. It also occurs between bifunctional compounds, which result from the opening of ring structures, e.g., ethylene oxide. Addition polymerisation does not involve liberation of small molecules.

Olefinic compounds of the type $H_2C=CHY$ (where Y = H, X, –COOR and CN etc) undergo addition polymerisation



$$n\,CH_2=\underset{Y}{\overset{H}{C}} \longrightarrow \left[-CH_2-\underset{Y}{\overset{H}{C}}-\right]_n$$

Addition polymerisation takes place in three possible ways:

(a) Head to tail $-CH_2.CHY-CH_2-CHY-$

(b) Head to head and tail to tail $-CHY\ CH_2-CH_2\ CHY-CHY\ CH_2-CH_2$ CHY–

(c) At random arrangement involving (a) and (b).

Addition polymerisation proceeds in the presence of catalyst. Polymerisation of olefins can be catalysed by ionic type or radical type catalyst.

Two important examples of addition polymerisation are represented as follows

(i) Ethylene to polyethylene

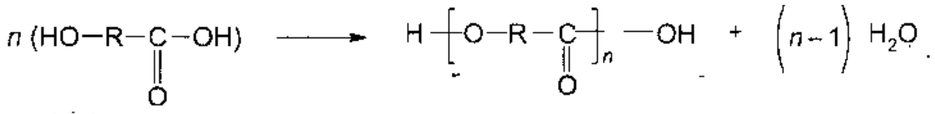
$$\underset{\text{Ethylene}}{H_2C=CH_2 + H_2C=CH_2} \longrightarrow \underset{\text{Dimer}}{CH_2-CH_2\ CH_2-CH_2} \xrightarrow{C_2H_4} \underset{\text{Polyethylene}}{\cdot\!\left[CH_2-\right]_n^{\cdot}}$$

(ii) Vinyl chloride to polyvinyl chloride (PVC)

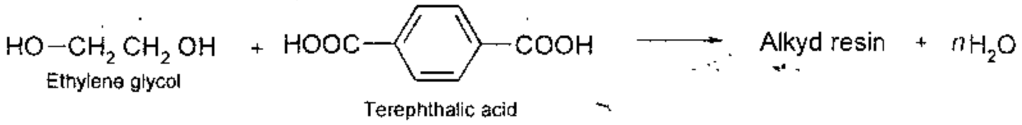
$$H_2C=CHCl + H_2C=CHCl \longrightarrow H_3C-CHCl-CH=CHCl \xrightarrow{H_2C=CHCl} \underset{\text{Polyvinyl chloride}}{\left[C_2H_3Cl\right]_n}$$

[II] Condensation Polymerisation (Polycondensation)

In this process, bi-or polyfunctional molecules condense with each other with elimination of small molecules (such as water, hydrogen chloride, ammonia etc.) as the reaction proceeds. For example,



$$n\,(HO-R-\underset{\|\atop O}{C}-OH) \longrightarrow H\left[O-R-\underset{\|\atop O}{C}\right]_n-OH + (n-1)\,H_2O$$



$HO-CH_2\,CH_2\,OH$ + HOOC–C₆H₄–COOH → Alkyd resin + nH_2O

Ethylene glycol

Terephthalic acid

1.28. SULPHONATION

Sulphonation is defined as a *process which introduces sulphonic acid group (—SO_2OH) or the corresponding salt or sulphonyl halide group (—SO_2Cl) into an organic compound.* These groups may be attached to carbon or nitrogen atom. Sulphonation reactions include :

(i) Sulphochlorination

(ii) Halosulphonation

(iii) Sulphoxidation

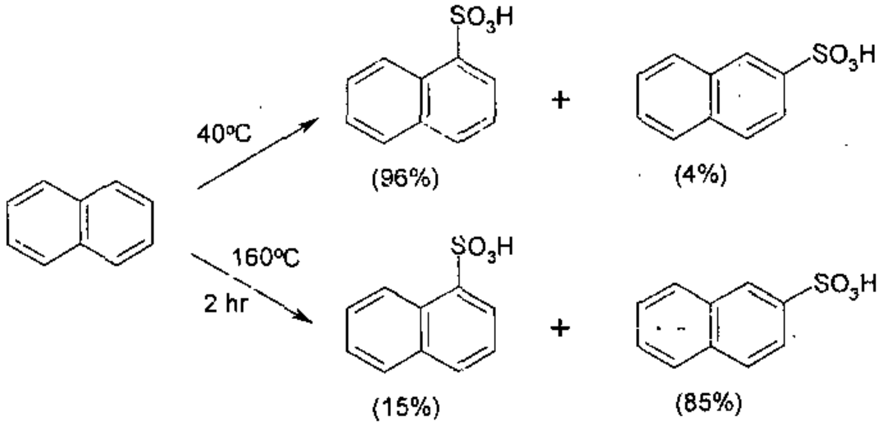
(iv) Sulphoalkylation, Sulphoacylation and Sulphoarylation.

Sulphonation reactions are carried out using sulphonating agents. The important sulphonating agents are represented as follows :

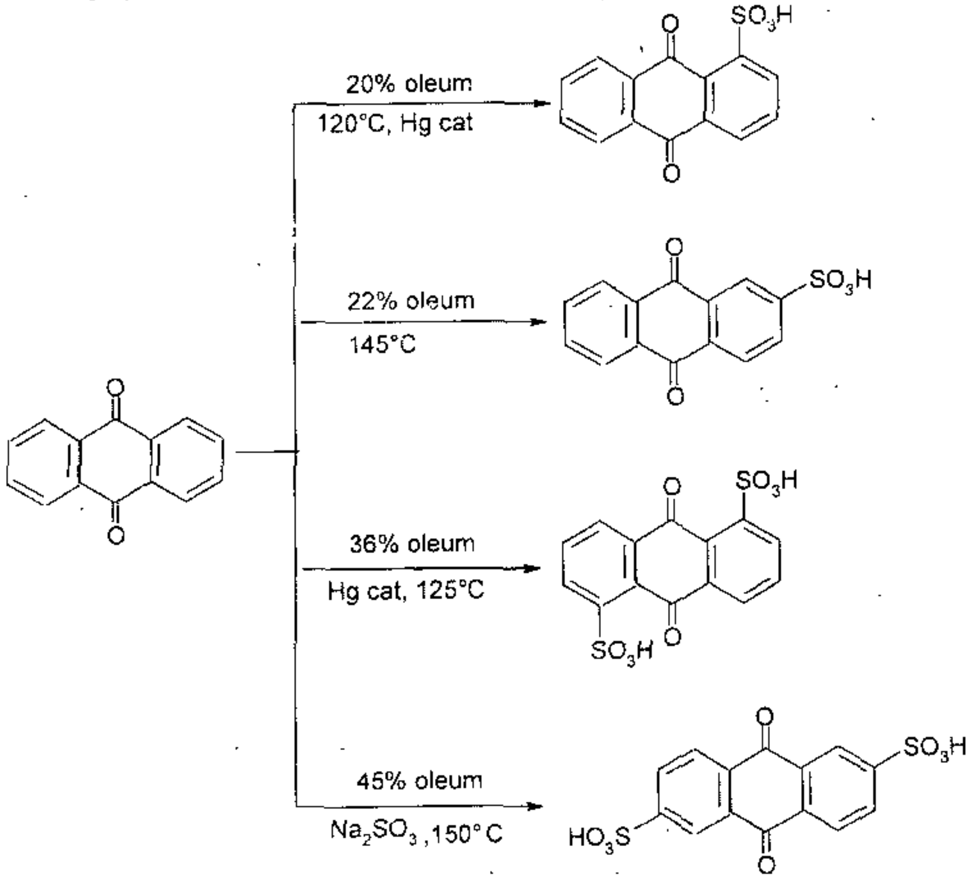
(a) SO_3 and compounds thereof (SO_3, oleum, conc. H_2SO_4, chlorosulphonic acid, SO_3 adducts with organic compounds)
(b) SO_2 group (Sulphurous acid, SO_2 with chlorine, SO_2 with oxygen etc)
(c) Sulphoalkylating agents (hydroxy-and aminomethane-sulphonates, ethylenesulphonic acid)

[I] Sulphonation of Aromatic Compounds

The sulphonic acids of naphthalene, naphthol and napthyl-amine are used as intermediate for the synthesis of azo and triphenylmethane dyes. Naphthalene undergoes sulphonation with acid or oleum.



Anthraquinone sulphonates are used as dye intermediates. Anthraquinone undergoes sulphonation in the presence of oleum to give different products.



[II] Sulphonation of Aliphatic Compounds

SO_3 and its hydrates are not suitable for sulphonation of saturated aliphatic compounds because oxidative decomposition takes place or the reaction does not take place. Long chain fatty acids are sulphonated with SO_3 to give α-sulpho acids.

$$RCH_2COOH + SO_3 \longrightarrow RCH_2(SO_2OH)COOH$$

[III] Sulphoxidation

It involves sulphonation of alkane by using SO_2 and O_2. The reaction proceeds in the presence of acetic anhydride.

$$RH + SO_2 + O_2 + (CH_3CO)_2O \longrightarrow RSO_2OOCOCH_3 + CH_3COOH$$

$$RSO_2OOCOCH_3 + SO_2 + 2H_2O \longrightarrow RSO_2OH + CH_3COOH + H_2SO_4$$

[IV] Sulphochlorination

It involves introduction of —SO_2Cl group into an alkane by using SO_2 and CI_2 in the presence of a catalysts such as actinic light

$$RH + SO_2 + Cl_2 \xrightarrow{\text{catalyst}} RSO_2Cl + HCl$$

[V] Sulphoalkylation

Sulphomethylation is one of the sulphoalkyation reactions. Phenols and ketones, and amines and amides undergo sulphomethylation by using sodium hydroxymethanesulphonate (sulphomethylating agent) as depicted in the following reactions

$$HOC_6H_5 + HOCH(R)SO_3Na \longrightarrow HOC_6H_4CH(R)SO_3Na + H_2O$$

$$R'NH_2 + HOCH(R)SO_3Na \longrightarrow R'NHCH(R)SO_3Na + H_2O$$

[VI] Uses of Sulphonates

Sulphonates are used as intermediates for the preparation of organic compounds not containing sulphur. Phenols (phenol, resorcinol, naphthol, hydroxyanthraqninoes and 8-hydroxyqninoline etc) are prepared by caustic fusion of various sulphonates. Naphthalene sulphonates and anthraquinone sulphonates are used as dye intermediates.

STUDENT ACTIVITY

1. What is leaching process ?

2. Define distillation.

3. What is esterification ? Give one common example.

4. How are products obtained by nitration process ?

5. Name the different types of polymerisation.

SUMMARY

- Conveying is a unit operation which carries out the transportation of solids and fluids.
- Crystallisation is a unit operation in which materials are obtained on a large scale.
- Distillation is a process in which a liquid mixture is separated into different components.
- Drying is the unit operation used for drying of materials before packing.
- Evaporation is the process used for the concentration of aqueous solutions.
- Filtration is a process used for separating a solid from a suspension.
- Leaching is a process used for the extraction of a soluble component from a solid by using a solvent.
- The particle size of a material can be reduced by crushing, grinding etc.
- The particle size of a material can be enlarged by pelletizing process.
- Screening is a process for the separation of solids of different sizes.
- Elutriation is a process used for the removal of fine particles from large solid particles by the passage of gas to fluidise and transportation of fine particles.
- Froth floatation process is used for metallurgical purposes. It is used to concentrate the sulphide ores.
- Esterification is a process is which an alcohol reacts with acid.
- Hydrolysis is a process is which a salt reacts with water to form an acid and a base.
- Halogenation is the process of introducing one or more halogen atoms into an aromatic compound.
- Halogenation involves addition, substitution and replacement reactions.
- When two compounds have same empirical formula but differ in molecular weight, then the more complicated compound is called a polymer. The process is known as polymerisation.

TEST YOURSELF

Answer the following questions :

1. In how many ways can addition polymerisation occur ?
2. What is condensation polymerisation ?

3. How are aromatic compounds sulphonated ?
4. Mention the uses of sulphonates.
5. What is halogenation ? How is it carried out for organic compounds ?
6. Define esterification. How is it carried out ion acid anhydrides, acid chlorides, nitriles ?
7. Give some examples of reaction which occur due to amination by reduction.
8. What is alkylation ?
9. Give one example of Friedel-Crafts reaction.
10. Write short notes on the following :
    (i) Solid-solid extraction (ii) Liquid-liquid extraction
    (iii) Membrane separation.
11. Define and explain the following terms :
    (i) Conveying (ii) Leaching
    (iii) Crystallisation (iv) Filtration
    (v) Distillation (vi) Evaporation
12. When ethanol is treated with HCl, we get
    (i) C_6H_5Cl (ii) C_2H_5Cl
    (iii) Cl_2 (iv) $C_2H_5.C_6H_5$
13. Primary alcohol on dehydrogenation gives
    (i) Ketone (ii) Aldehyde
    (iii) Hydrocarbon (iv) Both ketone and aldehyde
14. Toluene when treated with NH_3 at 500–550°C in presence of a catalyst it gives :
    (i) $C_6H_5NH_2$ (ii) C_6H_5COOH
    (iii) C_6H_5CN (iv) C_6H_5NC
15. **Fill in the blanks :**
    (i) $HC = CH + HF \xrightarrow[\text{Catalyst}]{\Delta} \ldots$
    (ii) Benzene sulphonic acid on hydrolysis by steam gives …… & ……
    (iii) …….. and …….. esters is obtained by hydrolysis of higher fatty acid esters,
    (iv) Ammonium carbonate is also known as ……….. .
    (v) Ethylene on polymerisation gives ………. .
    (vi) C_6H_5 . C_6H_5 is known as ………….

ANSWERS

12. (ii) **13.** (ii) **14.** (iii)

15. (a) $CHF{=}CH_2$, (b) benzene, H_2SO_4, (c) glycerol, (d) urea
(e) polyethylene, (f) Diphenyl.

❑❑❑

UNIT
2

PETROCHEMICALS AND POLYMERS

STRUCTURE

LEARNING OBJECTIVES

After studying this chapter, you will learn about petrochemicals, their manufacture and uses. Besides this, you will also learn about polymers, polymerisation techniques, types of polymers, introductory idea about rubber, vulcanisation etc.

2.1. INTRODUCTION

The relatively pure identifiable substance derived from petroleum and used in the chemical trade is called a **petrochemical.** Isopropyl alcohol (isopropanol) is the first organic chemical obtained on a large scale from petroleum base. The tremendous growth of petrochemicals is connected with research in the field of modern chemicals and chemical engineering.

The oil companies are entering into chemical business and chemical companies are entering into the oil business, and therefore, most of the organic chemicals are regarded as petrochemicals. More than 80% of organic chemicals are petrochemicals. The end products of petroleum industries are listed as follows :

- Adhesives
- Agrochemicals
- Alcohols
- Ammonia
- Dyes
- Explosives
- Fertilizers and pesticides
- Flavours and perfumes

- Detergents
- Industrial gases
- Lubricants
- Medicinal products
- Nitrogen industries
- Paints
- Industrial carbon
- Food additives
- Plastics and polymers
- Rubber and rubber chemicals
- Solvents
- Surface coatings
- Synthetic fibers
- Synthetic motor fuels

The basic raw materials, as mentioned in table 1, which are supplied by petroleum refineries or natural gas companies, are **liquefied petroleum gas LPG,** natural gas, gas from cracking operations, liquid distillate (C_4 to C_6), distillate from special cracking processes and selected or isomerised cyclic fractions from aromatics. Most of these substances are useful as fuels.

In petroleum refineries, the mixtures are generally separated into different components and then converted chemically into reactive precursors or converted into stable chemicals within the plant.

Table 1. Primary precursors: Petroleum – petrochemical complex

Raw materials by distillation	**Precursors by conversion**	**Intermediates by conversion**	**Finished products by conversion**
Paraffins and cyclics	Olefins, diolefins, acetylene, aromatics	Various inorganics and organics	Inorganics and organics
Natural gas			Carbon black
Sulphides	H_2S	S, H_2S	H_2SO_4
Hydrogen		Synthesic gas	NH_3
Methane			Methanol, Formaldehyde
Refinery gases	Acetylene	Acetic acid	Acetates
	Isobutene	Acetic anhydride	Fibers
Ethane	Ethylene	Isoprene	Rubber
Propane	Propylene	Ethylene oxide, etc	Rubber and Fiber
n-Butane	*n*-Butenes		Rubber
Hexane		Butadiene	
Heptanes			
Refinery naphthas			
Naphthalene	Cyclopentadiene	Adipic acid	Fibres
Benzene	Toluene	Ethylbenzene	Styrene
		Styrene	Rubber
		Cumene	Phenol, acetone
		Alkylbenzene	
Toluene	Toluene	Phenol	Plastics
		Benzonic acid	Phenol
Xylenes	*o*-, *m*-, *p*- xylenes	Phthalic Anhydride	Plastics
Methyl naphthanes	Naphthalene		

The lower members of the paraffin and olefin series (methane, ethylene, propylene and butylenes) and cyclic compounds (benzene, toluene, xylene, ethylbenzene) are the most economical sources of organic raw materials.

[I] Petrochemicals from Methane

The petrochemicals derived from methane are given in the chart shown in fig. (1). The uses of some of the petrochemicals derived from methane are as follows (figures in parenthesis show the use percentage) :

(i) **Ammonia:** Fertilizers (80), plastics and fibres (10), explosives (05).

(ii) **Carbon black:** Tyres (65), other rubber (25), colorant and fillers (10).

(iii) **Methanol:** Polymers (50), solvent (10).

(iv) **Methyl chloride:** Silicones (57), tetramethyl lead (19).

(v) **Methylene chloride:** Paint remover (30), aersol propellant (20) degreaser (10).

(vi) **Chloroform:** Fluorocarbons (90).

(vi) **Carbon tetrachloride:** Fluorocarbons (95), degreasing.

(vii) **Acetylene:** VCM (37), 1,4 butanediol (25), vinyl acetate (14).

(viii) **Hydrogen cyanide:** MMA (58), cyanuric chloride (17), chelating agents (13), NaCN (9).

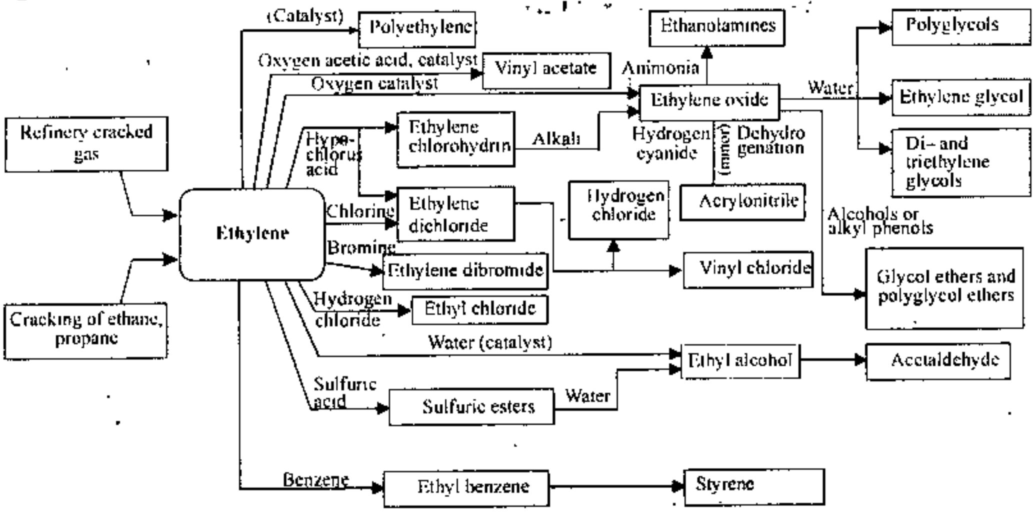


Fig. 1. Petrochemicals derived from methane

[II] Petrochemicals from Ethylene

The petrochemicals derived from ethylene are given in the chart shown in fig. (2)

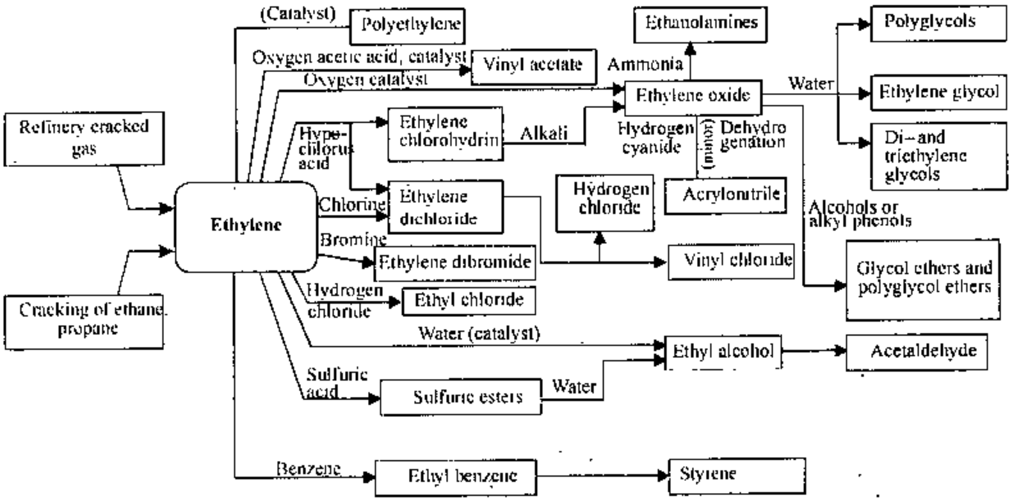


Fig. 2. Petrochemicals derived from ethylene.

The petrochemicals derived from ethylene are chemicals of great importance are described as follows (percentage use is given in parenthesis) :

(i) Ethylbenzene: Styrene (99), solvent (1).

(ii) Ethyl chloride: TEL (90), ethyl cellulose and pharmaceuticals (5).

(iii) Ethylene dichloride: VCM (84), solvent (7).

(iv) Ethylene glycol: Polyester fibers and films (49), antifreeze (38).

(v) Perchloroethylene: Textile cleaning (40), metal cleaning (21), chemical intermediates (6).

(vi) Polyethylene (LDPE): Film, sheet, molding and plastics.

(vii) Polyethylene (HDPE): Film, sheet, molding and plastics.

(viii) Styrene: Polystyrene: (52), polyester resin (6).

(ix) 1,1,1 Trichloroethane: Cold cleaning (40), adhesives (12), aerosols (10), electronics (6).

(x) Ethylene oxide: Glycol (60), glycol ethers (10), ethoxylates (10).

[III] Petrochemicals Derived from Propylene and Butylenes

Petrochemicals derived from propylene and butylenes are given in the chart shown in fig. (3).

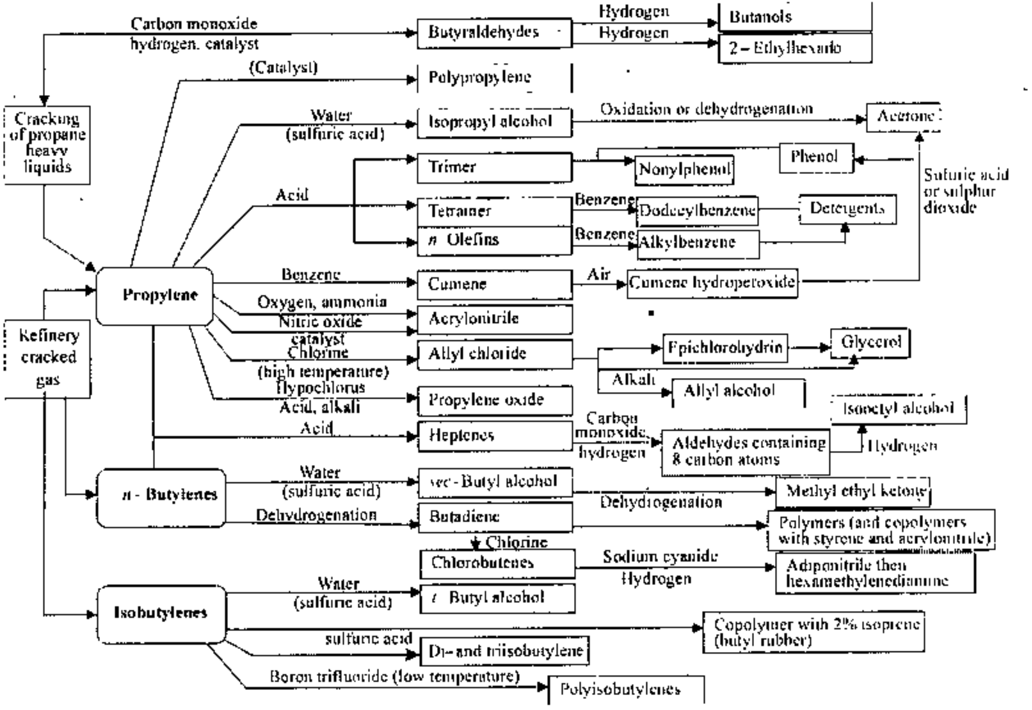


Fig 3: Petrochemicals derived from propylene and butylenes

The petrochemicals derived from propylene and butylenes are widely used as mentioned below (use percentage is given in parenthesis) :

(i) Acrylonitrile: Apparel (70), home furnishing (30).

(ii) Butadiene: SBR (40), polybutadiene (20), hexamethylene diamine (10).

(iii) *n*-Butanol: Acrylates (30), glycol ethers (22), butyl acetate (12), solvents (11), plasticizers (9) amino resins (7).

(iv) Butyl rubber: Tyres, high impact resins.

(v) Cumene: Phenol and acetone (98).

(vi) Isopropyl alcohol: Acetone (43), solvent (10), coating solvent (10), pharmaceuticals (6).

(vii) Polypropylene: Injection molding (30), fibers and filaments (26), extrusion (11).

(viii) Propylene oxide: Urethane polyols (54), propylene glycol (21), amines and ethers (13).

[IV] Petrochemicals Derived from Benzene, Toluene, Xylenes and Ethylbenzene

The cyclic materials are given in the chart shown in fig. (4).

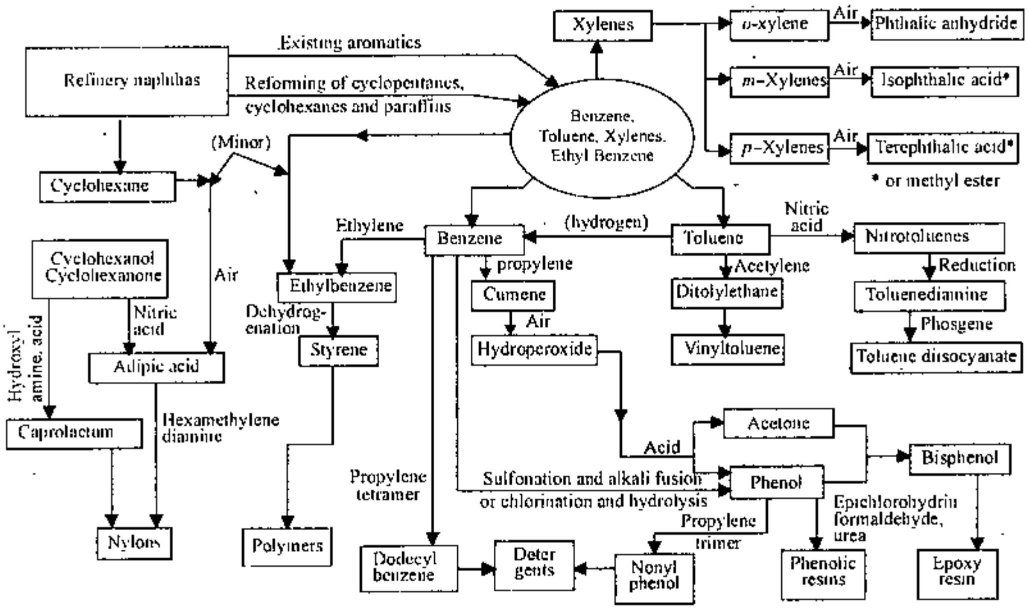


Fig. 4. Petrochemicals derived from cyclic materials

The uses of petrochemicals derived from cyclic materials are mentioned as follows. The figures in parentheses indicate use percentage.

(i) Benzene: Ethylbenzene (42), cumene (18), cyclohexane (15), nitrobenzene and aniline (5).

(ii) Cyclohexane: Adipic acid (60), caprolactam (30).

(iii) Ethylbenzene: Styrene (99).

(iv) Toluene: Octane improver, benzene, xylene.

(v) *p*-Xylene: dimethylterephthalate and terephathalic acid (100).

(vi) *o*-Xylene: Phthalic anhydride.

(vii) *m*-Xylene: Octane improver.

Ans 4

2.2 MANUFACTURE OF PETROCHEMICALS

The research and development divisions of various industries are actively engaged in the discovery of novel and efficient methods for the manufacture of petrochemicals. The problems such as quality control, environmental effects of the products and byproducts, sewage disposal, fire fighting producers, plant safety, packing and marketing etc are taken into account while suggesting a suitable method for the manufacture of a petrochemical.

[I] Alkylation, Dealkylation and Hydrodealkylation

Cumene (isopropylbenzene) is synthesised by the reaction of benzene with propylene at 250°C in the presence of phosphoric acid derivative as catalyst. A mixture of propylene-propane (a refinery fraction) is also used instead of pure propylene. An excess of benzene is added to avoid polyalkylation. Aluminum chloride as well as sulphuric acid are also used as catalyst in the reaction. Ethylbenzene is synthesised by reacting benzene and ethylene in the presence of aluminium chloride as catalyst (*Friedel Crafts reaction*).

Dealkylation and hydrodealkylation are used extensively for the conversion of available molecules into other more desired molecules. The two mostly used processes are represented as follows :

(i) The reaction of toluene or xylene or C_9 and heavier aromatics with H_2, in the presence of dealkylating catalyst, gives mainly benzene.

(ii) The reaction of two molecules of toluene with a little H_2, in the presence of a fixed bed catalyst, gives benzene and mixed xylenes.

Tetraethyl lead is prepared on a large scale by the following two processes as follows :

(i) By reaction between ethyl chloride and sodium lead alloy.

$$4PbNa + 4C_2H_5Cl \longrightarrow Pb(C_2H_5)_4 + 3Pb + 4NaCl$$

(ii) An electrolytic process using Grignard reagent to produce tetraethyl lead (TEL) or tetramethyl lead (TML).

$$4PbNa + 2RMgCl - 2RCl + Pb \xrightarrow[\text{current}]{\text{Electric}} PbR_4 + 2MgCl_2$$

[II] Cracking or Pyrolysis

Carbon black is produced on a large scale by cracking for the last 50 years or so. Olefins and diolefins are produced by catalytic cracking of various hydrocarbons. Ethylene (12.7 × 10^9 kg per year) and by-product propylene (5.9 × 10^9 kg per year) are being produced by cracking on a very large scale.

Acetylene is produced by cracking of natural gas or liquid hydrocarbon feed.

$$2\,CH_4(g) \longrightarrow C_2H_2(g) + 3\,H_2(g)$$

α–Olefins are produced by cracking heavy paraffins. Many α-olefins are produced by oglimerization of lighter hydrocarbons (for example, ethylene) by *alfol process* or the *Ziegler process*. α–Olefins are used in the manufacture of detergents.

[III] Dehydration

Generally, the ethers are prepared by the dehydration of alcohols. Diethyl ether is produced by dehydration of ethyl alcohol in presence of sulphuric acid as the dehydrating agent. Flowchart for the manufacture of diethyl ether by dehydration of ethanol is depicted in fig. (5).

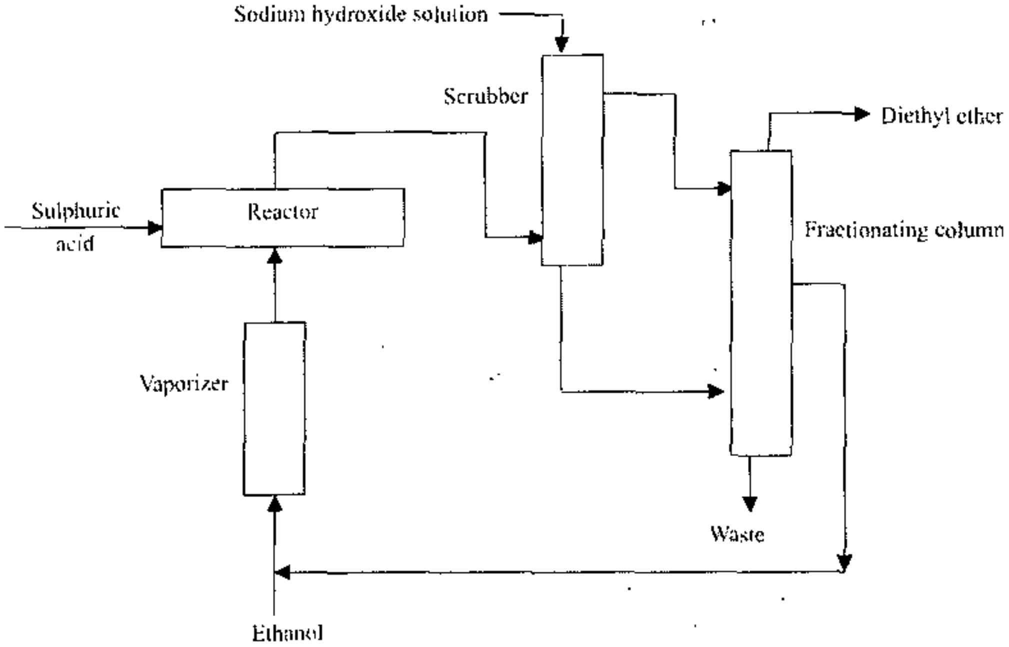


Fig. 5. Flowchart for the manufacture of diethyl ether

[IV] Esterfication of Organic Alcohols and Acids

Ethyl acetate is one of the important esters, which is manufactured on large scale by the reaction of ethanol and acetic acid in the presence of a little sulphuric acid.

$$CH_3COOH + C_2H_5OH \xrightleftharpoons{H_2SO_4} CH_3COOC_2H_5 + H_2O$$

The reaction is reversible and it is brought in forward direction for completion by using alcohol in excess and removing water formed in the reaction continuously. Esterification proceeds in a column, which takes a ternary azeotrope overhead. The ternary azeotrope boils at 70.2°C and has a composition 82.2 % ethyl acetate, 8.4 % ethanol and 9 % water. Alcohol can be added to the condensed overhead liquid to wash out the ethanol, which is then rectified and returned to the column to react.

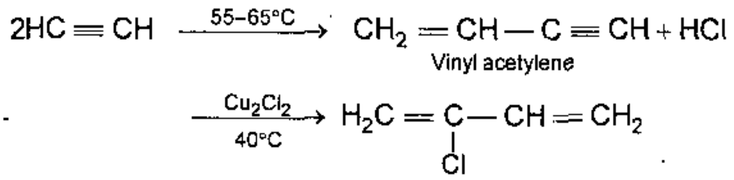
Other esters like amyl acetate, butyl acetate and isopropyl acetate are also produced by esterification reaction using acetic acid and appropriate alcohol. Esters have a wide range of applications. *For example, methyl salicylate,* methyl anthranilate, diethyl phthalate and dibutyl phthalate are used in perfumery and in plasticizers. Ethyl acetate is an important solvent particularly for lacquers. Vinyl esters are useful in polymerisation reactions.

Vinyl acetate is produced by the reaction between ethylene and acetic acid in vapour phase over a supported palladium catalyst. The reaction is performed in a fixed bed tubular reactor and is exothermic. The reaction proceeds at 175-200°C under pressure (475 to 1000 kPa).

$$H_2C=CH_2 + CH_3COOH + \frac{1}{2}O_2 \longrightarrow CH_3COOCH=CH_2 + H_2O$$

Chloroprene is synthesised by the following reaction. Acetylene is converted into vinyl acetylene (a weak solution containing ammonium chloride, Cu_2Cl_2 and potassium chloride is used as catalyst). Vinyl acetylene is then reacted with aqueous hydrochloric acid (35-40°C) in the presence of Cu_2Cl_2 as the catalyst to obtain chloroprene.

Ans4



$$2HC \equiv CH \xrightarrow{55\text{–}65°C} CH_2 = CH - C \equiv CH + HCl$$

Vinyl acetylene

$$\xrightarrow[40°C]{Cu_2Cl_2} H_2C = \underset{Cl}{\underset{|}{C}} - CH = CH_2$$

Esters of allyl alcohol are prepared by esterification of phthalic anhydride with allyl alcohol. They are used as bifunctional polymerisation monomers. Acrylic esters (ethyl and methyl acrylate) are prepared from acrylic acid and the appropriate alcohol.

[V] Halogenation and Hydrohalogenation

(1) **Chlorination of methane :** Chlorine and new and recycled methane are charged (in the ratio 0.6: 1.0) to the reactor and temperature is maintained at 340-370°C. The methane conversion is ~ 65%. The reaction product contains methyl chloride, methylene chloride, chloroform and carbon tetrachloride in the proportions 6:3:1:0.25 respectively. Unreacted methane, HCl, Cl_2 and chlorinated products are also present.

In secondary chlorination, methylene chloride is converted into chloroform in a secondary reactor and conversion of chloroform to carbon tetrachloride takes places in another secondary reactor. The applications of chlorinated methane are mentioned below Figures in paranthesis represent the percentage use.

(i) **Methyl chloride, CH_3Cl:** Silicones (57), tetramethyl lead (9), methyl cellulose (4).

(ii) **Methylene chloride, CH_2Cl_2:** Paint remover (30), aerosol propellant (20), detergent (10).

(iii) **Chloroform, $CHCl_3$:** Fluorocarbons (90).

(iv) **Carbon tetrachloride, CCl_4:** Fluorocarbons (95), degreasing.

(2) **Chlorination of ethane :** Ethane undergoes chlorination under the conditions very much similar to chlorination of methane to give mixed chlorinated ethanes. Ethyl chloride is used for the preparation of tetraethyl lead.

$$CH_3CH_3 + Cl_2 \longrightarrow CH_3CH_2Cl + HCl$$

(3) **Chlorination of ethylene :** Ethylene undergoes chlorination to give several derivatives like ethylene dichloride, dichloroethylene, trichloroethylene, tetrachloroethane and chloromethanes etc.

$$H_2C = CH_2 + Cl_2 \longrightarrow \underset{\text{Ethylene dichloride}}{CH_2ClCH_2Cl}$$

Ethylene dichloride is used in the preparation of ethylene diamine. Perchloroethylene (tetrachloroethylene), $CCl_2 = CCl_2$, is used in textile cleaning.

[VI] Hydration and Hydrolysis

Ethylene is used for the manufacture of ethyl alcohol. Ethylene dissolved in sulphuric acid to form ethyl sulphate, which is then hydrolyzed to from ethyl alcohol. This is an old process, which gives ethyl alcohol (90%) and diethyl ether (5 – 10%) as a by-product. Reactions taking place are shown below :

$$3H_2C = CH_2 + 2H_2SO_4 \longrightarrow C_2H_5HSO_4 + (C_2H_5)_2\,SO_4$$

$$C_2H_5HSO_4 + (C_2H_5)_2SO_4 + H_2O \longrightarrow 3C_2H_5OH + 2H_2SO_4$$

Ethyl alcohol is also manufactured by direct hydration of ethylene, in the presence of phosphoric acid as the catalyst, to give 85 % yield. Flowchart for the synthesis of ethyl alcohol from ethylene by direct hydration is depicted in fig. 6. Ethylene and water are mixed with a recycle stream (ethylene : water mole ratio 1 : 06) and heated to about 300°C. The gases react over phosphoric acid adsorbed on diatomaceous earth as the catalyst. Unreacted reagents are separated and recirculated. The by-product acetaldehyde is then hydrogenated over a suitable catalyst to form alcohol.

$$H_2C{=}CH_2 + H_2O \xrightarrow[300^\circ C,\ 6.8\ MPa]{H_3PO_4} C_2H_5OH$$

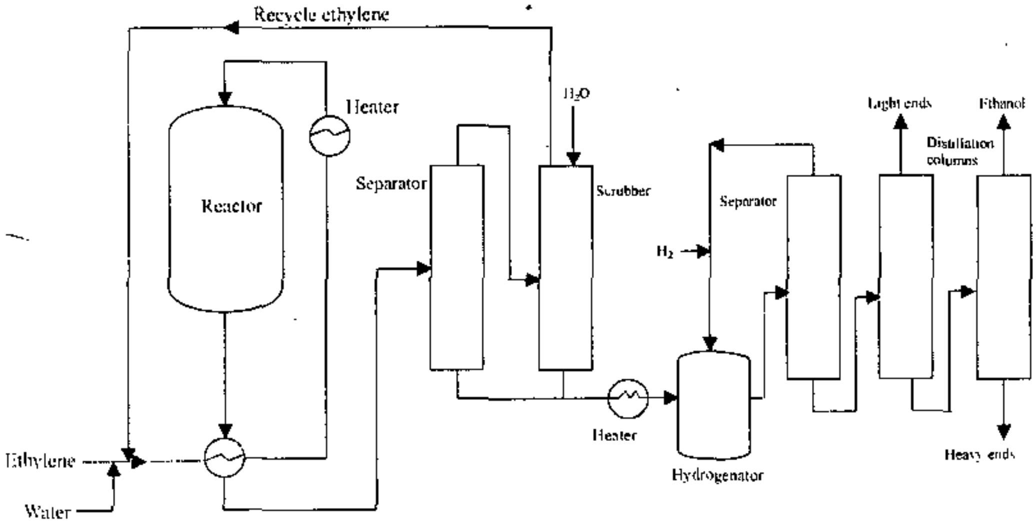


Fig. 6. Flowchart for the manufacture of ethyl alcohol from ethylene

Isopropyl alcohol is manufactured from propylene by using the following four different methods.

- **(i)** Sulphuric acid process similar to that for ethanol hydration.
- **(ii)** Gas phase hydration in the presence of a fixed bed supported phosphoric acid catalyst.
- **(iii)** Mixed phase reaction, in the presence of a cation exchange resin as catalyst.
- **(iv)** Liquid phase hydration in the presence of a dissolved tungsten catalyst.

$$CH_3CH{=}CH_2 + H_2O \xrightarrow{\text{Catalyst}} \underset{\text{Isopropyl alcohol}}{CH_3CHOHCH_3}$$

Isopropyl alcohol is used as a solvent. It is also used for preparing acetone and cosmetics.

[VII] Hydrogenation and Dehydrogenation

Generally, hydrogenation reactions are, carried out at high temperature and pressure and in the presence of a catalyst (noble metals, nickel, copper and various metal oxide combinations are the common catalysts). Dehydrogenation reactions are favoured by high temperature and low pressure. The catalysts used for dehydrogenation are the same as those for hydrogenation reactions.

(1) **Manufacture of methanol** : Methanol is manufactured from synthetic gas by using a copper based catalyst.

$$CO + H_2 \xrightarrow{\text{Cu catalyst}} CH_3OH$$

Flowchart for the manufacture of methanol is given in fig. (7). The reactor temperature is maintained at 250-260°C and pressure is five to eight MPa. Unreacted gas is recycled.

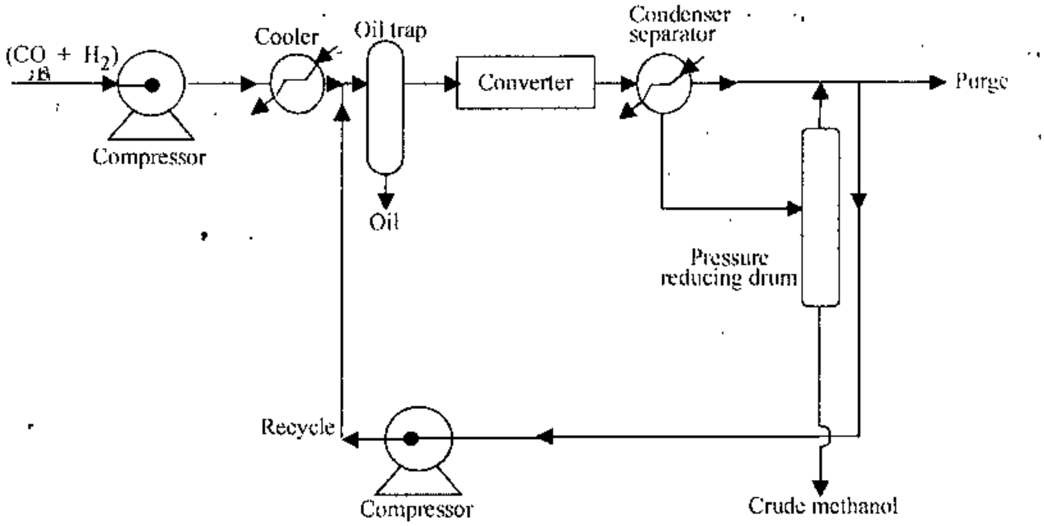


Fig 7. Flowchart for the conversion of synthetic gas to methanol

(2) Acetone : Acetone is manufactured from isopropyl alcohol. The reaction takes place at ~ 200 kPa and 350°C to give 80 to 90 percent conversion.

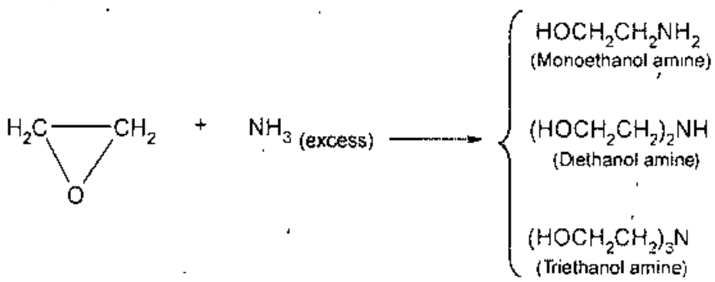
$$(CH_3)_2CHOH(g) \xrightarrow[\text{zinc acetate}]{\text{Copper or}} CH_3COCH_3(g) + H_2(g)$$

[VIII] Nitration and Amination

(a) Nitration is used for the conversion of unreactive paraffins into reactive compounds without cracking. Nitric acid and nitrogen oxides are strong oxidizing agents and therefore oxidation accompanies nitration. Aromatic nitration reactions are of great importance in the manufacture of explosives.

Vapour phase nitration of paraffin hydrocarbons (for example, propane) is performed by uncatalyzed reaction between a large excess of hydrocarbon and nitric acid vapour at 400°C, followed by quenching. The nitoparaffins are useful as fuel for race cars, submarines and model airplanes.

(b) Amination by reduction and amination by ammonolysis are used for the manufacture of amines. Ethanolamines are obtained by reacting ethylene oxide with ammonia. An equilibrium mixture of monoethanolamine, diethanolamine and triethanolamine is obtained when ethylene oxide is passed through aqueous ammonia (28 %) at 30-40°C. It is possible to get the desired ethanolamine by changing temperature, pressure and ratio of ammonia to ethylene oxide



[IX] Oxidation

Oxidation is one of the valuable conversion methods. Generally all oxidation reactions are exothermic. Vanadium pentoxide (V_2O_5) is the common catalyst used in oxidation reactions. Both liquid phase and vapour phase oxidation reactions are used industrially.

(1) Manufacture of phenol : *Phenol is synthesised by oxidation of* cumene to cumene hydroperoxide, followed by decomposition to phenol and acetone. The flowchart of the process is shown in fig. (8).

$$\underset{\text{Cumene}}{C_6H_5CH(CH_3)_2} \xrightarrow[130^\circ C]{\text{air + catalyst}} \underset{\text{Cumene hydroperoxide}}{C_6H_5C(CH_3)_2OOH}$$

$$\xrightarrow[35-65^\circ C]{10-25\%H_2SO_4} \underset{\text{Pheno)}}{C_6H_5OH} + \underset{\text{Acetone}}{CH_3COOCH_3}$$

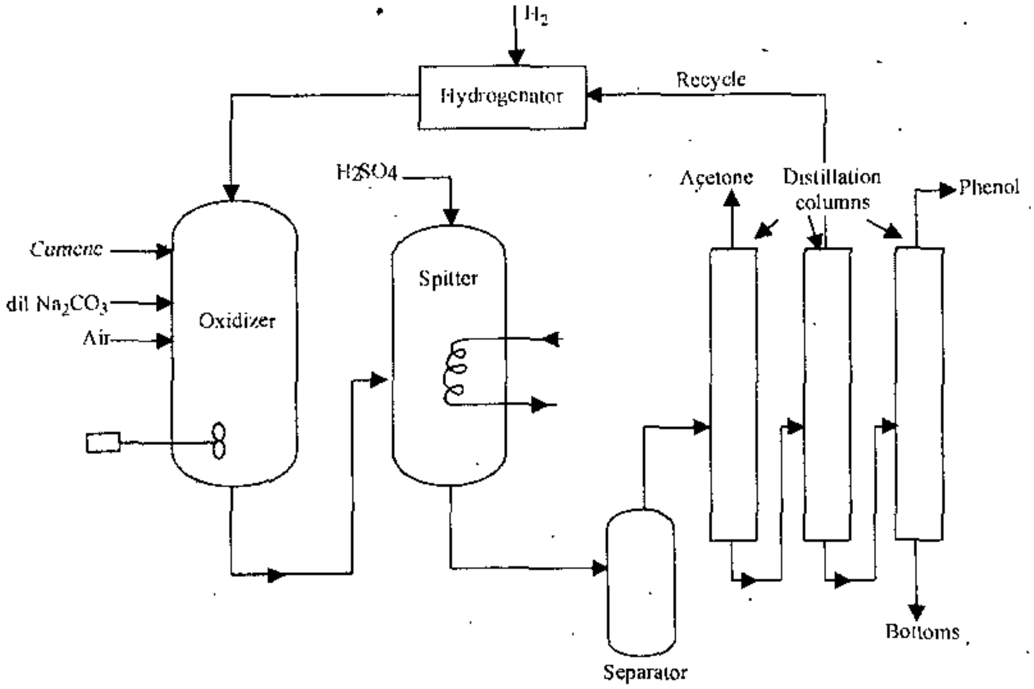


Fig. 8. Flowchart for the production of phenol from cumene

Phenol is also synthesised by the oxidation of toluene to benzoic acid, followed by decomposition to phenol.

$$\underset{\text{Toluene}}{C_6H_5CH_3} + \frac{3}{2}O_2 \xrightarrow[\text{Cobalt salt}]{150^\circ C} \underset{\text{Benzoic acid}}{C_6H_5COOH} + H_2O$$

$$C_6H_5COOH + \frac{1}{2}O_2 \xrightarrow[\text{Cu-Mg salt}]{280^\circ C} \underset{\text{Phenol}}{C_6H_5OH} + CO_2$$

(2) Manufacture of acetaldehyde : Acetaldehyde is used for the manufacture of acetic acid on a large scale. Acetaldehyde is produced by the most important Wacker process. Ethylene is oxidised by air or oxygen. The catalyst is palladium chloride with a copper chloride promoter. Ethylene gas is bubbled under atmospheric pressure through the solution at its boiling point. The heat of reaction is removed by boiling of water. Unreacted gas is recycled, followed by condensation of aldehyde and water. Both the components are then separated by distillation. Flowchart of the manufacturing process is shown in fig. (9).

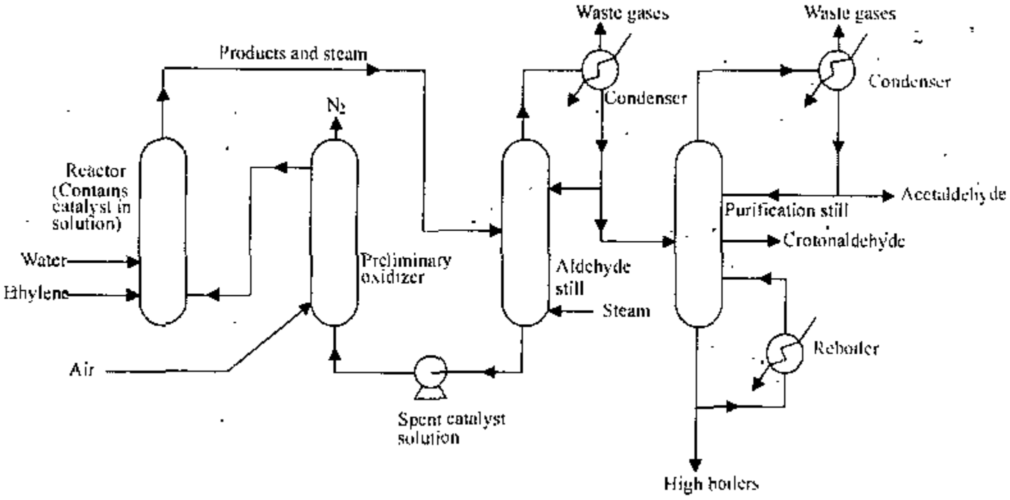
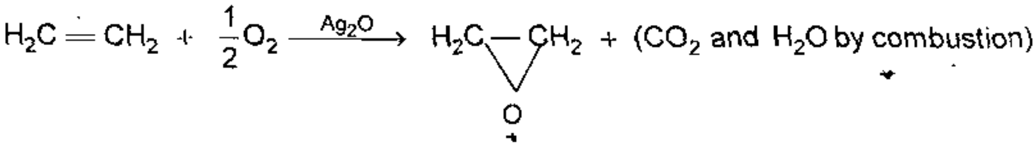
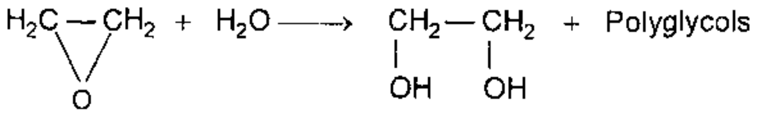


Fig. 9. Flowchart for the manufacture of acetaldehyde by air oxidation of ethylene

(3) Ethylene glycol : Ethylene glycol is one of the major petrochemicals and is widely used in antifreeze, and in fibres and films. It is prepared by reacting ethylene with oxygen or air in a tubular reactor over a silver oxide catalyst to obtain ethylene oxide. The ethylene oxide is then converted into ethylene glycol by hydration. During hydration, some polyglycols (diethylene glycol and triethylene glycol) are also formed.





(4) Maleic acid and maleic anhydride : Maleic acid and anhydride are obtained as by-product in the oxidation of xylenes and naphthalenes to form phthalic acid. They are also prepared by partial oxidation of benzene in the presence of vanadium pentoxide as catalyst.

[X] Hydroformylation (Oxo Reaction)

Olefins are converted into aldehydes and or alcohols containing an additional carbon atom by oxo reactions.

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + \underset{\text{Synthetic gas}}{(CO + H_2)} \longrightarrow \underset{\text{Butyraldehyde}}{CH_3CH_2CH_2CHO}$$

$$CH_3CH_2CH_2\,CHO + H_2 \longrightarrow \underset{n\text{-Butanol}}{CH_3CH_2CH_2CH_2OH}$$

Flowchart for the production of butyraldehyde and *n*-butanol by oxo reaction is depicted in fig (10). The propylene in liquid state is reacted (temperature: 150-170°C, pressure: 27-30 MPa) in the presence of a soluble cobalt catalyst. The aldehyde and a small amount of alcohol formed are flashed off along with the steam, and the catalyst is recycled. The reaction is exothermic.

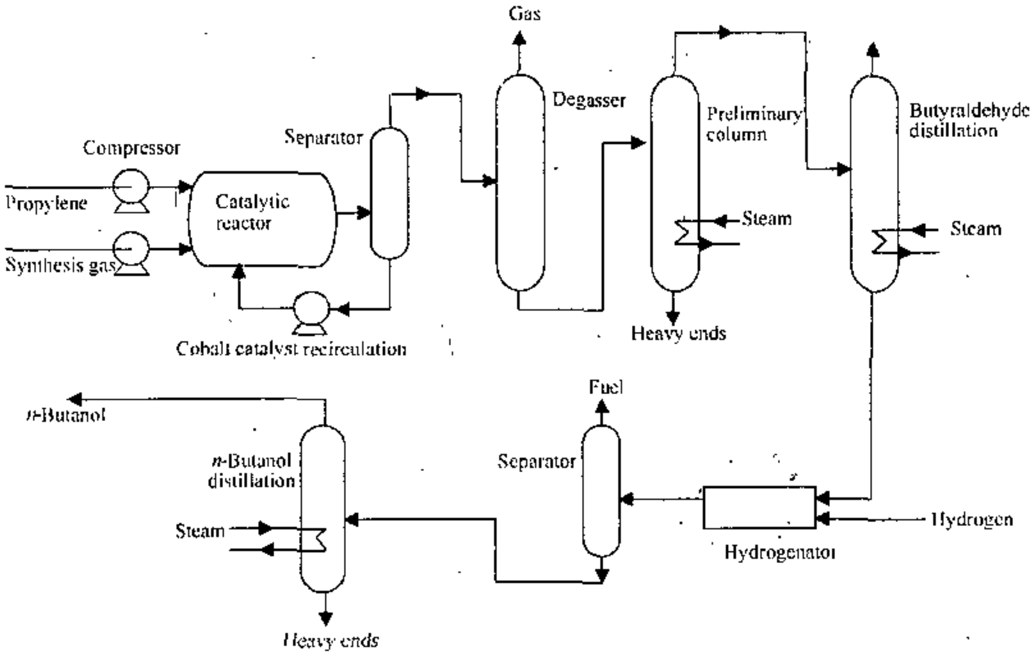


Fig. 10. Flowchart for oxo reaction

[XI] Polymerisation

Polymerisation reactions are discussed in unit 1 and succesding articles on polymers.

When the solution of triethyl aluminum ($AlEt_3$) and titanium tertrachlroide ($TiCl_4$) in a hydrocarbon solvent is reacted, a brown solid is obtained which is called the most important **Ziegler and Natta catalyst.** This catalyst is used for the polymerisation of ethene to polythene. For the discovery of this particular catalyst, both the scientists Ziegler and Natta received Nobel prize in the year 1963.

The $AlEt_3/TiCl_4$ catalyst is commercially very important for the production of stereoregular polymers which are stronger and possess higher melting points than atactic or random polymers.

A lot of work has been done to study the catalytic activity of Ziegler and Natta catalyst. *The active species is* Ti^{III}, *and* $AlEt_3$ *reduces* $TiCl_4$ *to* $TiCl_3$ *in* situ or $TiCl_3$ may be added instead. One of the Cl atoms is then replaced by an ethyl group. The possible mechanism is that the double bond in ethene attaches to a vacant coordination site on the titanium atom on the surface of the catalyst. A carbon shift reaction takes place, and migration of ethene and its insertion between titanium and carbon in the Ti—Et bond takes place. The carbon chain thus extends from two to four atoms leaving a vacant site on titanium.

The process is thus repeated to increase the carbon chain in length. A similar type of reaction takes place with other alkenes also, for example propylene ($CH_3—CH=CH_2$). When the double bond attaches to titanium the CH_3 group always points away from the surface because the reaction takes place on the surface. Thus the migration of the molecule and its insertion into the Ti—C bond has always the same orientation. This phenomenon is called ***cis* insertion** of alkene and it gives proper explanation for getting stereoregular polymers.

Uncatalysed polymerisation of ethene to polythene requires high temperature and pressure conditions. Ziegler and Natta catalysed polymerisation occurs at relatively low temperature (from room temperature to 93°C) and under atmospheric pressure upto 100 atmosphere. The product is hydrolyzed with water or alcohol and the catalyst is removed. The polythene so produced is called **high-density polythene** (density 0.95-0.97 g cm^{-3} and melting point 135°C). It is relatively hard and stiff. It consists of straight chains with very little branching and has a molecular weight ranging from 20,000 to 30,000. Ziegler and Natta catalysed polymerisation of ethene to polythene which is suggested in scheme VII shown in fig. (11).

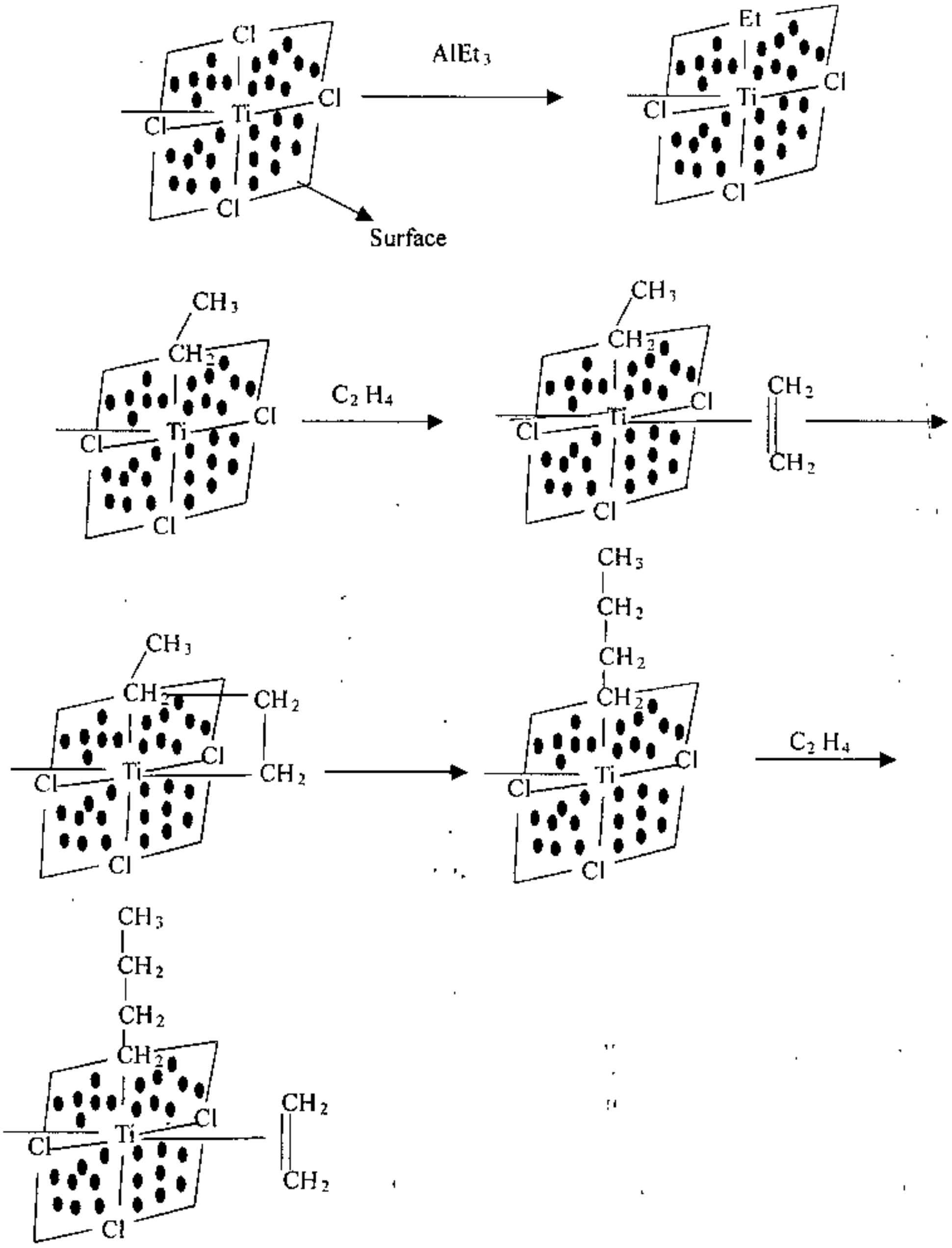


Fig. 11. Scheme VII : Ziegler and natta polymerisation of ethane to polythene.

Another variety of polythene called **low–density polythene** is soft (density 0.91–0.094 g cm^{-3} and melting point 115°C). It consists of much branched chains. It is produced by free radical polymerisation of ethene and promoted under rigid conditions of temperature 190-210°C and 1500 atmospheric pressure. More than 25 million tons of polythene is produced annually by Ziegler and Natta catalysed polymerisation process.

[XII] Some Miscellaneous Reactions

(1) **Manufacture of methyl tertiary butyl ether (MTBE)** : MTBE is used as a good octane enhancer for gasoline. Pure isobutylene and methanol are obtained by cracking of MTBE.

MTBE is produced by reacting mixed butene-butane fraction with methanol in liquid phase on a fixed bed of ion exchange resin catalyst. Flowchart is depicted in fig. (12).

$$CH_3OH + (CH_3)_2C=CH_2 \longrightarrow \underset{\text{(MTBE)}}{CH_3OC(CH_3)_3}$$

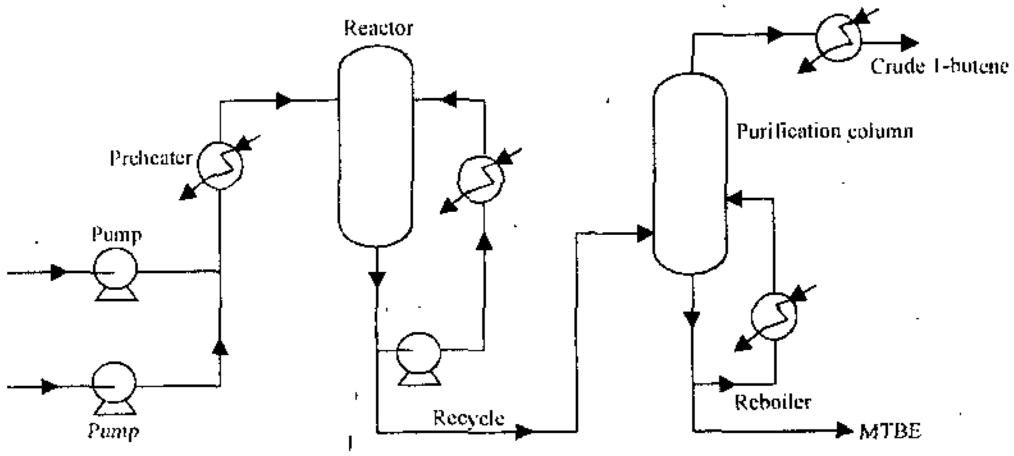


Fig. 12. Flowchart for the manufacture of MTBE and 1-butene.

(2) **Manufacture of carbon disulphide** : Carbon disulphide is used for the manufacture of rayon. It is prepared by the reaction between methane and sulphur in the presence of a catalyst (Al_2O_3 or Cr_2O_3). The yield, based on methane, is around 90%.

$$CH_2(g) + 4S(g) \xrightarrow[700°C,\ 270\ kPa]{Al_2O_3/Cr_2O_3} CS_2(g) + 2H_2S(g)$$

2.3. MAJOR PETROCHEMICAL INDUSTRIES IN INDIA

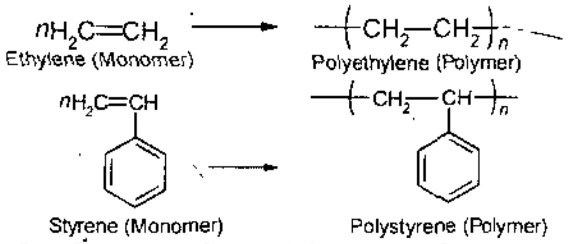
Some of the major petrochemical industries along with the names of their products are listed as follows :

1. Andhra Petrochemicals Ltd., Venkatarayapuram, Tanuku, Dist. West Godavari (Andhra Pradesh).
2. Auraiya Gas Cracker Complex, Uttar Pradesh.
3. Assam Petrochemicals Ltd, Lamb Road, Ambari, Guwahati (Assam).
4. Bongaigaon Refinery And Petrochemicals Ltd., Dhaligaon, Dist. Bongaigaon (Assam).
5. Bharat Petroleum Corporation Ltd., Bharat Bhavan, Ballard Estate, Mumbai (Maharashtra).
6. Cochin Refineries Ltd., Abalamnugal, Dist, Ernakulam (Kerala).
7. Cetex Petrochemicals Ltd., 12 Bishop waller avenue Mylapure, Chennai, (Tamilnadu).
8. Deepak Fertilizers and Petrochemicals Corporation Ltd, Taloja (Maharashtra).
9. Hindustan Petroleum Corporation Ltd., 17, Jamshedji Tata Road, Mumbai (Maharashtra).
10. Hindustan Organic Chemicals Ltd., Rasayani, Raigad, (Maharashtra).
11. Haldia Petrochemicals Complex, Haldia, West Bengal.

12. Haryana Petrochemicals Ltd., B-18, Adhitam Kendra, Qutab Institutional Area, New Delhi.
13. Herdillia Chemicals Ltd, Thane (Maharashtra).
14. IBP COMPANY Ltd., Gilander House, 8 Netaji Subhash Road, Kolkata (West Bengal).
15. Indian Oil Corporation Ltd., Indian Oil Bhavan, G-9, Ali Yawar Jung Marg., Bandra (E), Mumbai (Maharashtra).
16. IC Petrochemicals Ltd., 401/404, Raheja Centre, Nariman Point, Mumbai (Maharashtra).
17. Indian Petrochemicals Corporation Ltd., (IPCL), Petrochemicals Township, Dist. Vadodara (Gujarat).
18. Mysore Petrochemicals Ltd., 1/4 Jyoti Complex, 134/1 Infantary Road, Bangalore (Karnataka).
19. Mangalore Refinery and Petrochemicals Ltd., 7 Magadi Road, Bangalore (Karnataka).
20. Manali Petrochemicals Ltd., SPIC Annexe, 97 Mount Road, Guindy, Chennai (Tamilnadu).
21. National Aromatics and Petrochemicals Corporation, 480 Anna Salai, Nandanam, Chennai (Tamilnadu).
22. National Organic Chemical Industries Ltd., (NOCIL), Mafatlal Centre, Nariman Point, Mumbai (Maharashtra).
23. Niraj Petrochemicals Ltd., 6 – 3- 883 / 6D, Panjagatta, Hyderabad (Andhra Pradesh).
24. Oil India Ltd, Duliajan, Dist. Dibrugarh (Assam).
25. Rinki Petrochemicals and Indstries Ltd., 67, Race Course Circle, Vadodara (Gujarat).
26. Rama Petrochemicals Ltd., 51 / 52 Free Press House, Nariman Point, Mumbai (Maharashtra).
27. Relaince Industries Ltd., Hazira, Surat (Gujrat).
28. Supreme Petrochem Ltd., 17/18 Shah Industrial Estate, Andheri (W), Mumbai (Maharashtra).
29. Sree Rayalaseema Petrochemicals Ltd., Ashoknagar, Hyderabad (Andhra Pradesh).
30. Southern Petrochemical Industries Corporation Ltd., SPIC Centre, 97 Mount Road, Guindy, Chennai (Tamilnadu).
31. Saleempur Aromatic Complex, Aligrah (Uttar Pradesh).
32. Shree Ambuja Petrochemicals Ltd., 7-C, Surya Towers, 105 S.P. Road, Secunderabad, (Andhra Pradesh).

2.4. INTRODUCTION OF POLYMERS

A polymer is defined as a large molecule consisting of repeating structural units joined by covalent bonds. The word polymer is derived from Greek word **poly(many)** and **mers(parts)**. A large molecule is considered as one which has molecular weight of at least one hundred or one thousand or more structural units. *The structural unit is a relatively simple group of atoms joined together by covalent bonds in a specific spatial arrangement.* Polymers are distinguished from the solids or liquids in which the repeating units like ions, atoms or molecules are held together by ionic bonding, metallic bonding, hydrogen bonding, dipole moment or dispersion forces etc. Two examples of polymers are polyethylene and polystyrene represented as follows.



A **macromolecule** (the word derived from Greek, **macro-large**) is a large molecule and is often used with polymers. However, the macromolecules need not be made up of repeating structural units, though in actual practice, generally they are. The term **resin** is used to refer to a material whose molecules are polymers. For example: epoxy resin and novolak resin.

The different types of polymeric materials are represented in the following chart.

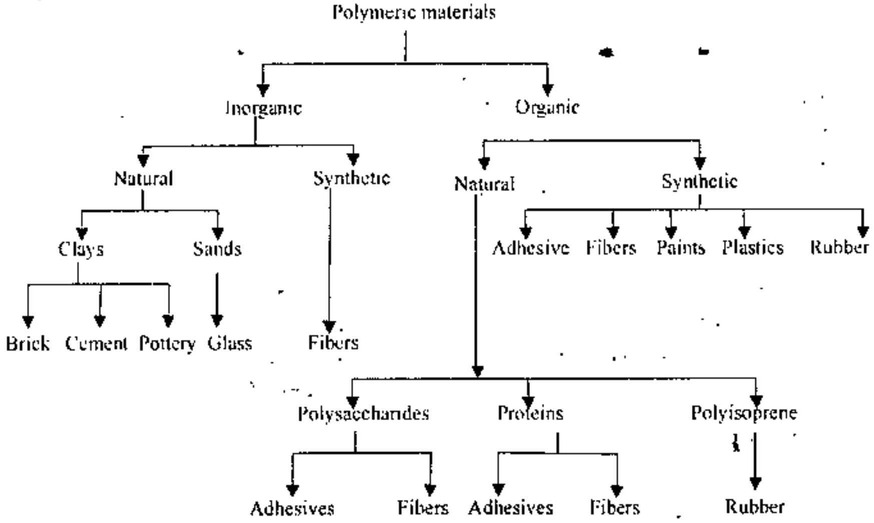


Fig. 1. Different types of polymeric materials

The physical properties of an individual polymeric material are determined by molecular weight, strength of intermolecular forces, regularity of polymer structure and flexibility of the polymer molecule.

2.5. NOMENCLATURE OF POLYMERS

A polymer may contain identical monomers or monomers of different structural units. Accordingly they are known as **homopolymers** or **copolymers.**

(i) Homopolymer

– – – A – A – A – A – A – A – A – A – – –

(ii) Copolymer

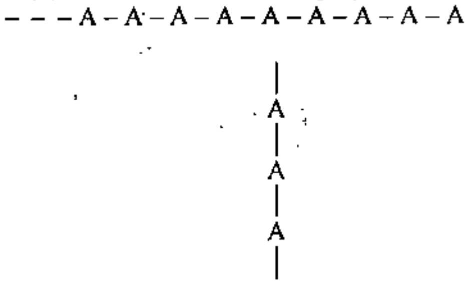
– – – A – B – A – B – A – B – A – – – –

The monomeric unit in a polymer may be present in either branched or cross-linked structure

(a) Linear homopolymer

– – – A – A – A – A – A – A – – – – – –

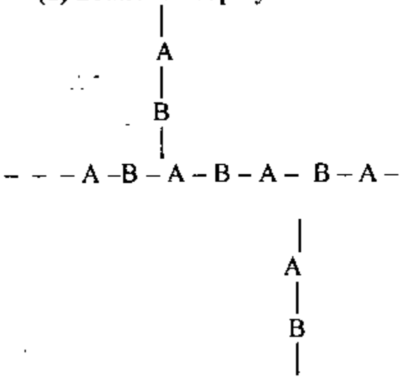
(b) Branched chain homopolymer



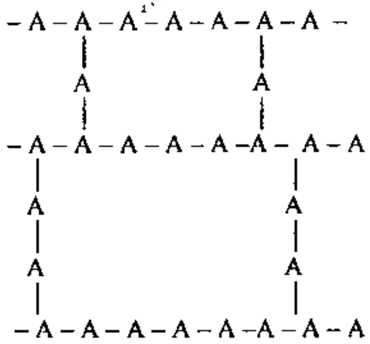
(c) Linear copolymer

– – – A – B – A – B – A – B – A – – – –

(d) Branched copolymer



(iii) Cross-linked homoploymer



If the polymer contains a main chain made up of similar type of atoms, then it is called **homochain polymer**. If the polymer contains the main chain made up of different atoms, then it is called **heterochain polymer.**

(a) Homochain polymer

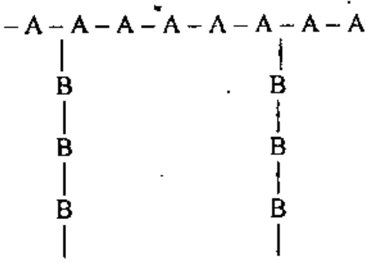
—— C – C – C – C – C – C – C – C – C —— —

(b) Heterochain polymer

——C – C – O – C – C – O – C – C – O —— —

(iv) Graft copolymer

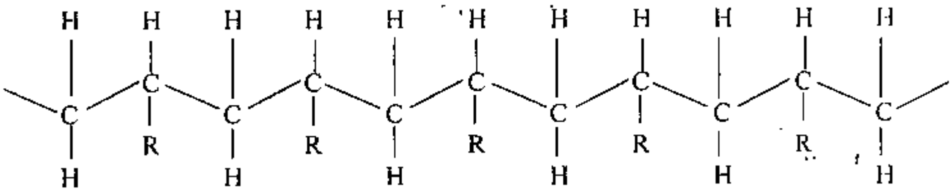
Graft copolymer possesses branched structures in which the monomer segments on the branches and on the backbone differ.



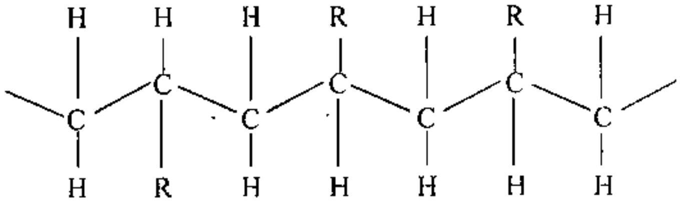
[I] Tacticity

The orientation of monomeric units in a polymer molecule may exist in an orderly or disorderly fashion with respect to the main chain. The physical properties of the polymers are affected by difference in configuration (**tacticity**).

(1) Isotactic polymers : They possess head-to-tail configuration in which the functional groups are all on the same side.

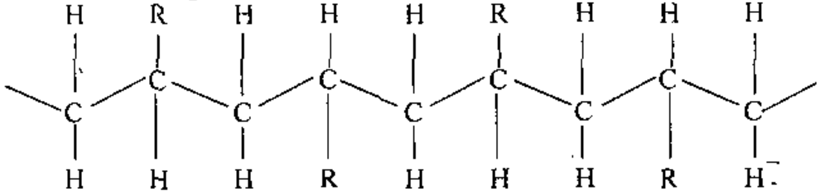


(2) Atactic polymers : In these polymers the arrangement of functional groups is at random around the main chain.



Example : Polypropylene.

(3) Syndiotactic polymers : In these polymers the arrangement of side groups is in alternating fashion.



Example : Gutta percha.

2.6. CLASSIFICATION OF POLYMERS

Polymers are classified in different ways as follows :

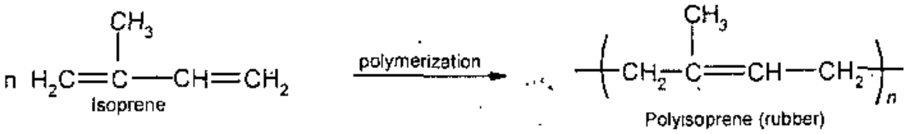
(i) Classification according to the source
(ii) Classification according to the structure
(iii) Classification according to the method of synthesis
(iv) Classification according to general physical properties

[I] Classification According to the Source

Polymers belonging to this class are of two types *viz.*, natural polymers and (ii) synthetic polymers.

(1) Natural polymers: These polymers occur in nature in plants and animals. A few examples are given below :

(i) ***Starch*** – It is a polymer of α-*D*-glucose.
(ii) ***Cellulose*** – It is a polymer of β-*D*-glucose.
(iii) ***Proteins*** – These are polypeptides and polyamides.
(iv) ***Natural rubber*** –It is a polymer of *cis*-isoprene.
(v) ***Gutta percha*** – It is a polymer of isoprene having *trans* configuration.



$$n\ H_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH{=}CH_2 \xrightarrow{\text{polymerization}} \left[CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}CH_2 \right]_n$$

(2) Synthetic polymers: These are prepared by synthetic methods. Examples : polyethylene, polypropylene, polystyrene, polyvinyl chloride, nylon, terylene and bakelite etc.

[II] Classification According to the Structure

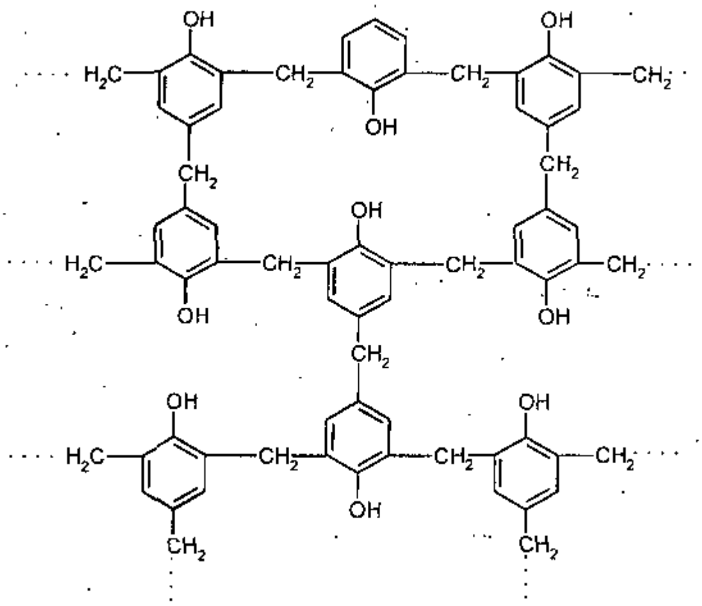
According to this type of classification, the polymers are of three types *viz.*, linear polymers, branched chain polymers and three dimensional network polymers.

(1) Linear polymers: These polymers contain monomeric units joined in form of a long straight chain. They have high melting point and density, and high tensile strength. Examples of these polymers are: high density polyethylene (HDPE), nylons and polyester.

(2) Branched chain polymers: These polymers contain branches along the main polymeric chain. They have low melting point and density as well as low tensile strength as compared to the linear polymers. For example: low density polyethylene (LDPE), glycogen etc.

(3) Three dimensional network polymers: These polymers contain monomers connected to each other by covalent bonds only. They are giant molecules having strong cross-links. These polymers are hard and rigid.

Examples of this kind of polymers are: urea–formaldehyde, melamine – formaldehyde and bakelite etc. A segment of bakelite is shown below :



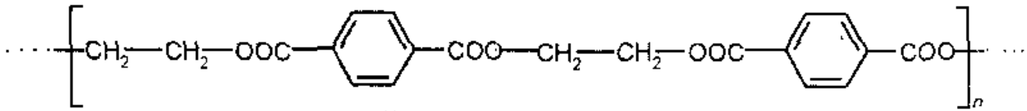
A segment of bakelite

[III] Classification According to the Method of Synthesis

According to this kind of classification, polymers are of two types, viz., addition polymers and condensation polymers.

(1) Addition polymers: These polymers are formed by the addition of monomer units. The monomer units are necessarily unsaturated compounds like ethylene or butadiene. Natural and synthetic rubbers, polyethylene. polyvinyl chloride are some of the examples of this type

(2) Condensation polymers: These polymers are obtained by condensation of similar or different types of monomers by elimination of some simple molecules such as water, ethyl alcohol etc. Starch. cellulose, polyester and polyamide fibers (terylene and nylon) are some of the examples of condensation polymers.



(A segment of terylene)

[IV] Classification According to General Physical Properties

According to this kind of classification, polymers are of four different types *viz.*, thermoplastic polymers, thermosetting polymers, elastomers and fibers.

(1) Thermoplastic polymers: These are linear long chain polymers. They become soft on heating and hard on cooling reversibly. The polymer chains in these polymers are very few and there is no cross linkage. The forces of attraction between polymer chains are weak Van der Waal's forces. and, therefore, they slide easily over one another. Polyethylene, polypropylene, polyvinyl chloride, polystyrene, nylons etc are some of the examples of thermoplastic polymers.

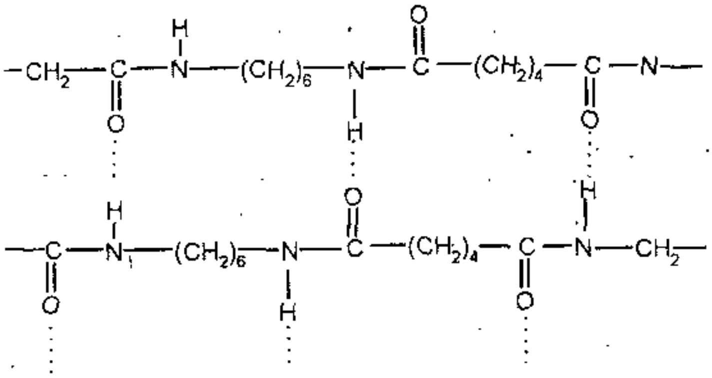
(2) Theromosetting polymers: The polymer chains in thermosetting polymers are highly cross-linked. Therefore, the sliding of chains over one another is restricted. The polymer thus *becomes hard, insoluble and infusible* with three dimensional space network of cross-linkage.

Thermosetting polymers can be heat-treated during their formation. They do not become soft on heating, and on strong heating they undergo decomposition. The solubility of these polymers is much decreased due to high degree of cross-linkage. Some of the thermosetting polymers absorb solvents and undergo swelling in size. Examples of thermosetting polymers are: polyester, bakelite, epoxy resin, urea-formaldehyde resin etc.

(3) Elastomers: Elastomers are rubber or rubber like substances. Similar to thermoplastics. Elastomers *in unstretched state contain very few cross* linkages. The polymer chains in them are not properly oriented. Elastomers are amorphous in unstretched state, and are more crystalline than thermoplastics.

An important character of elastomer is that on stretching, the chains get properly oriented and the polymer acquires the crystalline character. Elastomers become soft on heating and dissolve in certain solvents.

(4) Fibers: These are the polymers whose polymer chains are held together by hydrogen bonding. They are crystalline in nature and possess high *tensile strength. Nylon and polyester are the examples of fibers.*



(Hydrogen bonding in Nylon 66)

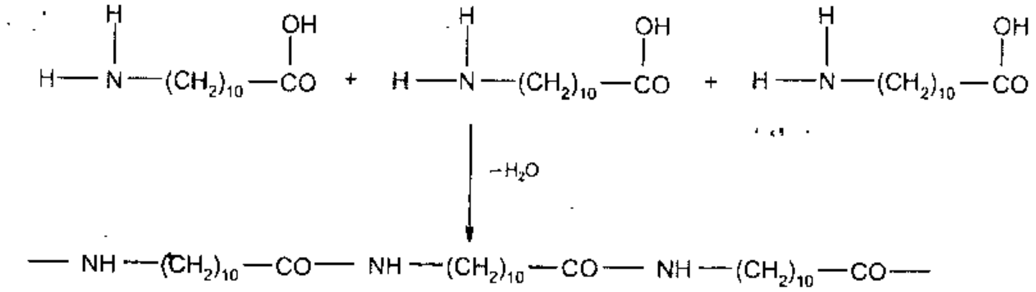
2.7. METHODS OF PREPARATION OF POLYMERS

There are *three general methods for the* preparation of polymers from relatively simple starting materials (monomers) :

- Polymerisation through *functional group*
- Polymerisation through multiple bonds
- Polymerisation through ring opening

[I] Polymerisation through Functional Groups

In this polymerisation, the reaction occurs between the pairs of functional groups associated *with two different molecules. A sequence of* reactions occurs to give a polymer provided all the reaction molecules have at *least two reactive groups. For example,* when ω-aminoundecanoic acid is heated then polymerisation of this kind takes place.



$$H-\overset{H}{N}-(CH_2)_{10}-\overset{OH}{CO} + H-\overset{H}{N}-(CH_2)_{10}-\overset{OH}{CO} + H-\overset{H}{N}-(CH_2)_{10}-\overset{OH}{CO} \xrightarrow{-H_2O} -NH-(CH_2)_{10}-CO-NH-(CH_2)_{10}-CO-NH-(CH_2)_{10}-CO-$$

OR

$$n\,H_2N-(CH_2)_{10}-COOH \longrightarrow \left[NH-(CH_2)_{10}-CO\right]_n + nH_2O$$

The resulting polymer (Nylon 11) contains a long chain of repeating $-HN-(CH_2)_{10}-CO-$ groups (in a typical commercial material n has a value of the order of 100). The resulting polymer is a polyamide because it contains amide (—CONH—) groups, which are not present in the starting material, at regular intervals along the chain.

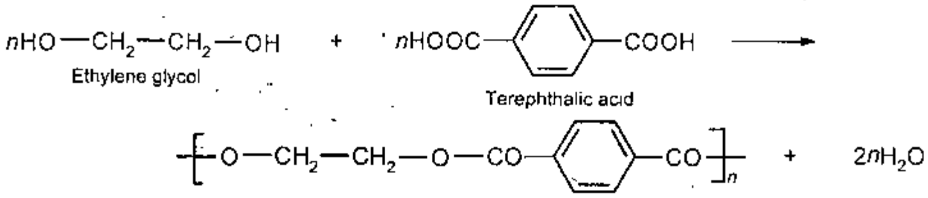
In the above example of polymerisation, the single monomer (ω-aminoundecanoic acid) possesses two functional groups (amino and carboxyl). It is more common to use a mixture of two monomers (each having only one type of functional group) for this type of polymerisation. A few examples are given below :

(1) Formation of polyamide

(i) $$\underset{\text{Hexamethylenediamine}}{nH_2N-(CH_2)_6-NH_2} + \underset{\text{Adipic acid}}{nHOOC\,(CH_2)_4\,COOH} \longrightarrow \underset{\text{Nylon 66}}{\left[NH-(CH_2)_6-NH-OC-(CH_2)_4-CO\right]_n} + 2nH_2O$$

(ii) $$\underset{\text{Hexamethylenediamine}}{nH_2N-(CH_2)_6-NH_2} + \underset{\text{Sebacic acid}}{nHOOC\,(CH_2)_8\,COOH} \longrightarrow \underset{\text{Nylon 6, 10}}{\left[NH-(CH_2)_6-NH-OC-(CH_2)_8-CO\right]_n} + 2nH_2O$$

(2) Formation of polyester



Polyethylene terephthalate

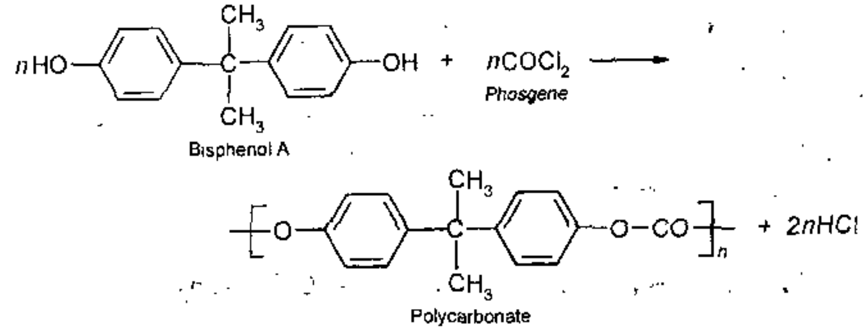
(3) Formation of polysulphide

$$\underset{\text{Ethylene dichloride}}{n\,Cl-CH_2-CH_2-Cl} + \underset{\text{Sodium disulphide}}{nNa_2S_2} \longrightarrow \underset{\text{Polysulphide}}{\left[CH_2-CH_2-S-S\right]} + n\,NaCl$$

In all the above examples, the polymers are formed along with a secondary product (water or hydrogen chloride). However, polymerisation through functional groups does not always occur with the formation of a secondary product. For example : reaction between 1.6 hexamethylene diisocyanate and 1,4-butanediol, polymer is the only product.

$$n\,OCN-(CH_2)_6-NCO + n\,HO-(CH_2)_4-OH \longrightarrow \left[OC-NH-(CH_2)_6-NH-CO-O-(CH_2)_4-O \right]_n$$

(4) Formation of polycarbonate



[II] Polymerisation through Multiple Bonds

This type of polymerisation is considered as the joining of unsaturated molecules through the multiple bonds. It is divided into the following categories :

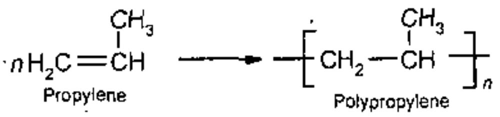
(i) Vinyl polymerisation
(ii) Diene polymerisation
(iii) Hetero-multiple bond polymerisation

(1) Vinyl polymerisation : Ethylene derivatives undergo polymerisation through carbon-carbon double bonds :

$$n\ H_2C{=}CH_2 \longrightarrow \left[CH_2-CH_2 \right]_n$$

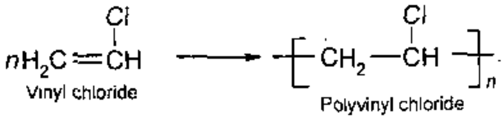
(Polyethylene)

The resulting polymer (polyethylene) contains long chain of repeating —CH$_2$—CH$_2$— groups. In a typical commercial material the value of n is of the order of 1000. Few more examples of polymerisation of ethylene derivatives are given as follows :



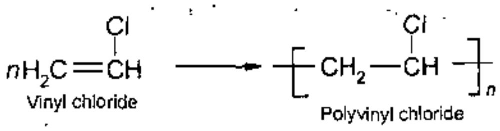
$$n\,H_2C{=}CH(CH_3) \longrightarrow \left[CH_2-CH(CH_3) \right]_n$$

Propylene → Polypropylene



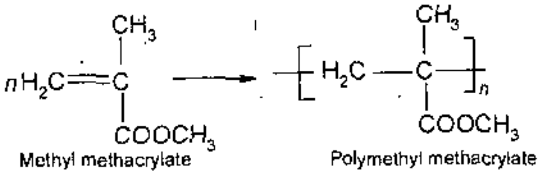
$$n\,H_2C{=}CH(Cl) \longrightarrow \left[CH_2-CH(Cl) \right]_n$$

Vinyl chloride → Polyvinyl chloride



$$n\,H_2C{=}CH(Cl) \longrightarrow \left[CH_2-CH(Cl) \right]_n$$

Vinyl chloride → Polyvinyl chloride



$$n\,H_2C{=}C(CH_3)(COOCH_3) \longrightarrow \left[H_2C-C(CH_3)(COOCH_3) \right]_n$$

Methyl methacrylate → Polymethyl methacrylate

$$n\,CF_2{=}CF_2 \longrightarrow \left[CF_2-CF_2 \right]_n$$

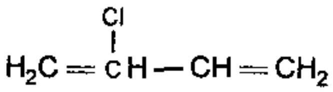
Tetrafluoroethylene → Polytetrafluoroethylene

The above polymerisation reactions are referred to as vinyl polymerisation. Vinyl compounds are only those containing $H_2C{=}CH$ group. However, it is convenient to consider all these polymerisation reactions under one heading.

(2) Diene polymerisation : The conjugated dienes undergo polymerisation through their multiple bonds. Butadiene, chloroprene and isoprene are the most common dienes used for the preparation of commercially important polymers :

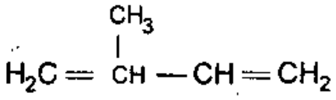
(i) Butadiene : $H_2C{=}CH{-}CH{=}CH_2$

(ii) Chloroprene :



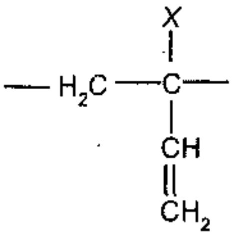
$$H_2C{=}\overset{\overset{\displaystyle Cl}{|}}{C}H{-}CH{=}CH_2$$

(iii) Isoprene :

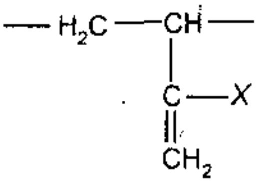


$$H_2C{=}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}CH{=}CH_2$$

Such type of monomers produce polymers containing various isomeric structural units. Each of the above monomer contains a 1,2-double bond and a 3,4-double bond, and there is a possibility that either double bond may participitate independently in polymerisation to give 1,2-units, and 3,4-units, respectively.



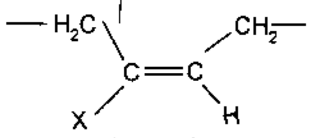
1,2-unit



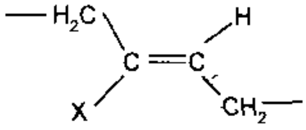
3,4-unit

(X = H, CH_3 or Cl)

In case of symmetrical dienes, for example butadiene, these two units are identical. Both the bonds are involved in polymerisation through conjugate reactions to give 1,4-units. The 1,4-unit may occur as **cis** or **trans** isomer

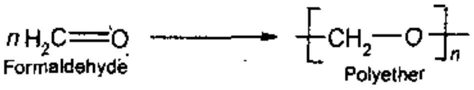


Cis 1,4-unit



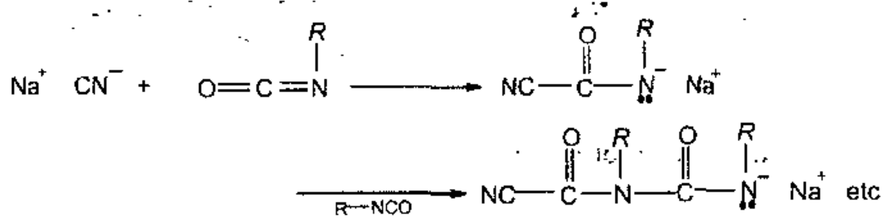
Trans 1,4-unit

(3) Hetero-multiple bond polymerisation : In the above types of polymerisation through multiple bond (vinyl and diene polymerisation), carbon-carbon double bond is the active site. The multiple bonds having elements besides carbon may also be utilized in the formation of polymers containing hetero-atom in the main chain. The carbonyl compounds are the most common unsaturated monomers used for the preparation of polymers of this kind. For example, formaldehyde, the product of polymerisation may be regarded as polyether.



$$\underset{\text{Formaldehyde}}{n\,H_2C{=}O} \longrightarrow \underset{\text{Polyether}}{\left[CH_2{-}O\right]_n}$$

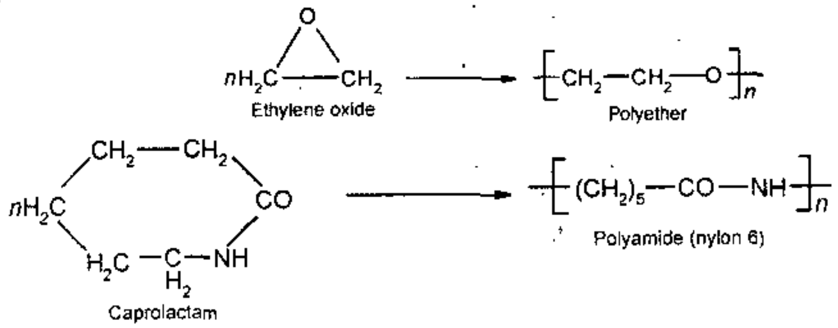
The polymerisation of monoisocyanate through the carbon-nitrogen double is the example of polymerisation of this category. The polymerisation is carried out at low temperature, to limit cyclisation, in the presence of sodium cyanide as an anionic initiator



[III] Polymerisation Through Ring Opening

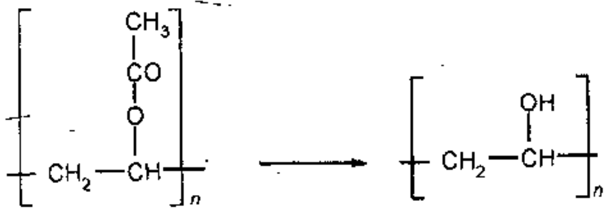
A number of cyclic compounds undergo ring opening reactions giving polymers. The structural units of the polymers thus prepared have the same composition as that of monomer and there is no change in the relative position of the atoms.

N-carboxy-α-aminoacid anhydrides, cyclic ethers, cyclic imines, cyclic sulphides, cyclopropanes, lactams and lactones undergo this kind of polymerisation. Generally, polymerisation through ring opening proceeds in the presence of anionic or cationic initiators. Polymerisation reactions of some of the cyclic compounds, for example cyclic ether and lactam, are given below :

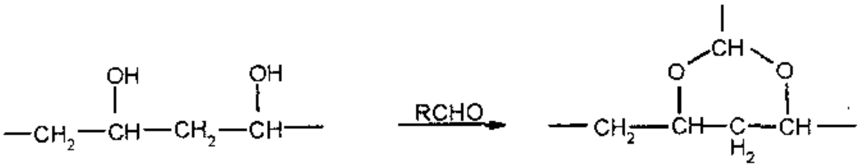


[IV] Polymer Modification

Polymer modification is not considered as the method of polymerisation. In this technique an existing polymer is subjected to such chemical reaction that a different polymer is obtained. For example, polyvinyl acetate on alcoholysis by treatment with methanol gives polyvinyl alcohol.



In the following case, the sequence of modification is extended by reacting a new polymer with an aldehyde to give polyvinyl acetal.



Cellulose may be modified through the hydroxyl groups to obtain esters and ethers. Cellulose acetate, cellulose nitrate and methyl cellulose are some of the important commercial materials.

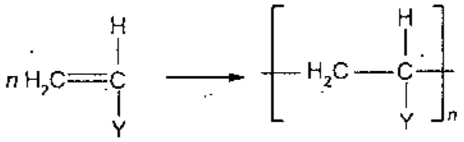
2.8. CLASSIFICATION OF POLYMERISATION REACTIONS

Polymerisation reactions are classified into two types, *viz.*, addition polymerisation and condensation polymerisation.

[I] Addition Polymerisation

Addition polymerisation occurs among the molecules that contain double or triple bonds. It also occurs between bifunctional compounds, which result from the opening of ring structures (for example, ethylene oxide). Addition polymerisation does not involve liberation of small molecules.

Olefinic compounds of the type $H_2C{=}CHY$ (where Y = H, X, $-COOR$ and CN etc) undergo addition polymerisation.



$$n\,H_2C{=}\underset{Y}{\overset{H}{C}} \longrightarrow \left[-H_2C-\underset{Y}{\overset{H}{C}}- \right]_n$$

Addition polymerisation occurs in the three following possible ways :

(i) Head to tail

$$-CH_2-CHY-CH_2-CHY-$$

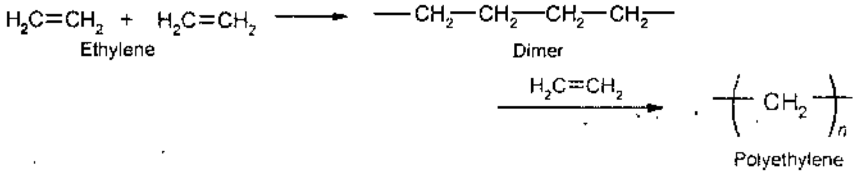
(ii) Head to head and tail to tail

$$-CHY-CH_2-CHY-CHY-CH_2-CH_2-CHY-$$

(iii) At random arrangement involving (i) and (ii)

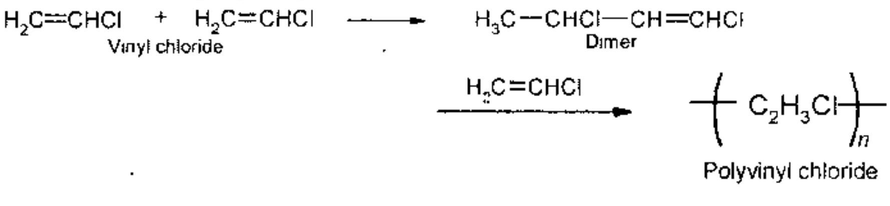
Addition polymerisation proceeds in the presence of a catalyst. Polymerisation can be catalysed by ionic type or radical type catalysts. Two important examples of this type of polymerisation are given below :

(a) Ethylene to polyethylene



$$\underset{\text{Ethylene}}{H_2C{=}CH_2 + H_2C{=}CH_2} \longrightarrow \underset{\text{Dimer}}{-CH_2-CH_2-CH_2-CH_2-} \xrightarrow{H_2C{=}CH_2} \underset{\text{Polyethylene}}{\left(CH_2 \right)_n}$$

(b) Vinyl chloride to polyvinyl chloride

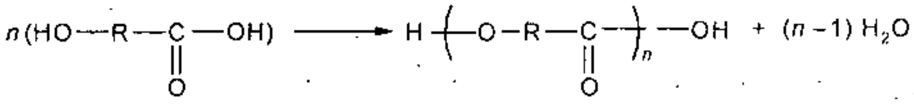


$$\underset{\text{Vinyl chloride}}{H_2C{=}CHCl + H_2C{=}CHCl} \longrightarrow \underset{\text{Dimer}}{H_3C-CHCl-CH{=}CHCl} \xrightarrow{H_2C{=}CHCl} \underset{\text{Polyvinyl chloride}}{\left(C_2H_3Cl \right)_n}$$

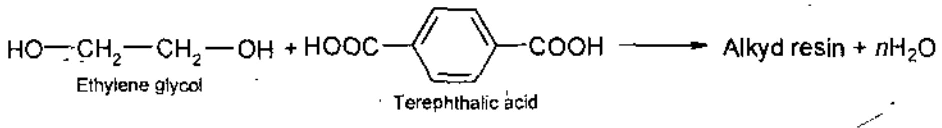
[II] Condensation Polymerisation (Polycondensation)

In condensation polymerisation, bi or polyfunctinal molecules condense with each other with elimination of small molecules (such as water, hydrogen chloride, ammonia etc.) as the reaction proceeds. Two examples of this type of polymerisation are represented as follows :

(i)



$$n(HO-R-\underset{\|\atop O}{C}-OH) \longrightarrow H\left(O-R-\underset{\|\atop O}{C} \right)_n-OH + (n-1)\,H_2O$$

(ii)


2.9. POLYMERISATION TECHNIQUES

Polymerisation reactions may be carried out in the solid phase, gas phase or liquid phase. Polymerisation techniques used in the production of some commercial polymers are given in table 2. Followings are the important polymerisation techniques :

(i) Bulk polymerisation
(ii) Solution polymerisation
(iii) Suspension polymerisation
(iv) Emulsion polymerisation

[I] Bulk Polymerisation

Polymerisation of the monomer in bulk may be carried out in the liquid or gas phase. The monomers and activators are mixed in a reactor and heated or cooled as required. Most of the polymerisation reactions are exothermic and therefore provision should be made to remove the excess heat. In some cases, the polymers are soluble in their liquid monomers causing an increase in the viscosity of the solution. In other cases, the polymer is insoluble in the monomer and it precipitates after a small amount of polymerisation has taken place.

[II] Solution Polymerisation

Solution polymerisation technique is used when the exothermic heat evolved is too high to be controlled in bulk polymerisation. The monomer and initiator are dissolved in a non-reactive solvent which makes the reaction slow and thus moderates the heat given off. The heat evolved may be controlled by refluxing the solvent. The polymer concentration should be low to avoid high viscosity. The polymers of low to medium molecular weight are produced by this kind of polymerisation.

[III] Suspension Polymerisation

In this technique, the monomer is suspended in water by agitation. Stabilisers such as talc, fuller's earth, and bentonite are added to stabilise the suspension and to prevent the adhering of polymer globules to each other. Generally, the initiator is soluble in monomer. Each monomer globule polymerises as a pearl of high molecular weight. The heat of polymerisation is removed by water. The stabiliser must be separated from the polymer. Sometimes, subsidiary polymerisation also occurs, because of partial miscibility of the monomer and water, producing a polymer having low molecular weight.

[IV] Emulsion Polymerisation

This technique is similar to suspension polymerisation but the monomer is broken into droplets that form aggregates (micelles). The monomer is on the initiator of the micelles, and the initiator is in water. Emulsifying agent (such as soap) is used to stabilise the micelles. The initiator diffuses into the micelle for starting polymer growth. Emulsion polymerisation is fast and can be performed at relatively low temperature. The heat evolved by the reaction is absorbed by the aqueous phase. By this process, polymers of high molecular weight can be prepared.

Table 2: Polymerisation techniques used in the production of commercial polymers

Polymer	Polymerisation technique
Polyamides	Bulk
Polycarbonate	Bulk
Polyethylene terephthalate	Bulk
Polysulphides	Suspension
Polyethylene (low density)	Bulk
Polyethylene (high density)	Solution
Polymethyl methacrylate	Bulk, suspension
Polypropylene	Solution
Polystyrene	Solution
Polyvinyl acetate	Emulsion
Polyvinyl chloride	Suspension
Styrene – butadiene copolymer	Emulsion
Polyformaldehyde	Solution
Polycaproamide (nylon 6)	Bulk

2.10. UTILIZATION OF COMMERCIAL POLYMERS

The following table 3 summarises the uses of commercial polymers :

Table 3: Uses of commercial polymers

Polymer	Use in
(1) Polyolefins Polystyrene Polyvinyl chloride Polymethyl methacrylate Fluoropolymers Polyethers	Plastics
(2) Polyamides Polyesters	Fibers
(3) Cellulosics	Films, fibers
(4) Phenol – formaldehyde Urea – formaldehyde Melamine – formaldehyde Polyurethanes Silicones	Plastics
(5) Phenol – formaldehyde Epoxides	Adhesives
(6) Polyesters Silicones	Paints
(7) Polydienes Polyesters	Plastics

2.11. THERMOPLASTIC POLYMERS

[I] Polyethylene or Polyethene

Polyethylene is prepared by the polymerisation of ethylene.

$$\underset{\text{Ethylene}}{n(CH_2{=}CH_2)} \xrightarrow{\text{Polymerisation}} \underset{\text{Polyethylene)}}{\left(-CH_2-CH_2- \right)_n}$$

Polyethylene is manufactured by two types of processes

High pressure process: This process produces flexible, semirigid and rigid polyethylene

Low pressure process: This process produces semirigid and rigid polyethylene. Flexible polyethylene can also be produced by this process.

(1) High pressure process : Industrially, polymerisation process is performed at high pressure (15000-30000 psi) and temperature (150-300°C). Pure ethylene is mixed with small percentage of oxygen (0.02 – 0.08 %) which acts as catalyst. The mixture is heated (150-300°C) and then delivered to a stainless steel reactor which is controlled to maintain the reaction at 150-300°C. The effluent from the reactor is passed to a separator in which unconverted ethylene is removed and recycled to an intermediate stage of the process. The liquid obtained from the separator is polyethylene. It is then chilled and *the solidified product is chopped and passed on to processing* steps like milling, rolling, compounding and pelletizing.

The polymerisation reaction is exothermic and requires control and safety measures for the prevention of decomposition of ethylene. The molecular weight of polyethylene can be controlled by reaction conditions. Higher pressure and purer ethylene produces polyethylene having higher molecular weight and higher melting point. The higher the oxygen content and the higher the temperature, the more vigorous the polymerisation reaction and the lower the degree of polymerisation.

High pressure process produces semirigid polyethylenes (density range 0.925 to 0.940 g cm^{-3}). The flowchart of high-pressure polyethylene process is *shown in fig. (12).*

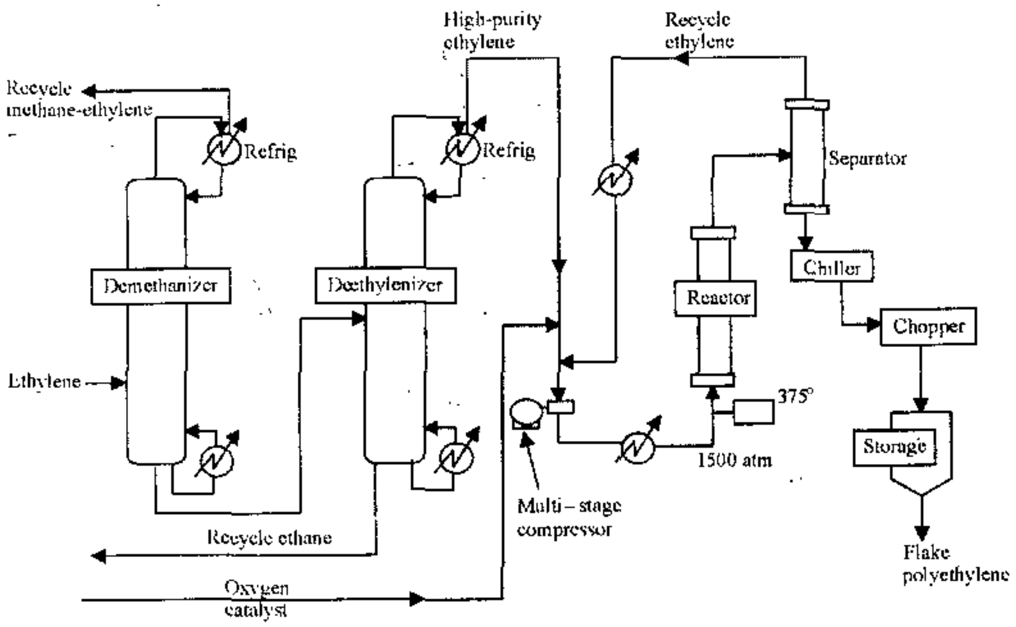


Fig. 12. Flowchart for high – pressure polyethylene process.

(2) Low pressure process : The commercial process for polymerisation of ethylene is performed at relatively low pressure (100-500 psi) in either fixed-bed or slurry-type operations. The catalyst consists of 2-3 weight percent chromium as oxide or silica alumina, and the reaction temperature varies from 90 to 180°C

(a) ***Fixed bed operation :*** Ethylene (purified) and hydrocarbon solvent streams are passed down flow, liquid phase over the catalyst bed. Solvent and polymer are collected and the solvent is flashed overhead. The unreacted gases are removed from the solvent and the solvent is recycled to the reactor. The solvent and polymer in the first receiver are cooled to room temperature in order to precipitate the polymer. The polymer thus obtained is filtered and dried in a vacuum oven.

(b) ***Slurry-type operation :*** The flowchart is shown in fig. (3). The solvent and small amount of fine catalyst (0.2 – 0.6 weight percent of solvent) are charged to the reactor. The reactor is closed and ethylene feed is started. Ethylene pressure is permitted to build up to 400 – 500 psi in less than an hour. At the end of the reaction, the polymer formed is removed. It is then dissolved in additional solvent and filtered to remove the catalyst. The polymer is precipitated by cooling the filtrate. The precipitated polymer is filtered and dried. Polyethylene formed possesses the density ranging form 0.91 to 0.965 g cm^{-3}.

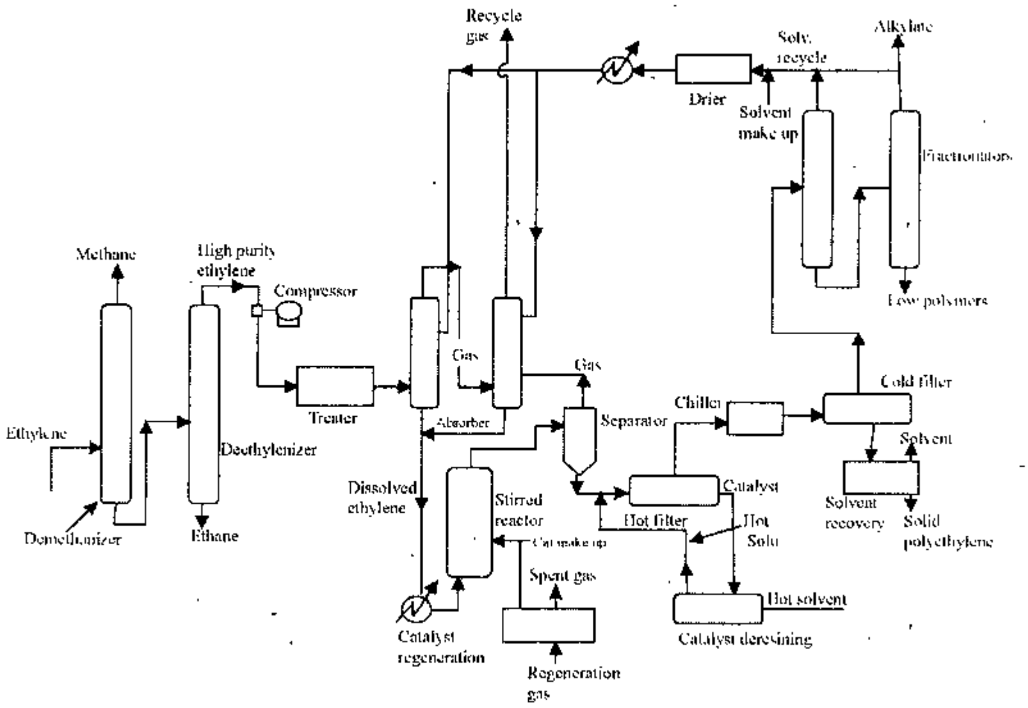


Fig. 13. Flowchart for low pressure polyethylene process (Philips)

In the Ziegler type of ethylene polymerisation, the catalyst can be prepared by adding diethylaluminium chloride (activator) and titanium tetrachloride (cocatalyst) to a dry hydrocarbon solvent under an inert atmosphere.

The flowchart for low-pressure polyethylene process (Ziegler) is shown in fig. (14). A small quantity of the dual catalyst (prepared in a dried paraffinic solvent)

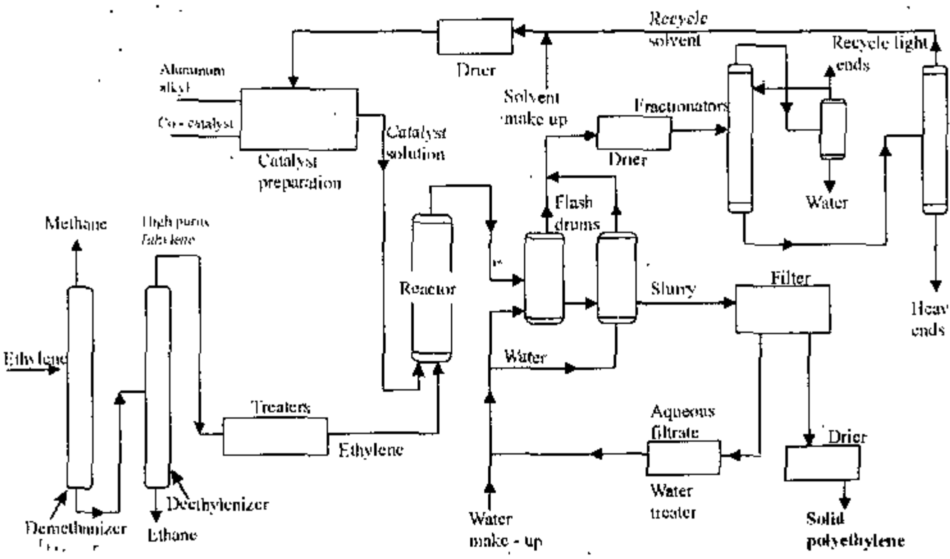


Fig. 14. Flowchart for the low-pressure polyethylene process (Ziegler)

is charged to the reactor. Ethylene (highly pure) is then delivered to the reactor to maintain a reactor pressure in the range of 15 – 100 psi. The temperature is maintained at 60-75°C. The reactor product is then passed through the series of flash drums in order to remove the solvent and to precipitate the polymer. The residual catalyst is then destroyed by adding water to the flash drums and polyethylene is removed as slurry. From this slurry, polyethylene is collected by filtration and then dried. Semirigid to rigid polyethylene is thus obtained (density in the range 0.93 to 0.96 g cm^{-3}).

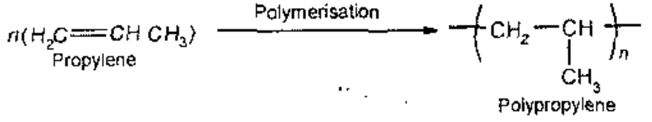
Properties :

(1) Polyethylenes are colourless, tasteless and odourless materials.
(2) Polyethylenes are inert and stable polymers.
(3) Polyethylenes are insoluble in all solvents at ordinary temperature.
(4) Polyethylenes are resistant to acids and alkalies. However, they are attacked by concentrated oxidizing acids.
(5) The solvents, which dissolve flexible polythene at 80°C only swell the rigid polyethylene at the same temperature.

Uses : Polyethylene is used for making bottle caps, flexible bottles, kitchen appliances, insulator parts, sheets for packing material, tubes, pipes, coated wires, cables and packing bags.

[II] Polypropylene (PP)

Polypropylene is prepared by polymerisation of propylene in the presence of Ziegler and Natta catalyst.



$$\underset{\text{Propylene}}{n(H_2C{=}CH\,CH_3)} \xrightarrow{\text{Polymerisation}} \underset{\text{Polypropylene}}{\left(CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}\right)_n}$$

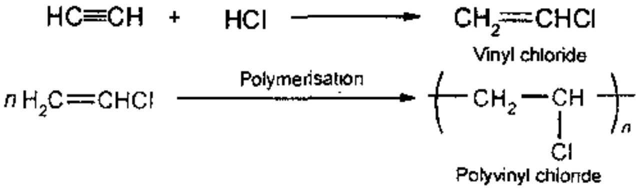
Properties :

(1) Polypropylene is isotactic and highly crystalline polymer
(2) Polypropylene has melting point 160-170°C.
(3) The hardness, strength, and stiffness of Polypropylene are better than those of polyethylene.

Uses : Polypropylene is used for making ropes, carpets, blankets, hand bags, water pipes, parts of the washing machines and hospital equipment etc.

[III] Polyvinyl Chloride (PVC)

Polyvinyl chloride is synthesised by heating water emulsion of vinyl chloride, in the presence of benzyl peroxide or hydrogen peroxide, in an autoclave under pressure. (Vinyl chloride is prepared by reacting acetylene at 01 to 1.5 atmosphere with HCl at 60-80°C, in the presence of metal chloride as catalyst).



$$HC{\equiv}CH + HCl \longrightarrow \underset{\text{Vinyl chloride}}{CH_2{=}CHCl}$$

$$n\,H_2C{=}CHCl \xrightarrow{\text{Polymerisation}} \underset{\text{Polyvinyl chloride}}{\left(CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}} \right)_n}$$

Properties :

(1) Polyvinyl chloride is a colourless, odourless, non-inflammable and chemically inert powder.

(2) The specific gravity of PVC is 1.33.

(3) PVC possesses resistance towards light, atmospheric oxygen, inorganic acids and alkalies.

(4) PVC has greater stiffness and rigidity as compared to that of polyethylene.

(5) Rigid PVC or unplasticised PVC has rigidity but is brittle. Plasticised PVC is obtained by addition of plasticisers like dibutyl phthalate, dioctyl phthalate etc.

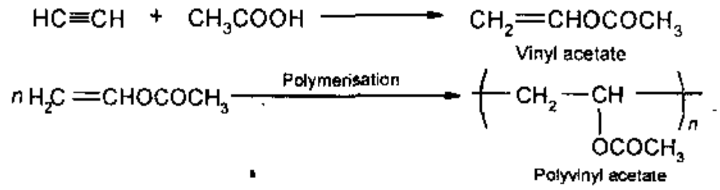
Uses:

(1) Rigid PVC is used for making sheets, light fittings, safety hamlets, tyres, mudguards of two wheelers, components of refrigerators etc.

(2) Plasticised PVC is used for making continuous sheets of different thickness (ranging from 0.1 to 8 mm) which are used for making raincoats, table-cloths and curtains etc, Plasticised PVC is also used for making toys, radio components, chemical containers, thermal insulating foam and conveyer belts useful in coal mines and industries.

[IV] Polyvinyl Acetate (PVA)

Polyvinyl acetate is synthesized by heating vinyl acetate in the presence of benzoyl peroxide or acetyl chloride as the catalyst. (Vinyl acetate is obtained by reacting acetylene with acetic acid in the presence of $HgSO_4$ as catalyst).



$$HC{\equiv}CH + CH_3COOH \longrightarrow \underset{\text{Vinyl acetate}}{CH_2{=}CHOCOCH_3}$$

$$n\,H_2C{=}CHOCOCH_3 \xrightarrow{\text{Polymerisation}} \underset{\text{Polyvinyl acetate}}{\left(CH_2-\underset{\displaystyle OCOCH_3}{\underset{|}{CH}} \right)_n}$$

Properties :

(1) Polyvinyl aretate is colourless and transparent.

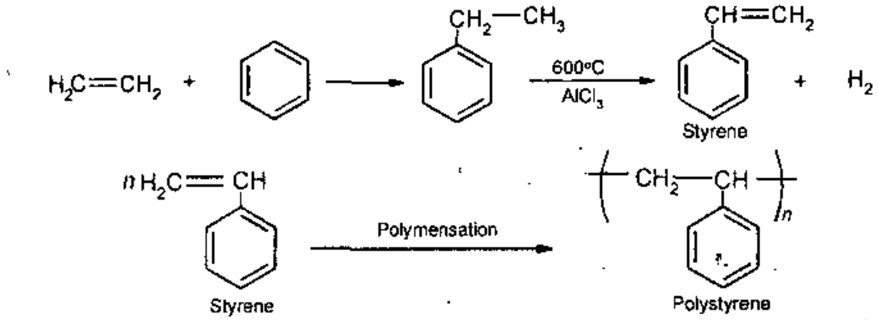
(2) Polyvinyl aretate possesses resistance towards water, atmospheric oxygen, and chemicals.

(3) Polyvinyl aretate is soluble in inorganic acids and organic solvents.

Uses : Polyvinyl acetate is used for making records, chewing-gums, paints, lacquers, coatings, card-boards, wrapping paper, surgical dressings, finishing textiles, leather and plastic emulsions etc.

[V] Polystyrene (PS)

Polystyrene is synthesised by polymerisation of styrene, dissolved in ethyl benzene, in the presence of benzoyl peroxide as catalyst. (Styrene is prepared from benzene and ethylene).



Properties :

(1) Polystyrene is a transparent substance having specific gravity 1.05 to 1.07 g cm^{-3}.

(2) Polystyrene cannot be nitrated by fuming nitric acid and sulphonated by concentrated sulphuric acid.

(3) Polystyrene has resistance towards moisture, acids and chemicals.

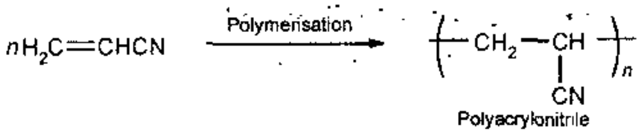
(4) Polystyrene is brittle and has low softening range (90-100°C).

Uses : Polystyrene is used for making toys, combs, buckets, parts of radio and television sets, battery cases, electric insulators, and various parts of refrigerators.

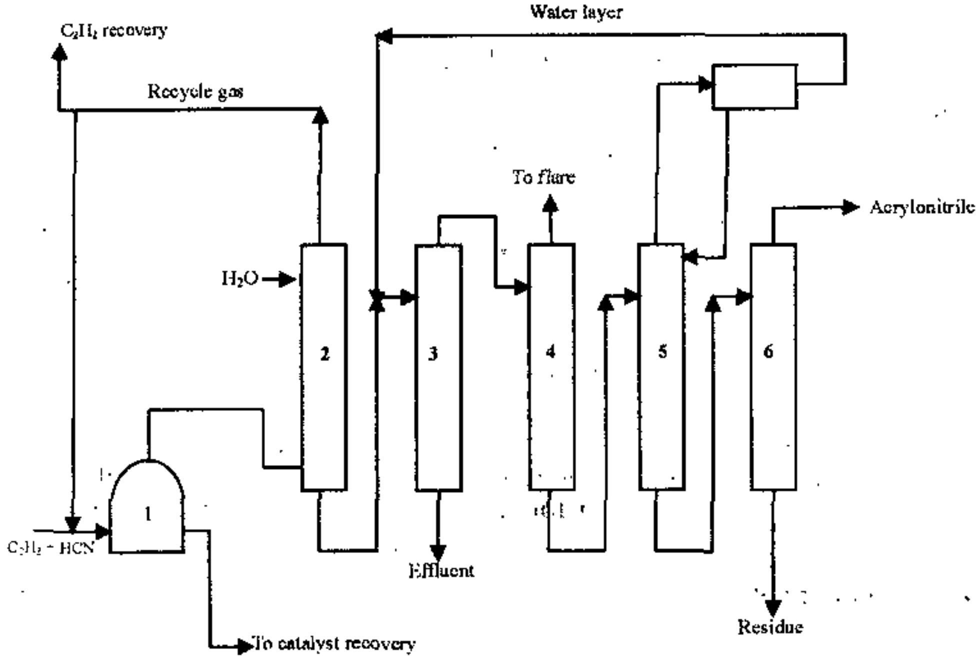
[VI] Polyacrylonitrile (PAN)

Polyacrylonitrile is prepared by the polymerisation of acrylonitrile in the presence of a peroxide. (Acrylonitrile is prepared by reacting acetylene with hydrogen cyanide).

$$HC \equiv CH + HCN \xrightarrow{CuCl} \underset{\text{Acrylonitrile}}{CH_2 = CHCN}$$



$$nH_2C{=}CHCN \xrightarrow{\text{Polymerisation}} \underset{\text{Polyacrylonitrile}}{\left(CH_2 - \underset{CN}{\underset{|}{CH}} \right)_n}$$



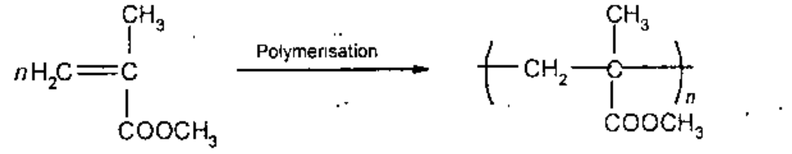
1 – Reactor, 2 Absorber, 3 – Stripper, 4 – Topper, 5 – Dryer, 6 – Rectifier

Fig.15. Flowchart for the manufacture of acrylonitrile.

Polyacrylonitrile is hard and possesses high melting point. It is used for making carpets, blankets and warm cloth. The flowchart for the manufacture of acrylonitrile is shown in fig. (15). Acetylene and hydrogen cyanide are reacted at ~ 90°C in an aqueous solution containing 35-60 percent cuprous chloride (CuCl). In order to increase the solubility of cuprous chloride, ammonium chloride is added.

[VII] Polymethyl Methacrylate (PMMA)

Polymethyl methacrylate is obtained by polymerisation of methyl methacrylate in the presence of acetyl peroxide or hydrogen peroxide



$$n\,H_2C{=}\overset{CH_3}{\underset{COOCH_3}{C}} \xrightarrow{\text{Polymerisation}} \left[CH_2-\overset{CH_3}{\underset{COOCH_3}{C}} \right]_n$$

Methyl methacrylate   Polymethyl methacrylate

Properties :

(1) PMMA is hard and rigid and possesses high softening point (130-140°C). It becomes rubber like at 65°C. (The wide span of temperature from rigid state to viscous state accounts for its outstanding shape forming property).

(2) PMMA has high resistance towards sunlight and low resistance towards chemicals, hot acids and alkalies.

Uses : Polymethyl methacrylate is used for making lenses, aircraft light fixtures, cockpit canopies, artificial eyes, emulsions, paints, adhesives, TV screens, and automotive appliances.

[VIII] Polytetrafluoroethylene (PTFE) or Teflon

Polytetrafluoroethylene is prepared by the polymerisation of water-emulsion of tetrafluoroethylene, under pressure, in the presence of benzoyl peroxide as catalyst.

$$n\,F_2C{=}CF_2 \xrightarrow{\text{Polymerization}} \left[CF_2-CF_2 \right]_n$$

Tetrafluoroethylene   Teflon

Properties :

(1) Teflon possesses high softening point (about 350°C) and high density (2.1-2.3 g cm^{-3}).

(2) Teflon has high resistance towards all chemicals except hot alkali metals.

(3) Teflon possesses good electrical and mechanical properties.

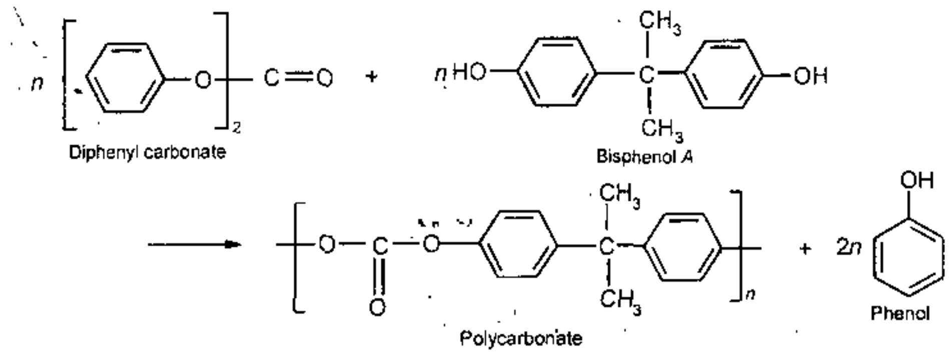
(4) Teflon has waxy touch and low coefficient of friction.

(5) At around 350°C, teflon forms viscous and opaque mass which can be moulded into desired form under pressure

Uses : Polytetrafluoroethylene is used for making gaskets, tank linings, packings, pipes (useful for carrying chemicals), and parts of pumps. It is also used as an insulating material for motors, transformers, cables, and wires etc.

[IX] Polycarbonates (PC)

Polycarbonates are prepared by reacting diphenyl carbonate with bisphenol-A.

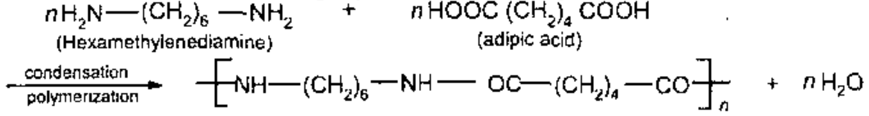


Polycarbonates possess high tensile strength over a wide range of temperature. They are soluble in organic solvents and alkalies. They are used for making electrical insulators and domestic wares etc.

[X] Polyamides

Polyamides are the synthetic polymers having recurring amide linkage (—CONH—). Nylons are polyamides. The different varieties of nylons are nylon 66, nylon 6, and nylon 11.

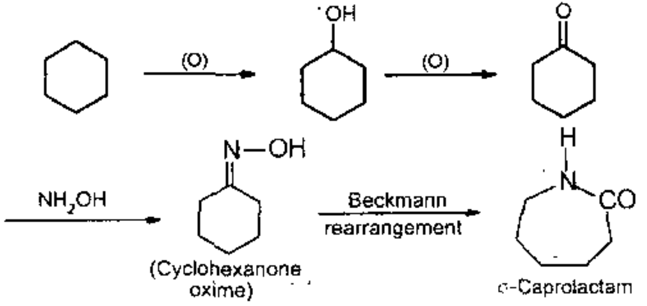
(1) Nylon 66 (Polyhexamethylene adipate) : This polyamide fibre is obtained by condensation polymerisation of two monomers namely hexamethylenediamine and adipic acid. Both the monomers contain six carbon atoms and hence the resulting nylon is called nylon 66.



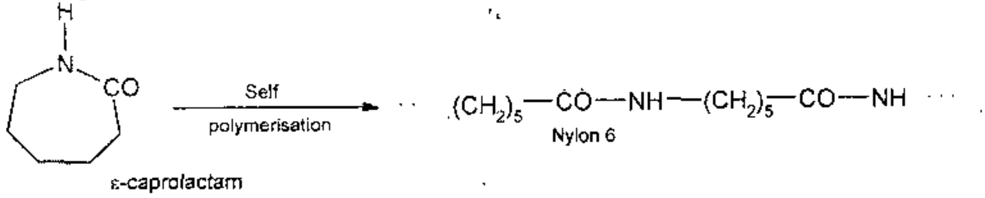
$$\underset{\text{(Hexamethylenediamine)}}{nH_2N—(CH_2)_6—NH_2} + \underset{\text{(adipic acid)}}{nHOOC(CH_2)_4COOH} \xrightarrow[\text{polymerization}]{\text{condensation}} \left[NH—(CH_2)_6—NH—OC—(CH_2)_4—CO\right]_n + nH_2O$$

(Nylon 66)

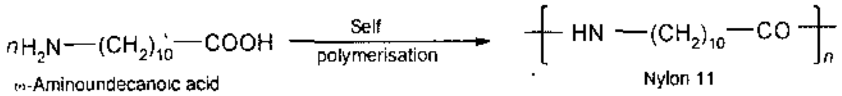
(2) Nylon 6 (Perlon L) : This polyamide fibre is synthesised by self polymerisation of ∈ caprolactam. (∈ caprolactam is obtained by Beckmann rearrangement of cyclohexanone oxime).



∈ caprolactam further undergoes self polymerisation to produce nylon 6.



(3) Nylon 11 : Nylon 11 is synthesised by self condensation of ω-aminoundecanoic acid



$$\underset{\text{ω-Aminoundecanoic acid}}{nH_2N—(CH_2)_{10}—COOH} \xrightarrow[\text{polymerisation}]{\text{Self}} \underset{\text{Nylon 11}}{\left[HN—(CH_2)_{10}—CO\right]_n}$$

Properties :

(1) Nylons are high melting polymers (160–240°C).

(2) Nylons possess high thermal stability.
(3) Nylons are insoluble in common organic solvents (benzene, acetone etc) and soluble in phenol and formic acid.

Uses :

(1) **Nylon 66:** It is used for making socks, under garments, dresses and carpets etc.
(2) **Nylon 6 and Nylon 11:** These are used mainly for moulding purposes for gears, bearings and electrical mountings. Nylon bearings and gears function properly.

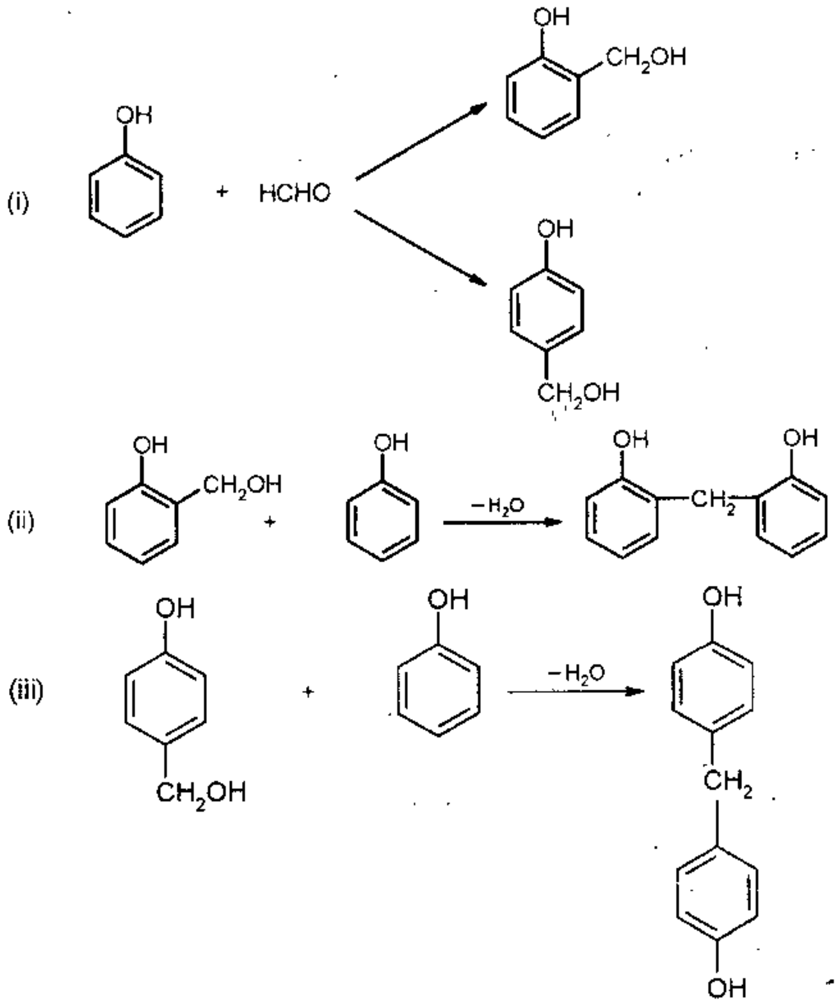
2.12. THERMOSETTING POLYMERS

Following are some of the important thermosetting polymers :

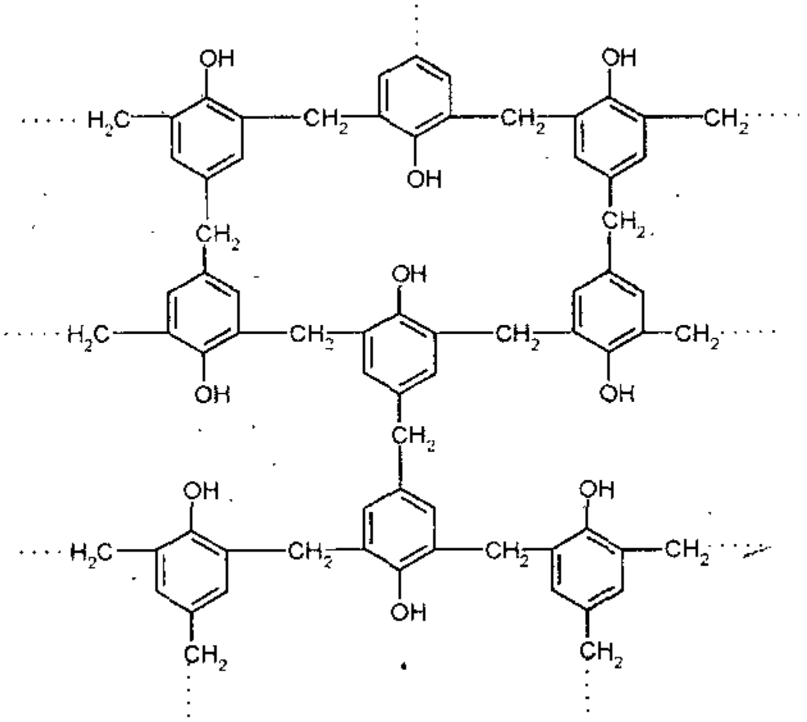
(i) Phenol-formaldehyde resin (Bakelite)
(ii) Urea-formaldehyde resin
(iii) Malemine-formaldehyde resin
(iv) Polyester resins
(v) Epoxy resins
(vi) Polyurethanes

[I] Phenol–Formaldehyde Resin (Bakelite)

Phenol–formaldehyde resin is synthesised by condensation of phenol and formaldehyde in alkaline or acidic medium.



In this way, $—CH_2—$ cross-linkages are introduced at ortho and para positions with respect to phenolic group and finally the following three dimensional structures (**Bakelite**) are obtained :



A segment of bakelite

Properties :

(1) Phenol-formaldehyde resin is rigid, hard, infusible and water resistant insoluble solid

(2) Bakelite has resistance towards non-oxidizing acids, and many organic solvents. It is attacked by alkalies.

(3) Bakelite is a good electrical insulator.

Uses : Bakelite is used for making electrical insulator parts (switches, plugs, switch boards etc) and parts of radios and television sets. It is used as hydrogen exchanger resin for softening of water. It is also employed in paints and varnishes.

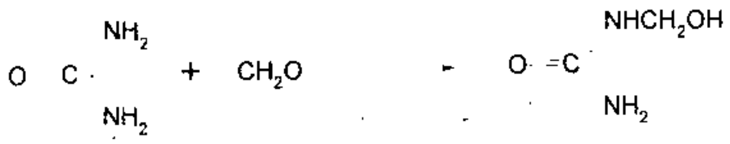
[II] Amino Resins

The following are commercially important amino resins :

(i) Urea-formaldehyde resin

(ii) Melamine-formaldehyde resin

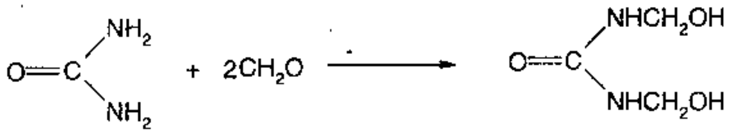
The other resins of this category use aniline, sulphonamide and thiourea. *methylolureas and methylolmelamines are the simplest condensates.* A low-stage resin is formed by the reaction of urea (or melamine) with formaldehyde. The reaction of urea (or melamine) with formaldehyde is a simple addition to yield methylol compounds.



$$O=C\begin{matrix}NH_2\\ NH_2\end{matrix} + CH_2O \longrightarrow O=C\begin{matrix}NHCH_2OH\\ NH_2\end{matrix}$$

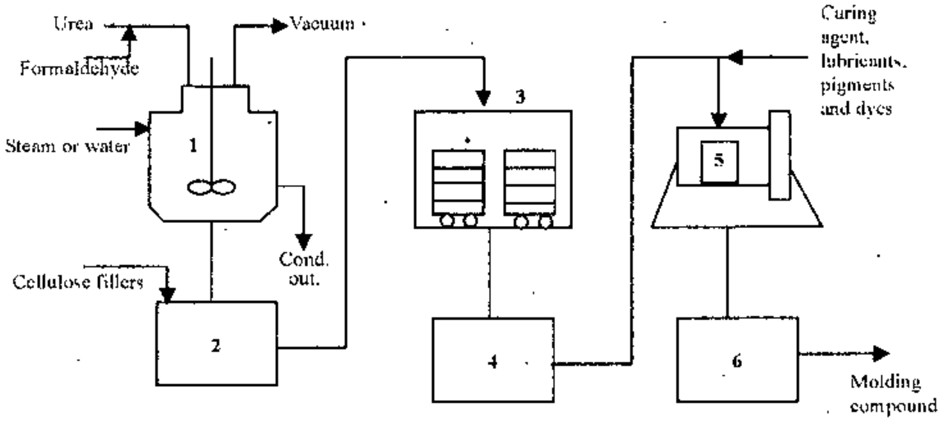
(Methylolurea)

Some dimethylolurea is also formed



(Dimethylolurea)

The mechanism of subsequent intercondensation of methylol compounds is not known definitely. However, there is evidence for the formation of methylene linkages, —NH, —CH_2, —NH— or either bridges —NH.CH_2—O—CH_2. NH— as condensation and curing proceeds. These water- soluble water-white intermediates are mixed with cellulose fillers before the final reaction and curing to obtain an infusible and insoluble product. The reaction requires a suitable catalyst and controlled temperature conditions. As the melamine is not quickly soluble in water or formalin at room temperature, it is essential to heat the reaction mixture at ~ 80°C to get methylol compounds for melamine-formaldehyde resin. The flowchart for the manufacture of a molding compound of urea–formaldehyde is shown in fig. (16).



1: Stainless steel reaction kettle
2: Mixer
3: Tray dryers
4: Low humidity cooling room
5: Ball mill
6: Granulator

Fig. 16. Flowchart for the manufacture of molding compound

The raw materials required to produce 100 kilogram of molding compound of urea-formaldehyde are as follows :

(i) Urea : 42 kg (ii) Formaldehyde : 42 kg

(iii) Cellulose filler : 40 kg (iv) Curing agent, lubricant and dye : 1.8 kg.

Properties :

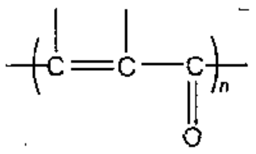
(1) Amino resins are resistant towards heat, solvent and chemicals, and discolouration.

(2) They possess extreme surface hardness.

Uses : Amino resins are widely used in molding compounds adhesives, paper coatings, textile treatment, manufacture of plywood, dinner waves and decorating strictures.

[II] Polyester Resins

Polyester resins are complex esters. They are formed by reacting difunctional alcohol with dibasic acid or anhydride. The reaction takes place at both ends of the chain, and therefore long molecules are possible and a plurality of ester groups is obtained. When one of the reactants contains unsaturation, then unsaturated polymers are obtained, for example,

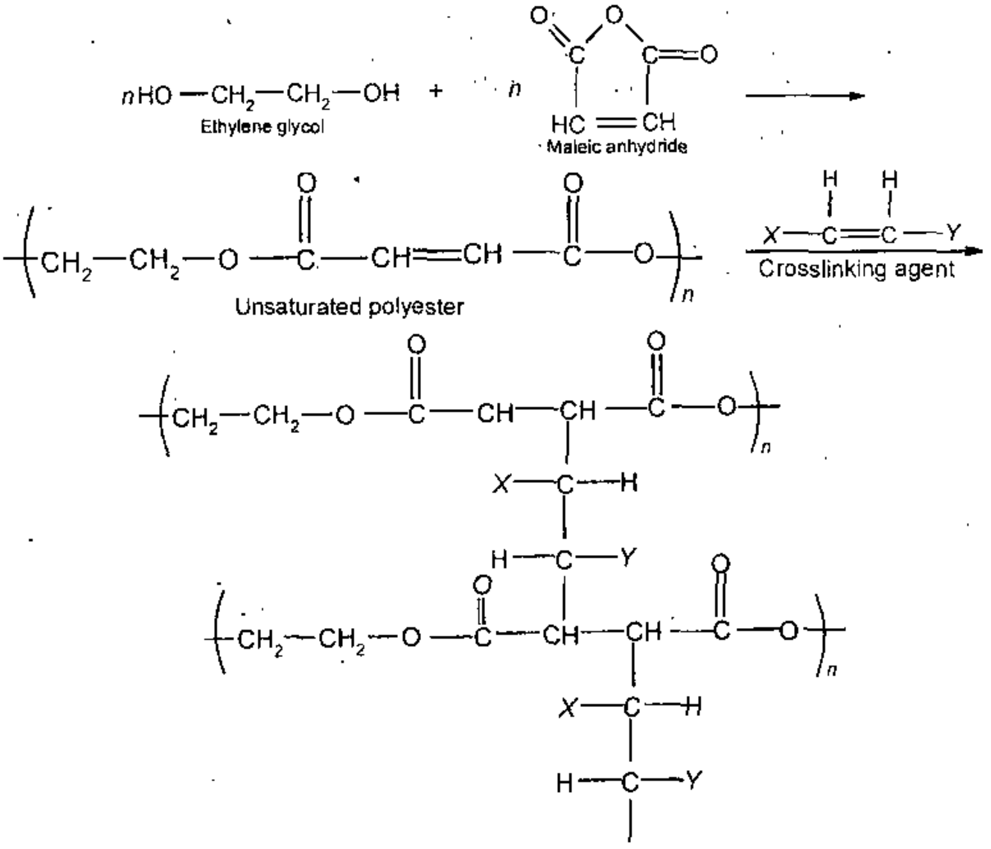


$$\left(-\overset{|}{C}=\overset{|}{C}-\underset{\underset{O}{\|}}{C}-\right)_n$$

Unsaturated polyesters are formed in two steps :

Step I – Condensation of the acid and alcohol to form a soluble resin and

Step II – *Addition of a cross-linking agent to form the thermosetting* resin. Some typical reactions are represented below :



The condensation reaction is performed in an insulated stainless steel or glass-lined kettle. Nitrogen gas (an inert gas) is bubbled through the reactants in order to keep out oxygen (which may cause gelation and decolouration of the resin).

The reaction mixture is heated to ~200°C for 4 to 20 hours. The water (by-product) *and the inert gas are removed continuously during the reaction.* When the desired degree of condensation is attained, generally under vacuum, the product is cooled to avoid gelation. The viscous polycondensation product is delivered to blending tanks and mixed with cross-linking agent for 2 to 4 hours. The resin thus obtained is filled in drums for storage and transportation.

Properties :

(1) Polyester resins possess extreme versatility in processing.

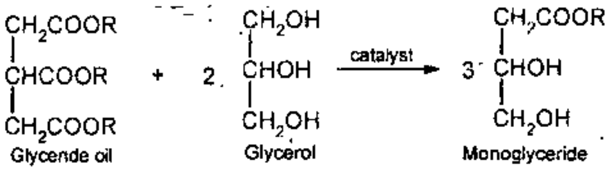
(2) Polyester resins possess excellent resistance towards heat, chemicals and flame.

(3) Polyester resins possess excellent mechanical and electrical properties.

Uses : Polyester resins are used in construction, laminates, finishing rods, aircraft components, coatings, decorative fixtures and bottles.

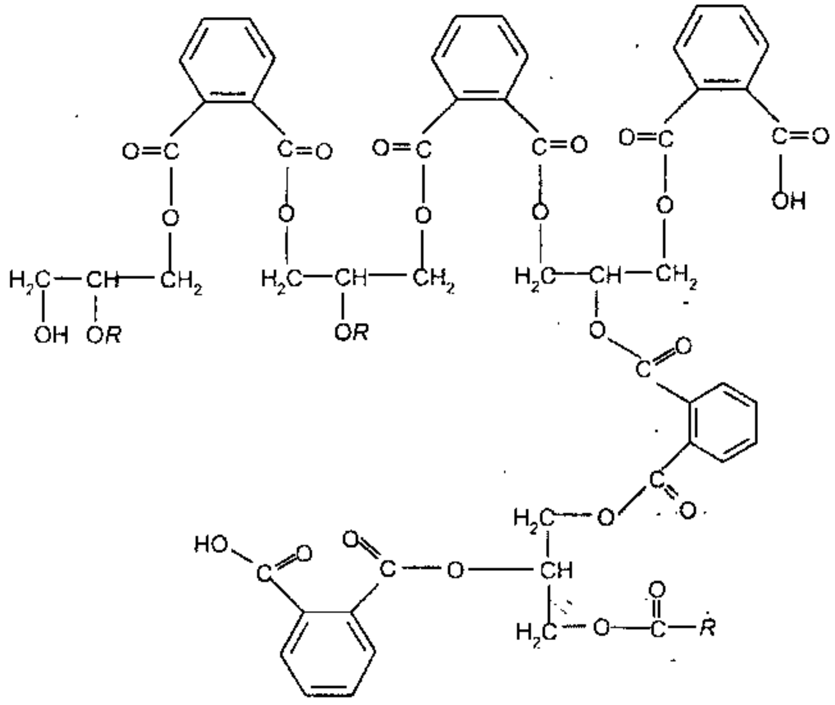
[IV] Alkyd Resins

Alkyd resins are particular kind of polyester formed by the reaction of polyhydric alcohols with polybasic acids. The most common method of preparation is the "fatty acid" method. In this method the glyceride oil is catalytically treated with glycerol at 225-250°C. The glyceride oil is simultaneously esterified and de-esterified to a monoglyceride.



$$\begin{matrix} CH_2COOR \\ | \\ CHCOOR \\ | \\ CH_2COOR \end{matrix} + 2\ \begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix} \xrightarrow{\text{catalyst}} 3\ \begin{matrix} CH_2COOR \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix}$$

The monoglyceride, on reaction with a dibasic acid, yields an alkyd resin



(Alkyd resin)
(R = fatty acid chain)

Properties :

(1) Alkyd resins have excellent electrical and thermal properties.

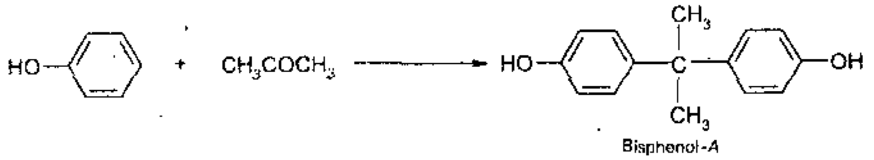
(2) Alkyd resins exhibit good chemical resistance.

(3) Alkyd resins possess rigidity.

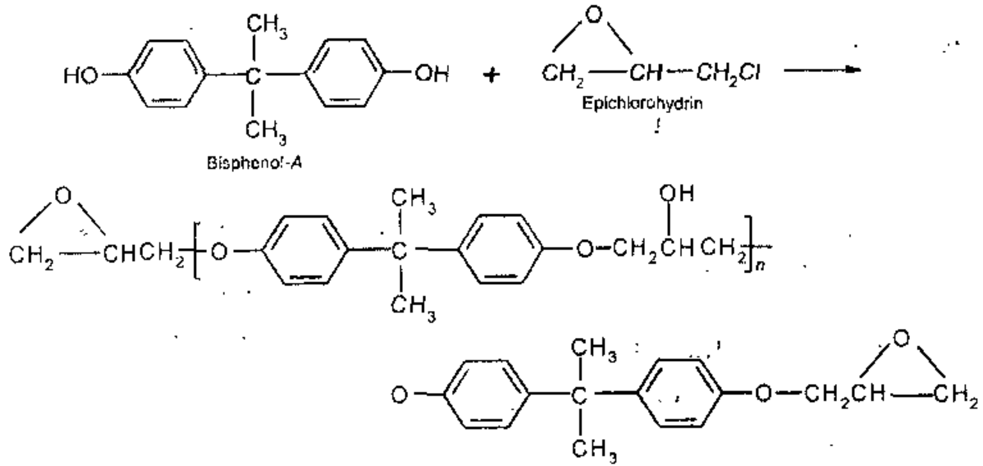
Uses : Alkyd resins are used in electrical insulation, electronic components, glass reinforced parts, and paints.

[V] Epoxy Resins

Epoxy resins are formed by the reaction of bisphenol–*A* with epichlorohydrin. Bisphenol–*A* is prepared by reacting phenol and acetone



Bisphenol–*A* on reaction with epichlorohydrin produces resins of the following general structure.



The resin is liquid (when *n* has low value) and hard, tough solid (when *n* value is 25). A resin containing one or more epoxide group is an epoxy resin.

(Epoxide group)

The most commercial resins are not 100 % diepoxides but may contain some terminal groups (glycol, phenolic or chlorohydrin). To obtain a useful resin, the expoxy resins must be cured or cross-linked. The cross linking may *occur due to opening of epoxide* ring caused by addition of curing agent having active hydrogen atoms (for example: amines, acid anhydrides and mercaptans etc).

Properties :

(1) Epoxy resins possess excellent chemical resistance.

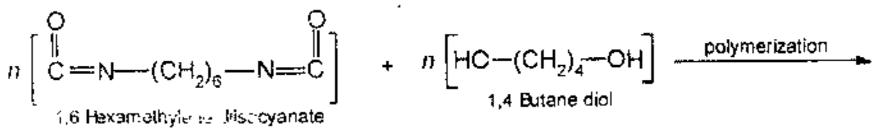
(2) Epoxy resins have good adhesion properties as well as excellent electrical properties.

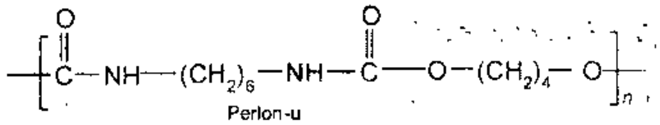
(3) Epoxy resins exhibit good heat resisting properties.

Uses : Epoxy resins are used in laminates, adhesives, flooring, linings propellers, and surface coating.

[VI] Polyurethanes

Commercially, polyurethanes are obtained by reacting di-isocyanate and diol. **Perlon-u** is one of the important examples of polyurethanes. It is obtained by reacting 1,4-butane diol with 1,6 hexamethylene-diisocyanate. Reaction is shown below.





$$\left[-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-O-(CH_2)_4-O-\right]_n$$

Perlon-u

Properties :

(1) Polyurethanes possess extreme versatility when combined with other resins

(2) Polyurethanes have good physical, chemical and electrical properties.

Uses : Polyurethanes are used in adhesives, rocket fuel binders, insulators, elastomers and foam inner liners for clothing.

2.13. RUBBER

Rubbers are high polymers having elastic properties. There are two types of rubber, viz., natural rubber and synthetic rubber.

[I] Natural Rubber

The milky fluid obtained from rubber tree **Hevea** is the colloidal solution of rubber in water. On coagulation with acetic acid, a soft solid is separated, which is called natural rubber. Natural rubber can be rolled into sheets.

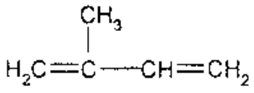
(1) Structure of Natural Rubber

(1) Empirical formula: C_5H_8.

(2) Natural rubber undergoes thermal decomposition in the absence of air to give isoprene and dipentene as the main products.

(3) Isoprene on polymerisation gives a rubber like product.

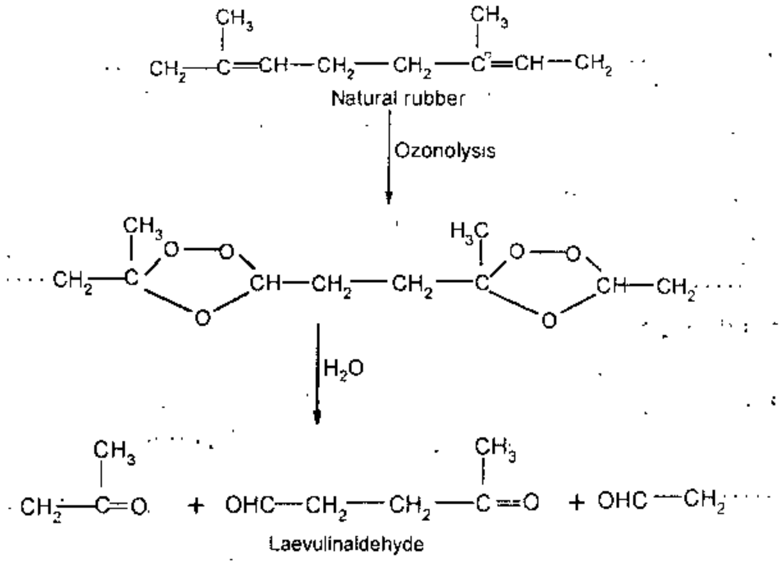
It is, therefore, indicated that natural rubber is a high polymer of isoprene (C_5H_8) units,



$$H_2C=\overset{CH_3}{\overset{|}{C}}-CH=CH_2$$

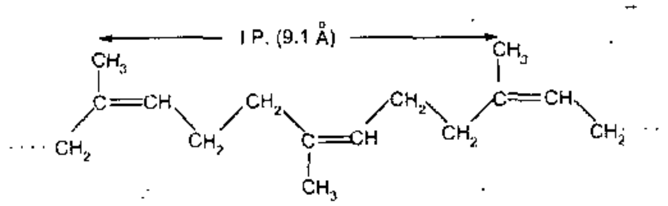
Isoprene

Natural rubber on, ozonolysis, gives laevulinaldehyde. This confirms the structure of natural rubber as represented :

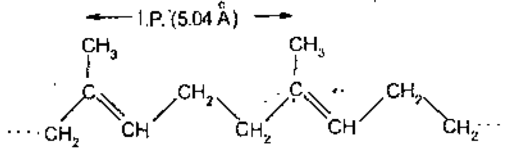


(2) Stereostructure of natural rubber : X-ray studies have suggested that natural rubber, in unstretched condition, is amorphous. The stretched rubber, however, is found to be oriented.

The elasticity of rubber is attributed to its *cis* configuration and large identity period (9.1 Å). On the other side, the isomeric natural polymer **Gutta percha** is non-elastic because of its *trans* configuration and low identity period (5.04Å).



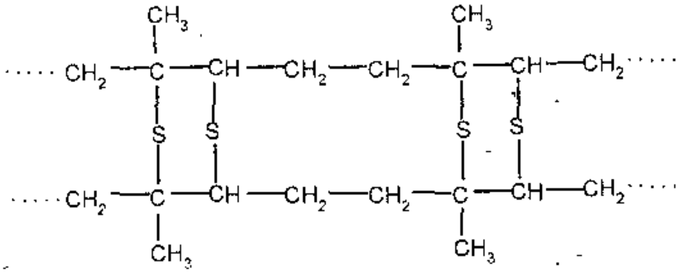
Natural rubber (*cis*)



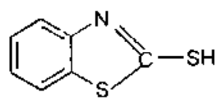
Gutta-percha (*trans*)

(3) Vulcanisation of rubber : The raw natural rubber is very soft and sticky. It has low tensile strength and low resistance towards friction. It undergoes auto-oxidation on exposure to air. Because of these qualities of natural rubber, the articles made from it are not durable.

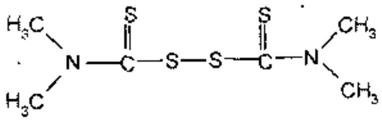
In order to convert natural rubber into a tough and elastic rubber, Charles Goodyear (1893) discovered a process known as **vulcanisation.** The vulcanisation process involves the heating of raw natural rubber with desired quantity of sulphur (5 to 8%). If more quantity of sulphur is added, then the toughness of rubber increases after vulcanisation. Addition of 50% sulphur gives **ebonite.** The vulcanised rubber possesses higher elasticity and more resistance to abrasion as compared to the raw rubber. Due to vulcanisation, the sulphur cross-links are introduced between the polymer chains. The sliding of polymer chains is, therefore, restricted and the rubber becomes tough.



The vulcanisation process is accelerated by adding 0.5 to 1% compounds such as mercaptobenzothiazole, tetramethyl thiuram disulphide etc known as **accelerators.**



Mercaptobenzothiazole

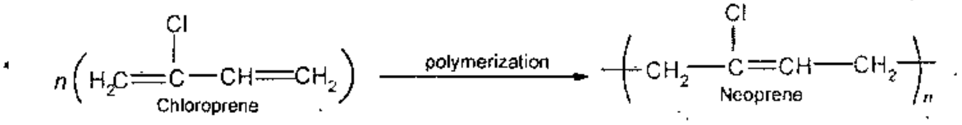


Tetramethyl thiuram disulphide

The accelerators enhance the rate of reaction between rubber and sulphur and also make vulcanisation process to occur at relatively lower temperature. Fillers (zinc oxide or carbon black) are also used to increase the efficiency of accelerator.

[II] Synthetic Rubber

(1) Neoprene rubber : Neoprene rubber is synthesised by polymerisation of chloroprene



$$n\left(H_2C{=}\overset{Cl}{\overset{|}{C}}{-}CH{=}CH_2\right)\ \xrightarrow{\text{polymerization}}\ \left(\!-CH_2{-}\overset{Cl}{\overset{|}{C}}{=}CH{-}CH_2-\!\right)_n$$

Chloroprene — Neoprene

Neoprene rubber possesses resistance towards water, solvents, chemicals and air oxidation. It is used for making gaskets, tubes for carrying corrosive gases and oils, conveyer belts, adhesives and linings of reaction vessels.

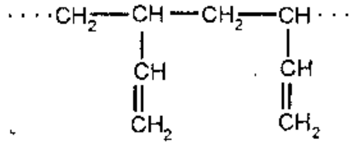
(2) Buna rubber : Buna rubber is synthesised by addition polymerisation of butadiene (BU) using sodium (Na) as the polymerizing agent. Hence it is called **BUNA** rubber.

$$H_2C{=}CH{-}CH{=}CH_2 + H_2C{=}CH{-}CH{=}CH_2 + H_2C{=}CH{-}CH{=}CH$$

$$\Big\downarrow \text{Polymerisation} \mid \text{Na}$$

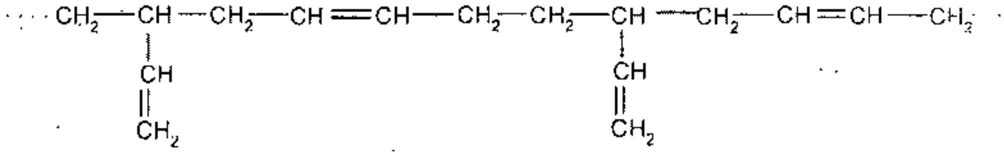
$$\cdots CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2\cdots$$

Apart from 1:4 addition, 1:2 addition polymerisation of butadiene occurs to a certain extent.



$$\cdots CH_2{-}\underset{\underset{CH_2}{\overset{\|}{CH}}}{\underset{|}{CH}}{-}CH_2{-}\underset{\underset{CH_2}{\overset{\|}{CH}}}{\underset{|}{CH}}\cdots$$

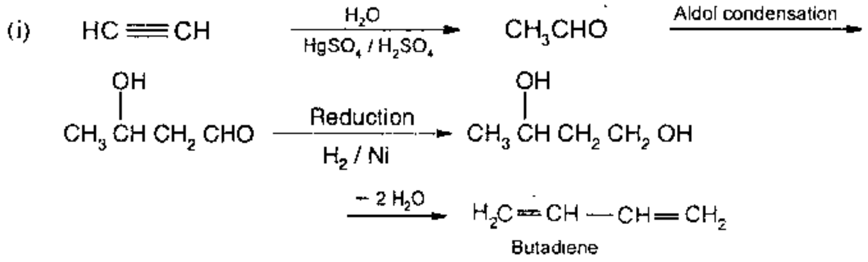
The Buna rubber, therefore, possesses some 1:4 addition and 1:2 addition linkages between the butadiene units.



$$\cdots CH_2{-}\underset{\underset{CH_2}{\overset{\|}{CH}}}{\underset{|}{CH}}{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\underset{CH_2}{\overset{\|}{CH}}}{\underset{|}{CH}}{-}CH_2{-}CH{=}CH{-}CH_2\cdots$$

Buna rubber

The monomer **butadiene** is synthesised by using the following methods :

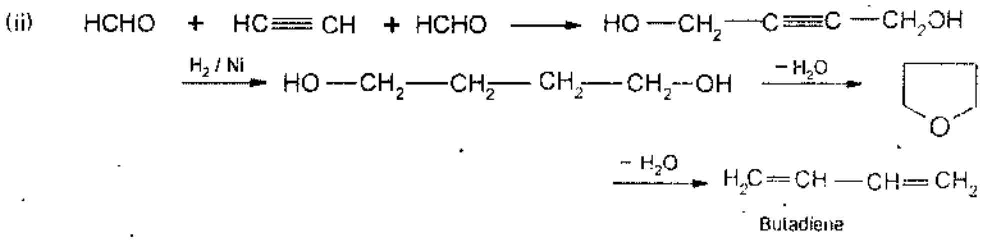


$$\text{(i)}\quad HC{\equiv}CH\ \xrightarrow[HgSO_4/H_2SO_4]{H_2O}\ CH_3CHO\ \xrightarrow{\text{Aldol condensation}}$$

$$CH_3\overset{OH}{\overset{|}{C}H}CH_2CHO\ \xrightarrow[H_2/Ni]{\text{Reduction}}\ CH_3\overset{OH}{\overset{|}{C}H}CH_2CH_2OH$$

$$\xrightarrow{-2H_2O}\ H_2C{=}CH{-}CH{=}CH_2$$

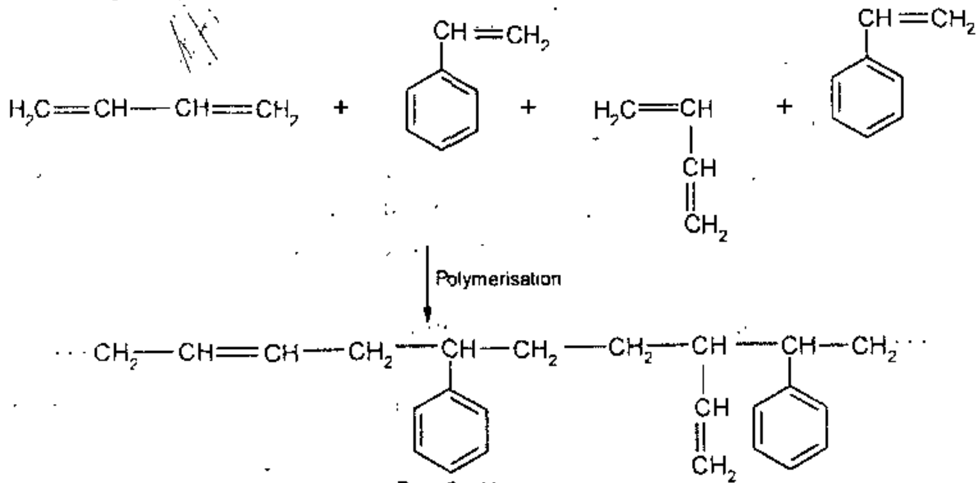
Butadiene



$$\text{(iii)}\quad C_2H_5OH + CH_3CHO \longrightarrow H_2C{=}CH{-}CH{=}CH_2 + 2H_2O$$

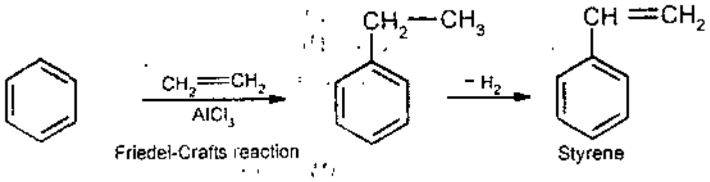
Butadiene

(3) Buna-S rubber (Government Rubber Styrene GRS) : Buna-S rubber is synthesized by copolymerisation of butadiene and styrene. Ozonolysis of this rubber suggests that butadiene undergoes 1 : 4 as well as 1 : 2 addition with styrene units. Butadiene (75% by weight) and styrene (25% by weight) are taken for synthesis.



Buna-S rubber

One of the monomers (styrene) is synthesized by the following method :



Properties :

(1) Buna – S rubber possesses high abrasion-resistance and high load-bearing capacity.

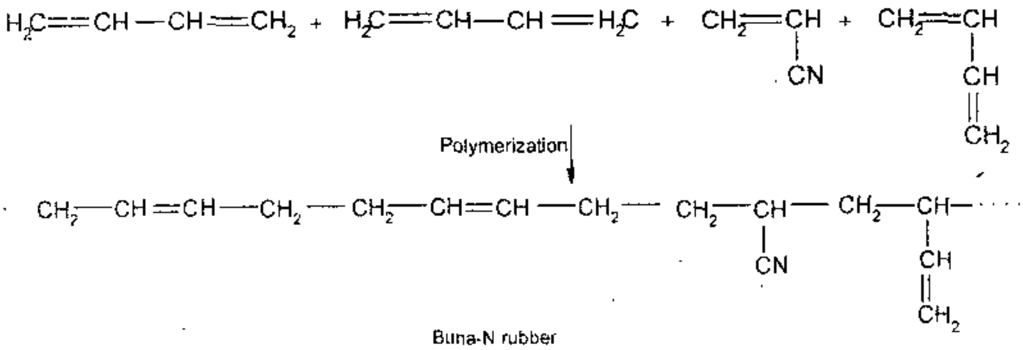
(2) Buna – S rubber undergoes swelling in oils and solvents

(3) Buna – S rubber undergoes oxidation readily, especially in the presence of traces of ozone present in the atmosphere.

(4) Buna – S rubber can be vulcanized in the presence of sulphur.

Uses : Buna– S rubber is used for making motor tyres, shoe soles, gaskets, components of foot-wares, wire and cable insulations, adhesives and tank-linings.

(4) Buna-N rubber (Perbuna, Government Rubber Acrylonitrile) : Buna-N rubber is synthesized by addition polymerisation of butadiene and acrylonitrile in the ratio 3 : 1 respectively. 1 : 4 and 1 : 2 addition of the monomers *takes place to give this rubber. Emulsion polymerisation technique* is used



Buna-N rubber

Properties :

(1). Buna–N rubber is resistant to heat, sunlight, oils, and acids.

(2) Buna–N rubber has low resistance towards alkalies due to the presence of cyano group

(3) Buna–N rubber can be vulcanised.

Uses : Buna–N rubber is used for making conveyer belts, components of aircrafts, tank linings, gaskets, adhesives and various automobile parts.

2.14. INORGANIC POLYMERS

Inorganic polymers are important compounds because they possess wide range of applications. These polymers are giant molecules composed of atoms excluding carbon atoms. Examples of inorganic polymers are :

- Silicones
- Phosphazenes and cyclophosphazenes
- Polythiazyl

Silicones and their applications are not covered in the syllabus. The phosphazenes and polythiazyl are discussed here as follows.

[I] Phosphazenes

Nitrogen and phosphorus bond together to form a large number of compounds known as ***phosphazenes.*** In these compounds, phosphorus exists in **+5** and nitrogen in +3 oxidation state. The compounds are formally unsaturated.

Monophosphazenes are obtained by reacting an azide ($C_6H_5N_3$) with phosphorus trichloride (PCl_3) or triphenyl phosphine (PPh_3),

$$PCl_3 + C_6H_5N_3 \longrightarrow Cl_3P{=}N{-}C_6H_5 + N_2$$

$$P(C_6H_5)_3 + C_6H_5N_3 \longrightarrow (C_6H_5)_3P{=}N{-}C_6H_5 + N_2$$

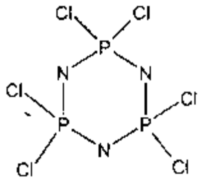
Diphosphazenes are obtained as follows :

$$3PCl_5 + 2\ NH_4Cl \longrightarrow \left[Cl_3P{=}N{-}PCl_2{=}N{-}PCl_3\right]^{+}\overset{-}{Cl} + 8\ HCl$$

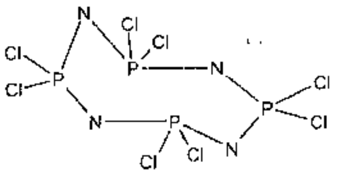
Nitrogen and phosphorus catenate together to form a series of polymers.

$$n\,PCl_5 + n\,NH_4Cl \xrightarrow{120\text{-}150^{\circ}C} \underset{\text{Cyclophosphazenes}}{\left[NPCl_2\right]_n} + 4n\,HCl \quad \text{and} \quad \underset{\text{Chain polyphosphazenes}}{Cl_4P{-}\left[NPCl_2\right]_n{-}NPCl_3}$$

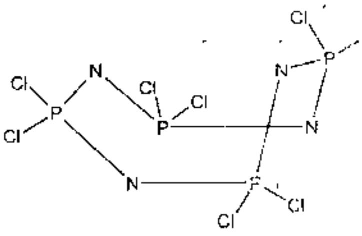
Some examples of **cyclophosphazenes** are represented below (structures I, II and III) :



I



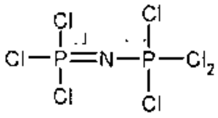
II



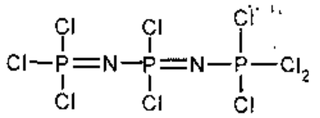
III

In cyclophosphazenes, $(NPCl_2)_n$, the value of n corresponds to 3,4,5,6 ……

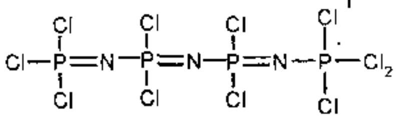
A large number of chain compounds are well known. They contain chains ranging from P_2NCl_7, $P_3N_2Cl_9$, $P_4N_3Cl_{11}$ to those upto 10^4 units ($NPCl_2$) linked together. Few examples are represented below (**IV**, **V**, **VI**, **VII**). These compounds are called **poly(chlorophosphazenes)**.



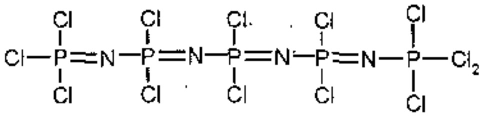
IV



V



VI



VII

In phosphazenes, the nature of bonding is not understood. The P-N and P=N bonds are equivalent (1.56-1.59 Å). This bond length is much shorter than the usual single bond distance (1.77Å).

High molecular weight phosphazenes are waterproof, fireproof, and are unaffected by petrol, oils and solvents. Because of these properties, phosphazenes are used as plastic, expanded foam and fibres. Thin films of poly(amino-phosphazene) are used in hospitals to cover severe burns and wounds because these films prevent the loss of body fluid and also protect from germs.

[II] Polythiazyl (SN)x

Polythiazyl is obtained by slow polymerisation of disulphur dinitrogen (S_2N_2).

$$S_2N_2 \xrightarrow[\text{polymerization}]{\text{slow}} \underset{\text{Polythiazyl}}{(SN)_x}$$

The crystal structural studies suggest that the four membered rings in disulphur dinitrogen (S_2N_2) have opened and polymerized into a long chain polymer. The atoms have zig-zag arrangement and the chains are flat.

Polythiazyl, $(SN)_x$, is a bronze coloured shiny solid. It conducts electricity and as temperature decreases, the conductivity increases. At 0.26 K, polythiazyl behaves as **superconductor**.

2.15. SCENARIO OF POLYMER INDUSTRIES IN INDIA

1. Astron Rubbers (P) Ltd., B-475-476, Nehru Ground, NIT, Faridabad, Haryana.
2. Ambad Engg Works, F-123, Ambad MIDC, Ambad, Nashik, Maharashtra.
3. Accumet Products, 348, Abdul Rehman Street, Jhaveri House, 4th Floor, Mumbai, Maharashtra.
4. ABS Industries Ltd., Kirthi Towers, Tilak Road, Baroda-390001.
5. BLS Polymer Ltd., 604, Indra Prakash Building, 21, Delhi.
6. B.A.S.F. India Ltd., Rhone Poulenc House, S.K. Ahire Marg, Mumbai-400025.
7. Baroda Rayon Corp. Ltd., 193, Nariman Point, Mumbai-400021.
8. Bhansali Engineering Polymers Limited, Ambaji Industrial Estate, Riico, Rajasthan.
9. Cariyon Chemical Pvt. Ltd., 802, Galav Chambers, Sayajigunj, Gujarat.
10. Century Inka Ltd., 9, Water 100 Street, Kolkata-700069.
11. Corel Pharma-Chem., 2-A, Vijay Colony, Stadium Road, Naranpu, Ahmedabad, Gujarat.

12. Classic Polymers & Resins, 4, Devdarshan, Mogul Lane, Mahim [W], Mumbai, Maharashtra.
13. Creative Components Pvt. Ltd. S-31, MIDC., Bhosari,, Maharashtra.
14. Croda Chemicals (I) Pvt. Ltd. 1/1,. Ttc Iindustrial Area, Thane Belapur, Navi Mumbai, Maharashtra.
15. Creative Polymers, MIDC, Phase II, Dombivli (East), Maharashtra.
16. DMS Global Inc, 115, Phase 1, Palm Meadows, Whitefield, Bangalore.
17. Dhiren Chemical Industries, FF/18 Panorama, R.C. Dutt Road, Baroda 3, Gujarat.
18. Daman Polymers (India) Pvt. Ltd., 703, 7th Floor, C-2, Satellite Classic, Near Railway Station, Jogeshwari (e), Maharashtra.
19. Damodar Tradelinks Pvt. Ltd., No.6, Sylvan Lodge Colony, 1st Cross Street, Kilpauk, Tamil Nadu.
20. Dr. Beck and Co. Ltd., 796/189-B, Bhandarkar Road, Pune-411004.
21. Ester Industries Ltd., Pilibhit Road, Khatima, US Nagar, Uttarakhand.
22. Extrusion Techniks, Plot No. 3207, Phase IV, GIDC, Vatva, Gujarat.
23. Expanded Polymer Systems Pvt. Ltd., C-44/1, Midc, Pawne, Ttc Area, Vashi, Navi Mumbai, Maharashtra.
24. Exxonmobil Company India Pvt. Ltd., Plot No. 107, Road No. 8, Kalpataru Point, Sion (East), Mumbai.
25. Flamingo Additives & Colourants Pvt. Ltd, 511-514, Raikar Chamber, Next to Jain Temple, (e), Mumbai-400088, Maharashtra.
26. Gyani Polymers, Circuit House Road, Jagdalpur, Chhattisgarh.
27. Garware Plastics And Polyester Ltd., Vile Parle (e), Mumbai-400057.
28. HPL Additive Ltd., Plot 8, Sector 25, Ballabgarh, Haryana.
29. HPL, Haldia, West Bengal.
30. High Polymer Labs Ltd., 803, Vishal Bhawan, 95, Nehru Place, New Delhi.
31. Hindustan Polymer Ltd., 3 Second Line Beach, McDowell House, Chennai-600001.
32. Indian Petrochemicals Corp. Ltd., Petrochemical Town, Baroda.
33. Igus India Pvt. Ltd., 199/1, 22nd Main Hosur Layout, Agara,
34. India Polyfibers Ltd., 9, Laxmi Road, Lucknow-226001.
35. Jai Aravali Industries, 29, Khadak Street, Room No. 36, 3rd Floor, Masjid Bunder Road, Masjid, Mumbai - 400 009, Maharashtra.
36. J P Polymers Pvt. Ltd., J.P. House, Plot No.11, Opp. S.N.D.T. College, Liberty Garden Road, Malad (West), Mumbai-400064. Maharashtra.
37. KPL International, Statesman House, 10th Floor, 148, Barakhamba Road, New Delhi.
38. Lakshmi Rubber Industries (An ISO 9001 Certified Company), 12, 2nd Street, 2nd Lane, Harbour Colony, Kodungaiyur, Chennai, Tamil Nadu.
39. Mercury Synthetic Resins, Plot No.157/A. IDA, Bollaram, Zinnaram, Medak-Dt., Hyderal
40. MAC Coating Private Limited, H-35/a, Kirti Nagar, New Delhi-15.
41. Manorama Packaging Industries, J-118, Adarsh Nagar, Jaipur-302004, Rajasthan.
42. Mitvision Industries, Unit No. 18, 2nd Floor, Satam Industrial Estate, C.G. Road, Chakala, Andheri (e), Mumbai - 400099, Maharashtra.
43. National Rayon Corp. Ltd., 1, Jamshedji Tata Road, Mumbai-400023.
44. Omega Speciality Techno-Chem Pvt. Ltd., B-155, Midc, Wai, Satara-412803, Maharashtra
45. PTFE Rubber Works, 8, Geeta Indl. Est., I.B. Patel Road, Mumbai, Maharashtra.
46. Parnami Rubber & Plastic Works Pvt. Ltd., B-63 Bais Godam, Industrial area, Jaipur, Rajasthan
47. Performance Polymers And Coatings, 260A, Bommasandra Indl. Area, Hosur Road, Bang
48. Raymond Synthetics Ltd., USIDC Industrial Area, Kailashnagar, Dist. Allahabad-212301.
49. Radiant Ele-Lite Company, Shapar (Veraval), Rajkot, Gujarat.
50. Raghav Polymers, Pocket J-3326, Narela Industrial Area, Dsidc, Delhi – 110009.
51. Reliance Industries Ltd., 222 Nariman Point, Mumbai-400021.
52. Sunbeam Rubber Linings, 15A, D1 Block, Midc Chinchwad, Pune, Maharashtra.
53. Sun Polymers, W-269, Midc Ind. Area, Thane-Belapur-Road, Navi Mumbai-400701, Maharashtra.

54. Sarandot Polymers, 2/25, Lakshmi Nagar North, Tirupur, Tamil Nadu.
55. Sima (India) Extrusion Technologies Pvt. Ltd., Office No. 102, 1st Floor, Kaalika Tower, Opp. Pratap Cinema, Gupta Deshpande Estate, Kolbad, Thane-400602, Maharashtra.
56. Sharan Polyplast, Sangli, Maharashtra.
57. Segma Industries, 97/501Poonam Complex, Santipark Road, Miraroad (Mumbai), Maharashtra.
58. Shree Synthetics Ltd. Naulakhi, Maksi Road, Vjjain, Madhya Pradesh.
59. Vikas Profin Limited, F-6, Vikas Apartments, 34/1, East Punjabi Bagh, New Delhi-26.
60. Zydex Industries, 25-A, Gandhi Oil Mill Compound, Vadodara, Gujarat.

STUDENT ACTIVITY

1. Name any four petrochemicals.

2. What is Buna-S rubber ? How it is prepared ?

3. Differentiate between thermosetting and thermoplastic polymers.

4. What is Zeigler-Natta catalyst ? Where it is used ?

5. Define monomer, macromolecule and co-polymer.

6. How is polythene obtained from ethene ? Give reaction only.

7. Give the structure of polystyrene.

SUMMARY

- The relatively pure identifiable substances derived from petroleum and used in the chemical trade are known as a petrochemicals.
- Adhesives, agrochemical, lubricants, alcohols, benzene, coal tar, dyes, explosives, industrial carbon, rubber and rubber chemicals etc. are all petrochemicals.
- Methane gives the following petrochemicals : Ammonia, carbon black, methanol, methyl chloride, methylene chloride, chloroform, carbon tetrachloride, acetylene, hydrogen cyanide.
- Petrochemicals from ethylene are : Ethylbenzene, ethyl chloride, ethylene dichloride, ethylene glycol, perchloroethylene, polyethylene, styrene, ethylene oxide, 1, 1, 1 trichloroethane.
- Petrochemicals from propylene and butylenes are : Acrylonitrile, butadiene, *n*-butanol, butyl rubber, isopropyl alcohol, polypropylene, propylene oxide.
- Petrochemicals from benzene, toluene, cylenes and ethylbenzene are : Benzene, cyclohexane, ethylbenzene, toluene, *p*-xylene, *m*-xylene, *o*-xylene.
- Heating at a very high temperature in a closed cover is called cracking or pyrolysis.
- Methanol is manufactured from synthetic gas in presence of a copper based catalyst.

$$CO + 2H_2 \xrightarrow{\text{Catalyst}} CH_3OH$$

- Phenol is manufactured by oxidation of toluene to benzoic acid followed by decomposition.

$$C_6H_5CH_3 + \frac{3}{2}O_2 \xrightarrow[\text{Co salt}]{150°C} C_6H_5COOH + H_2O$$

$$C_6H_5COOH + \frac{1}{2}O_2 \xrightarrow[\text{Cu-Mg salt}]{280°C} C_6H_5OH + CO_2$$

- A polymer is a large molecule consisting of repeating structural units joined by covalent bonds.
- A polymer may contain identical monomers or monomers of different structural units. They are then also known as homopolymers or copolymers.
- The physical properties of the polymers are affected by difference in configuration. This is known as tacticity.
- Thermoplastic polymers are linear long chain polymers having no cross linkages. They become soft on heating and hard on being cooled.
- Thermosetting polymers are highly cross-linked polymers. They become hard, insoluble and infusible with three-dimensioned space network of cross linkages.

- Elastomers are rubber or rubber like substances. In unscratched state, elastomer contains very few cross linkages. The polymer chains are not properly oriented. They become soft on heating and dissolve in certain solvents.
- Fibers are polymers whose polymer chains are held together by hydrogen bonding.
- The milky fluid obtained from rubber tree is a colloidal solution of rubber in water. On coagulation with acetic acid, a soft solid is separated. This solid is called natural rubber.
- Vulcanisation is done to convert natural rubber into a tough and elastic rubber. The heating of natural rubber with desired quantity of sulphur (5-8%) is called vulcanisation.
- If more quantity of sulphur is added during vulcanisation, the toughness of rubber increases.
- Addition of 50% sulphur to natural rubber gives a product called ebonite.

TEST YOURSELF

Answer the following questions :

1. What are petrochemicals ? Name any four of them.
2. What petrochemicals are obtained from ?
   (a) Methane (b) Ethylene
   (c) Propylene (d) Benzene
3. How are petrochemicals manufactured ?
4. Write a note on pyrolysis ?
5. Mention the esterification of organic acids and alcohols.
6. What products are obtained from the chlorination of methane ?
7. How is isopropyl alcohol manufactured ?
8. How is ethanol manufactured ?
9. How will you manufacture the following organic compounds ?
   (a) Methanol (b) Phenol
   (c) Acetaldehyde (d) Ethylene glycol
   (e) Carbon disulphide (f) MTBE
10. What are Zeigler-Natta catalysts ?
11. How will you represent the types of different polymeric materials ?
12. Mention the nomenclature of polymers.
13. Define tacticity, istactic polymers and atactic polymers ?
14. What are natural polymers ? How are they classified ?
15. How are polymers prepared ?
16. What are thermosetting and thermoplastic polymers ?
17. Discuss diene polymerisation.
18. How will you prepare the following polymers ?
   (a) Polyethene (b) Polypropylene
   (c) Polystyrene (d) PVC
   (e) Teflon (f) Nylon 66
   (g) Nylon 6 (h) Bakelite
   (i) Epoxy resins (j) Polyester resins

19. What is natural rubber ?
20. Define vulcanisation.
21. Write short notes on the following :
    (a) Buna-N rubber (b) Buna-S rubber
22. Write a note on inorganic polymers.
23. Natural rubber is :
    (a) Soft (b) Hard
    (c) Brittle (d) Ductile
24. Mixing of sulphur with natural rubber is called :
    (i) Melting (ii) Vulcanisation
    (iii) Hydration (iv) Hydrogenation
25. Bakelite is a :
    (i) Epoxy resin (ii) Urea-formadehyde resin
    (iii) Phenol-formaldehyde resin (iv) Polyurethane
26. Nylon 66 is obtained from :
    (i) Hexamethylene diamine and adipic acid
    (ii) Self polymerisation of caprolactam
    (iii) Self condensation of ω-aminoundecanoic acid
    (iv) Hexamethylene amine and acetic acid
27. **Fill in the blanks :**
    (a) Phenol is manufactured by the oxidation of ....
    (b) Starch is a polymer of ....
    (c) Thermoplastic polymers have .... cross linkages.
    (d) Ethylene on polymerisation gives ....
    (e) The starting compound for obtaining PVC is ....
    (f) Natural rubber is a high polymer of ....
    (g) Heating of natural rubber with 50% sulphur gives ....

ANSWERS

23. (i) **24.** (ii) **25.** (iii)

26. (i)

27. (a) toluene (b) d-D-glucose (c) no (d) polyethylene
(e) acetylene (f) isoprene
(g) ebonite.

UNIT
3

DYES AND DRUGS

STRUCTURE

LEARNING OBJECTIVES

After studying this chapter, you will learn about the different types of dyes and their applications. You will also learn about drugs, types of drugs, some antibiotics, antimalarials, antipyretics, arsenical etc as well as the manufacture of aspirin.

3.1. INTRODUCTION OF DYES

A dye is a substance, which must fulfil the following conditions :

(i) It must be coloured.

(ii) It must have strong ability to fix itself or must be capable of being fixed onto the fabric.

(iii) When it is fixed onto the fabric, it must not be fugative (*i.e.*, it must be fast to light and must possess resistance to the action of water and to a certain extent to dilute acids and alkalies).

Many natural dyes are well known since long. During ancient times people were using natural dyes obtained from vegetable and animal sources to dye their clothes. Some of the examples of natural dyes are *Turkey red* or *alizarine* (obtained from the roots of maddar tree), *indigo* (a blue dye obtained from the leaves of the indigoid tree) and *saffron* (a yellow dye obtained from the dried flowers of the colour thistle).

The first synthetic dye **mauve** was prepared by W.H. Perkin in the year 1856. While preparing the compound quinine by the action of acidified potassium dichromate on aniline sulphate, he obtained a dark precipitate (instead of quinine), which, on washing and then followed by extraction with hot alcohol, gave a violet dye (mauve). Later on a number of synthetic dyes namely **magenta** (1859) **aniline yellow** (1863) and **alizarin** (1869) were prepared. At present, a number of synthetic dyes are available in the market, which are prepared from aromatic compounds (benzene, phenol, aniline and naphthalene).

3.2. COLOUR AND CHEMICAL CONSTITUTION

When white light (750-4000 Å) falls on a substance, the light may be totally absorbed or totally reflected by the substance. When the light is totally reflected then the substance appears white and when the light is totally absorbed then the substance appears black. When a certain portion of the light is absorbed by the substance and the rest is reflected then the substance retains the colour of the reflected light. Thus, when a substance absorbs only a single band then it possesses the complementary colour of the absorbed band. The following table 1 displays the wavelength region, colour absorbed and visible (complementary) colour.

Table 1: Colour absorbed and colour visible

Wavelength (Å)	Colour absorbed	Visible (complementary) colour
4000-4350	Violet	Yellow-green
4350-4800	Blue	Yellow
4800-4900	Green-blue	Orange
4900-5000	Blue-green	Red
5000-5600	Green	Purple
5600-5800	Yellow-green	Violet
5800-5950	Yellow	Blue
5950-6050	Orange	Green-blue
6050-7500	Red	Blue-green

When a substance absorbs all visible light except one band, which is reflected, then the substance will be having the colour of that reflected band. For example, a substance appears blue because it absorbs only the yellow portion of the spectrum. In other words, the substance absorbs all the visible spectrum except blue. However, the shades will be different. Apparently a dye does not give a pure shade that means it does not reflect only one band of wavelength. For example, malachite green reflects green light but also to a certain extent reflects red, blue and violet light. The substances which are colourless exhibit absorption spectra but they absorb in the ultraviolet and infrared region and not in the region of visible spectrum.

O.N. Witt (1876) for the first time suggested that an organic compound appears coloured when that compound contains certain unsaturated groups. Let us consider two examples of organic compounds namely diazomethane and glyoxal. Both these compounds are coloured and they contain unsaturated groups. On reduction, diazomethane gives methylhydrazine and glyoxal gives glycol. Both the compounds methylhydrazine and glycol are colourless. It is very important to note that the carbonyl group is referred to as an unsaturated group by Witt. Its presence in a compound, however, does not give rise to unsaturatation. A more appropriate term than unsaturated group would have been a group with multiple bonds. Witt called these groups with multiple bonds as **chromophores**. Some of the important chromophores are mentioned below :

- **(i)** Nitro group : $-NO_2$
- **(ii)** Nitroso group : $-N=O$
- **(iii)** Azo group : $-N=N-$
- **(iv)** Azoxy group : $-N=N^+-O^-$
- **(v)** Azoamino group : $-N=N-NH-$
- **(vi)** Carbonyl group : $>C=O$
- **(vii)** Thiocarbonyl group : $C=S$

A compound containing chromophoric group is termed as a **chromogen.** It is observed that when the chromogen contains only one chromophore, then it is usually coloured (yellow) and the depth of the colour generally increases with the number of chromophores. A compound containing a single $C=C$ group is colourless, but if a number of such groups are present in *conjugation* then colour may be developed. For example, ethylene ($CH_2=CH_2$) is colourless but $CH_3(CH=CH)_nCH_3$ is yellow in colour. Another example is that acetone (CH_3COCH_3) is colourless, but diacetyl ($CH_3COCOCH_3$) is yellow and triketopentane ($CH_3COCOCOCH_3$) is orange.

Witt also suggested that the presence of certain groups in the chromogen deepens the colour even though these groups are chromophores. These groups are known as **auxochromes**. The auxochromes are acidic (phenolic) and basic in nature. Some of the important auxochromes are $-OH$, $-NH_2$, $-NHR$ and $-NR_2$ groups.

The groups, which cause deepening of the colour, are called **bathochromic groups**. *The groups which cause opposite effect that is* diminishing or lightening of colour are called **hypsochromic groups**. The deepening of colour is nothing but the change in colour as: yellow → orange → red → purple → violet → blue → green → black. Visible colour is the complementary color of the absorbed band. The bathochromic group shifts the λ_{max} from violet towards red that means they lower the frequency of the absorbed light. On the other hand, hypsochromic groups shift the λ_{max} from red towards violet, *i.e.,* they raise the frequency of the light absorbed. Auxochromes are generally bathochromic. The replacement of hydrogen in the $-NH_2$ group by aryl shows exhibits **bathochromic effect** and the replacement of hydrogen in the $-OH$ or $-NH_2$ group by acetyl group shows ***hypsochromic effect.***

3.3. CLASSFICATION OF DYES

Dyes are classified in two ways, *viz.*,

- Classification of dyes according to the applications.
- Classification of dyes according to the chemical constitution.

[I] Classification of Dyes According to Their Applications

The dyes are *classified according to their applications* to the fiber as follows :

(i) Acid dyes	(ii) Basic dyes
(iii) Direct dyes or Substantive dyes	(iv) Mordant dyes
(v) Vat dyes	(vi) Ingrain dyes or developed dyes
(vii) Sulphur dyes	(viii) Solvent dyes
(ix) Organic pigments	

(1) Acid dyes : The acid dyes are the sodium salts of sulphonic acid and nitrophenols. They are used for dyeing protein fibers such as wool, silk and nylon. They are also applied for dyeing leather and fiber.

(2) Basic dyes : Basic dyes are mostly salts of colour bases with hydrochloric acid or zinc chloride. They are used to dye wool or cotton with a mordant but are also useful for duplicator inks, carbon paper and typewriter ribbons. In solvents, except water, they form writing and printing inks.

(3) Direct dyes or substantive dyes : These dyes are used to dye cotton directly without a mordant. They are also applicable for dyeing mixed cotton, wool or silk. These dyes are mostly salts of azo compounds derived from benzidine or similar bases. They are soluble in water.

(4) Mordant dyes : These dyes do not dye the animal or vegetable fibers directly but they require a mordant for this purpose. If the dye is acidic then the mordant must be basic and if the dye is basic then the mordant must be acidic. The metallic hydroxides (hydroxides of chromium, aluminum, iron and tin) are used as mordant for acidic dyes, and tannic acid (tannin) is used as a mordant for basic dyes. In case of metal mordanting, the fabric is dipped into a solution of the metallic salt and then the padded fibre is dipped into the solution of the dye. This produces an insoluble coloured lake, which is fast to washing. In the case of tannin mordanting, the fibre is immersed into the tannin bath and potassium antimonyl tartrate is added to the bath. This produces brighter and insoluble lakes.

The colour of the lake is dependent upon the metal used. The lakes are nothing but the chelates formed between the metal and the dye.

(5) Vat dyes : Vat dyes are insoluble in water. They are reduced by alkaline sodium hyposulphite to alkali soluble compounds, which are readily reoxidized to the dye. These reduced compounds are white or colourless and are called leuco vats. The leuco vats are used to impregnate cotton fibers, which are further treated with an oxidant or exposed to air to develop the colours. The vat dyes are expensive and are used for fabric in service with frequent washing. Some vats are used as pastes for printing.

(6) Ingrain dyes or developed dyes : These dyes are produced in the fibre. They belong to three broad categories :

(a) *Ice colours* : These are produced on cotton fibre by soaking it in the secondary component (phenol or amine) of the azo dye and then colour is developed by dipping in the solution of diazonium salt.

(b) A direct cotton dye having a free amino group is applied to the fibre. It is then diazotized by dipping into a nitrous acid solution, followed by dipping in the solution of secondary component (phenol or amine). The azo dye is then produced.

(c) *Aniline black:* It is produced by the oxidation of aniline hydrochloride by heating the fibre with aniline hydrochloride solution containing oxidizing agent.

(7) Sulphur dyes : Sulphur dyes are high and low cost group of dyes. They produce dull shade on cotton. They possess good fastness to light, washing and acids. However, they are sensitive towards chlorine or hypochlorite. The sulphur dyes are colorless in the reduced form in a sodium sulphite bath but they gain colour on oxidation.

(8) Solvent dyes : The solvent dyes are generally azo, triarylmethane bases or anthraquinones. These dyes are used to colour oils, waxes, varnishes, shoe polishes, lipsticks and gasolines.

(9) Organic pigments : Organic pigments are not dyes in the sense that they dye fibres, but they are solid substances, which are generally insoluble in water and are useful for colouring paints and varnishes. Some pigments have been made water-soluble and then they are used as dyes, for example, phthalocyanine dyes.

Ans 2-

[I] Classification of Dyes According to Their Chemical Constitution

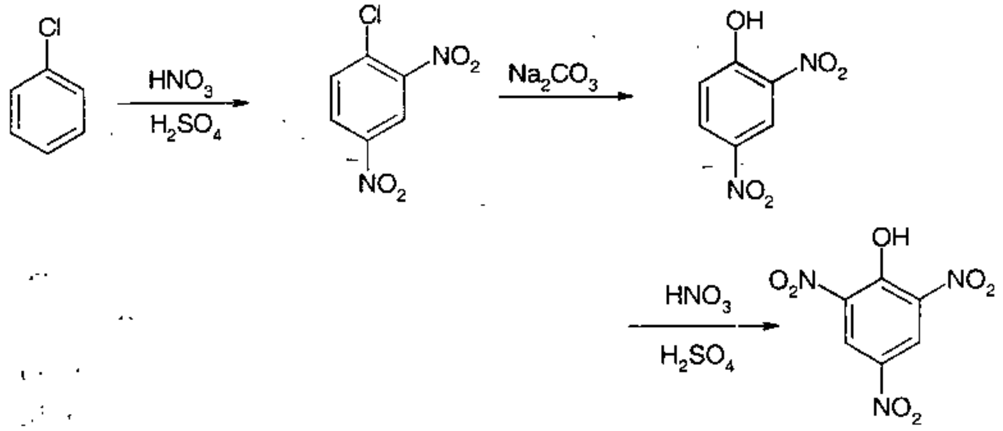
The dyes are classified according to their chemical constitution as follows :

(i) Nitro dyes (ii) Nitroso dyes
(iii) Azo dyes (iv) Diphenylmethane dyes
(v) Triphenylmethane dyes (vi) Xanthen dyes
(vii) Diphenylamine dyes : indamines, indophenols
(viii) Heterocyclc dyes: acridine group, quinoline group, azine group, thiazine group, oxazine group.
(ix) Vat dyes : indigoid group, anthraquinone group.
(x) Anthraquinoid dyes (xi) Sulphur dyes
(xii) Phthalocyanine dyes

(1) Nitro dyes : Nitro dyes contain $-NO_2$ group as the chromophore and $-OH$ group as the auxochrome Examples: picric acid, martius yellow, naphthol yellow S etc.

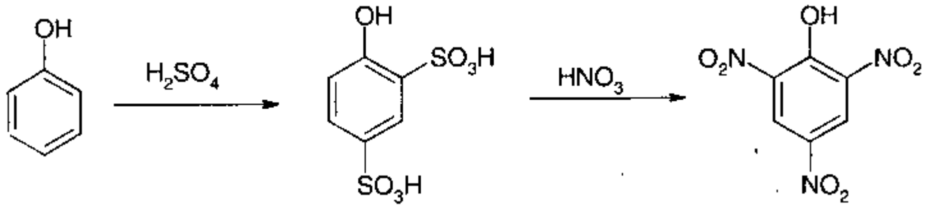
(a) ***Picric acid (2,4,6 Trinitrophenol)*** : Picric acid is a yellow crystalline solid having melting point 122°C. It is the simplest nitro dye used to dye silk bright yellow, but the colour is fugitive. It is prepared by using chlorobenzene or phenol as follows :

(i) Synthesis of picric acid from chlorobenzene



Picric acid

(ii) Synthesis of picric acid from phenol



Picric acid

(2) Nitroso dyes : Nitroso dyes contain nitroso group as the chromophore and the hydroxyl group as the auxochrome. Examples: Fast green O, Gambine Y and Gambine R.

(3) Azo dyes : The azo dyes contain azo group (—N═N—) as the chromophores and —NH_2, NR_2 and —OH groups as auxochromes. Azo dyes are prepared by the diazotization of an amino compound to get diazonium salt and then coupling the diazonium salt with phenol in alkaline solution or with an amine in neutral or slightly acidic solution. The structure of azo dye can be studied by reduction in the presence of stannous chloride and hydrochloric acid. The azo group undergoes rupture to give primary amines, which are then identified

$$ArN = NAr' \xrightarrow{\text{Reduction}} Ar\,NH_2 + Ar'\,NH_2$$

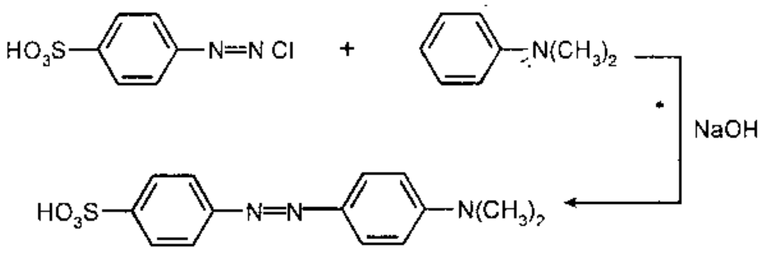
The azo dyes are classified as :

(a) Basic azo dyes
(b) Acid azo dyes
(c) Direct azo dyes
(d) Ingrain azo dyes
(e) Mordant dyes

(a) Basic azo dyes : These dyes contain —NH_2 or NR_2 as the auxochrome. Examples are aniline yellow (aminoazobenzene), butter yellow (*p*-dimethylaminoazobenzene), Bismarck Brown G, and Chrysoidine G. Aniline yellow and butter yellow are the simplest basic azo dyes but are very sensitive to acids.

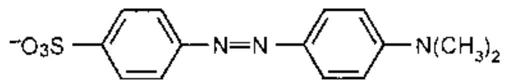
(b) Acid azo dyes : These dyes contain —SO_3H group. Some examples of these dyes are methyl orange, orange I and orange II, fast red AV, naphthol blue black B etc.

Methyl orange : Methyl orange is prepared by reacting diazotized sulphanilic acid with dimethlaniline.

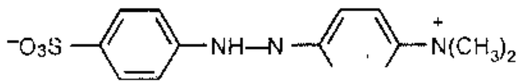


Methyl orange

Methyl orange dyes only in fugitive shades. It is used as an indicator in volumetric analysis (it is orange in alkaline solution and red in acidic solutions).



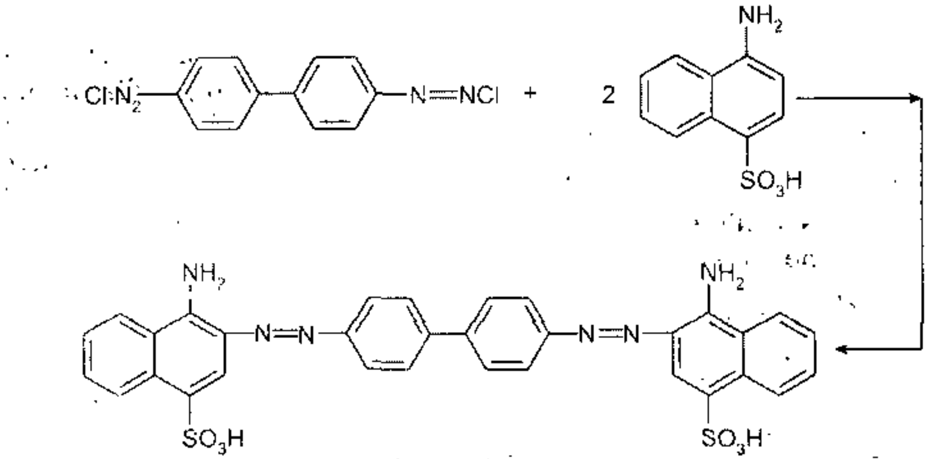
orange



red (red)

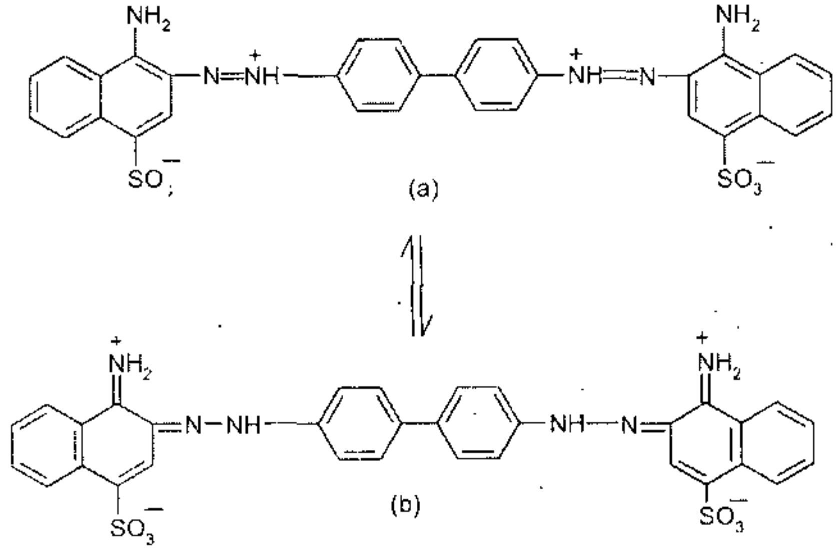
(c) Direct azo dyes : The direct azo dyes are used to dye cellulose fibres directly without a mordant. Some of the examples are discussed below.

Congo red : Congo red is a bisazo dye and it is prepared by reacting tetrazotised benzidine with two molecules of 1-naphthylamine-4-sulphonic acid.



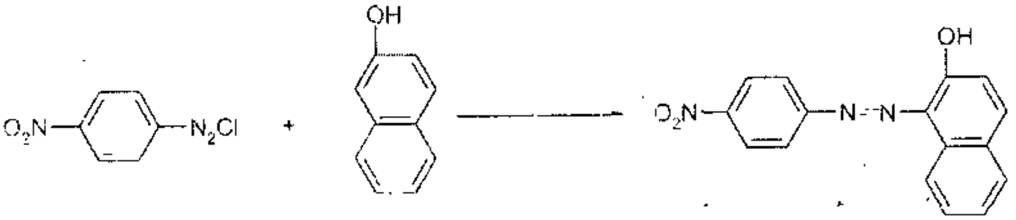
Congo red

Congo red is the first synthetic dye and it dyes cotton directly. It is red in alkaline solution. Its sodium salt dyes cotton red in colour. Congo red is sensitive to acids. It changes its colour from red to blue in the presence of inorganic acids. The change in colour may be due to the resonance hybrid of structures (a) and (b).



Ans 2

(d) Ingrain azo dyes : These dyes are insoluble azo dyes and are known as **azoic dyes.** A well know example of ingrain azo dye is **Para Red.** Dyeing with Para Red is performed by padding the fibre with an alkaline solution of 2-naphthol containing Turkey red oil, the fibre is dried and then immersed in an ice bath of diazotised *p*-nitroaniline.



The colour of ingrain azo-dye varies from orange to blue on account of changing the amine component, for example

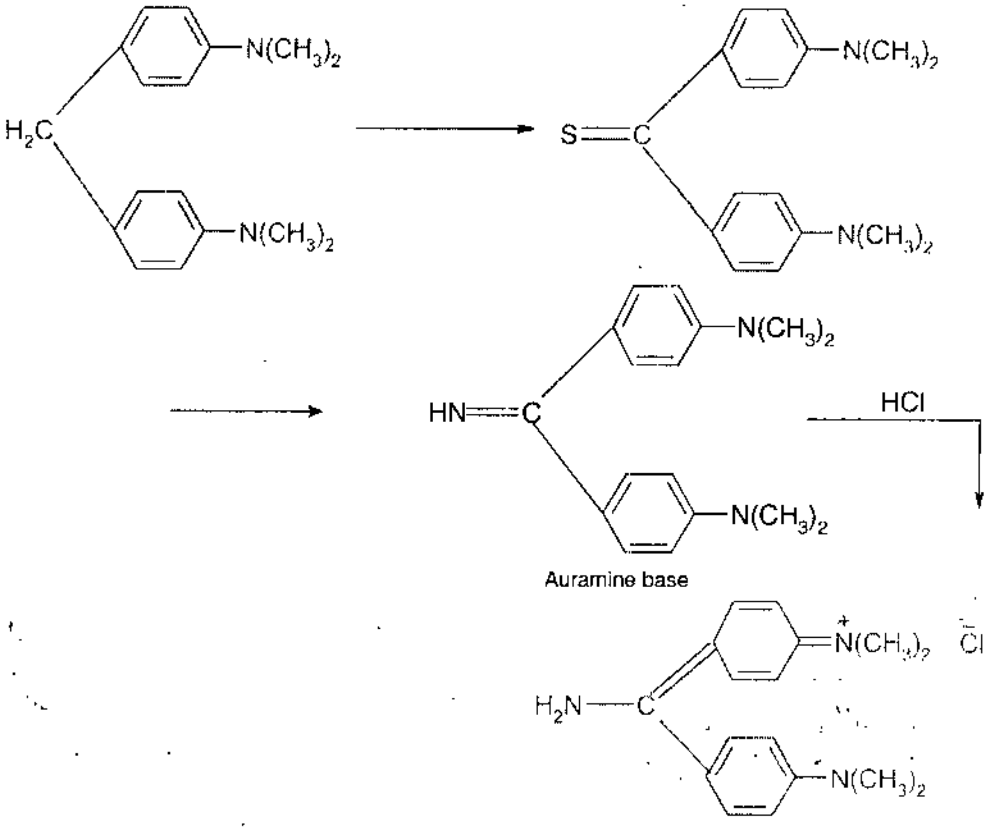
(i) 2-Naphthol + *m*-Nitroaniline = Nitroaniline orange
(ii) 2-Naphthol + 2,4 Dinitroaniline = Permanent red 2G
(iii) 2-Naphthol + Dianisidine = Dianisine blue

(e) Mordant azo dyes : The important metal used in mordanting azo-dyes is chromium, which produces the so called azo-chrome mordant dyes. The fibre is mordanted by boiling with $K_2Cr_2O_7$ solution, generally with a reducing agent *e.g.*, formic, lactic or oxalic acid.

(4) Diphenylmethane dyes : Auramine O and Auramine G are the examples of diphenylmethane dyes.

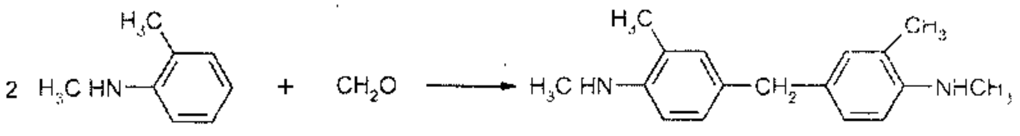
(a) Auramine O : It is a yellow basic dye. It has low fastness. It undergoes hydrolysis readily to give corresponding ketone. It is used for dyeing cotton, paper, leather, wool, silk and jute.

Auremine O is prepared by heating *p,p'*-tetramethyldiaminodiphenylmethane with sulphur, NH_4Cl and a large excess of NaCl in a current of ammonia at ~ 200°C. Auramine base is thus produced, which with HCl forms the hydrochloride, Auramine O.



(Auramine O)

(b) Auramine G : It is a greenish yellow basic dye. It is synthesized in similar way from the condensation product of monomethyl-o-toluidine and formaldehyde, which is heated with sulphur in a current of NH_3.



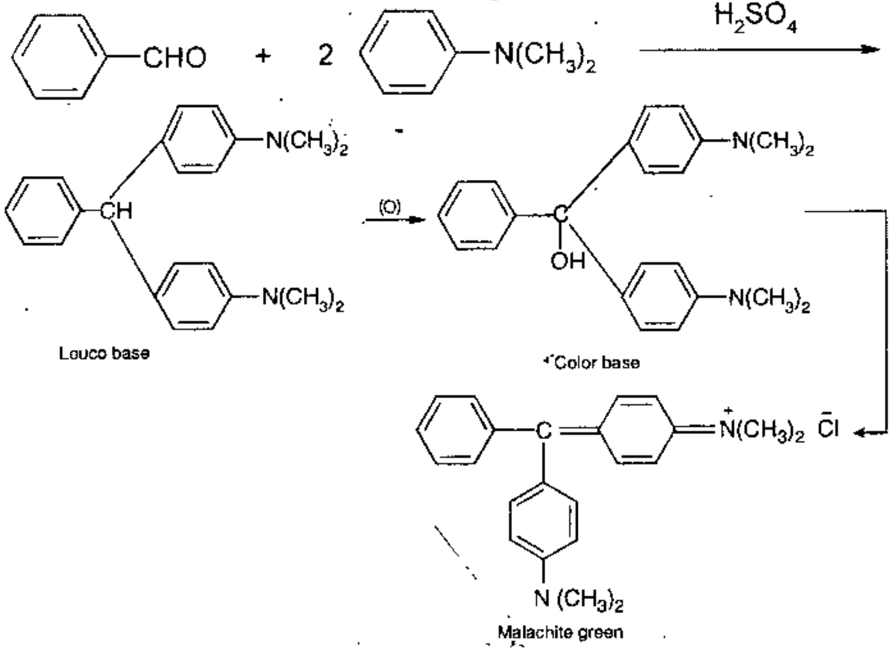
(Auramine G)

(5) Triphenylmethane dyes : Triphenylmethane dyes are obtained by introducing —NH_2, NR_2 or —OH group into the rings of triphenylmethane. The compounds thus obtained are colourless (*leuco compounds*) and these are converted into corresponding tertiary alcohols (*colour bases*). The colour bases readily change from the colourless benzenoid forms to the quinonoid dyes in the presence of acid, due to salt formation. The salts are reconverted into luco bases.

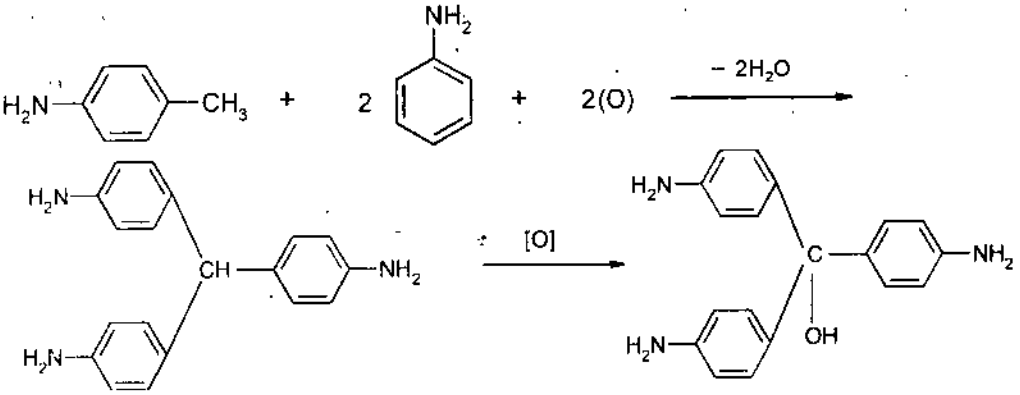
$$\underset{\text{(Colourless)}}{\text{Leuco base}} \underset{\text{Reduction}}{\overset{\text{Oxidation}}{\rightleftharpoons}} \underset{\text{(Colourless)}}{\text{Colour base}} \underset{\text{Alkali}}{\overset{\text{Acid}}{\rightleftharpoons}} \underset{\text{(Coloured)}}{\text{Dye}}$$

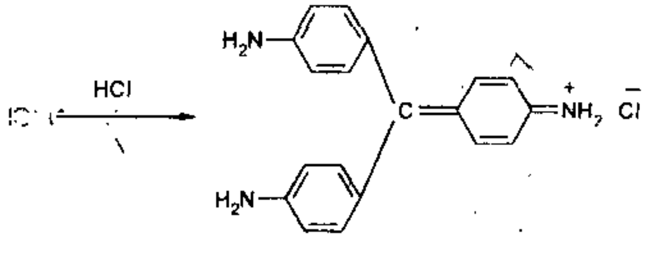
Some of the examples of triphenylmethane dyes are : malachite green; pararosaniline; rosaniline (Magenta, Fuchsine) crystal violet methyl violet, aurin, victoria blue B and patent blue V etc.

(a) Malachite Green : Malachite Green dyes wool and silk directly. However, cotton requires previous mordanting with tannin. It is synthesized by reacting dimethylaniline (2 moles) with benzaldehyde (1 mole) at 100°C in the presence of concentrated H_2SO_4. The leuco base thus obtained is oxidized with lead dioxide in a solution of CH_3COOH containing HCl. The resulting colour base on treatment with excess HCl gives malachite green.



(b) Pararosaniline : It dyes wool and silk directly but in case of cotton previous mordanting with tannin is needed. It is synthesized by oxidizing a mixture of *p*-toluidine (one mole) and aniline (two moles) with arsenic acid or nitrobenzene.

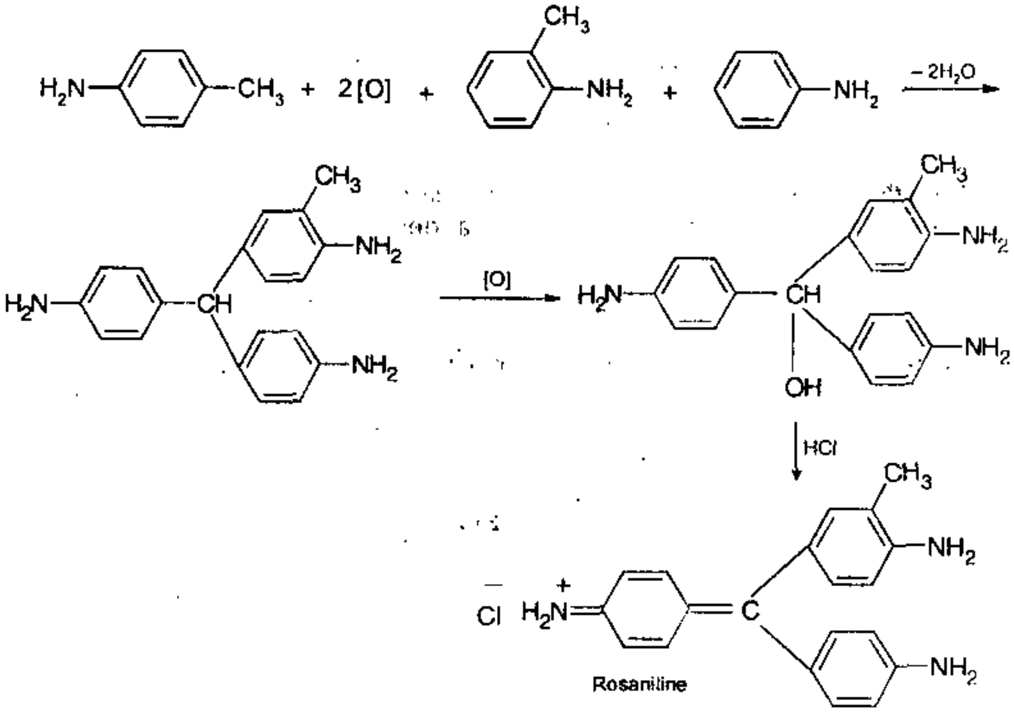




Pararosaniline

(c) ***Rosaniline :*** Rosaniline is used for dyeing wool and silk directly, however, cotton must be first mordanted with tannin.

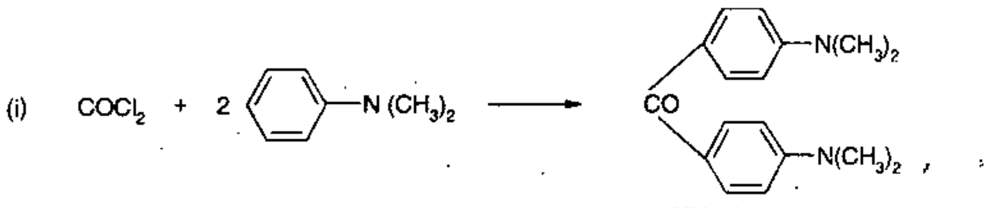
Rosaniline is the *o*-methyl derivative of pararosaniline. It is synthesized by oxidizing an equimolar mixture of aniline, *o*-and *p*-toluidines and their hydrochlorides, with nitrobenzene in the presence of iron filings.



Rosaniline

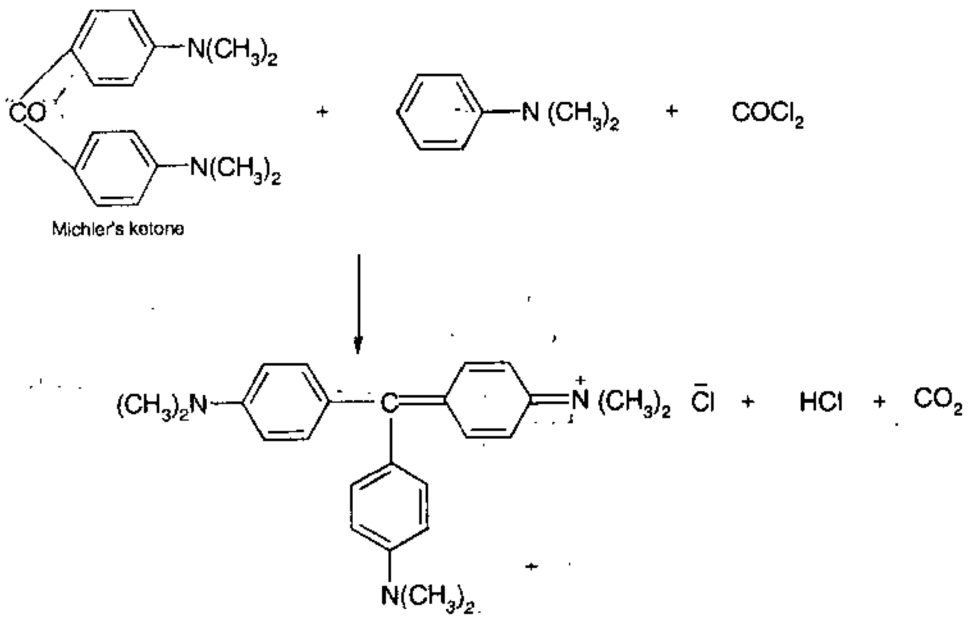
Rosaniline crystals exhibit a green metallic lustre and are soluble in water to from a deep red solution. The solution is decolourized by sulphur dioxide and is then known as **Schiff's reagent,** which is used for testing aldehydes.

(d) Crystal Violet : It is used for dyeing wool and cotton. It gives bluish violet colour on wool and tannined cotton. It is synthesized by fusing Michler's ketone (tetramethyldiamin-obenzophenone) with dimethylaniline, in the presence of phosphoryl chloride or carbonyl chloride. When carbonyl chloride is used, then crystal violet may be synthesized directly by heating carbonyl chloride with dimethylaniline.



Michler's ketone

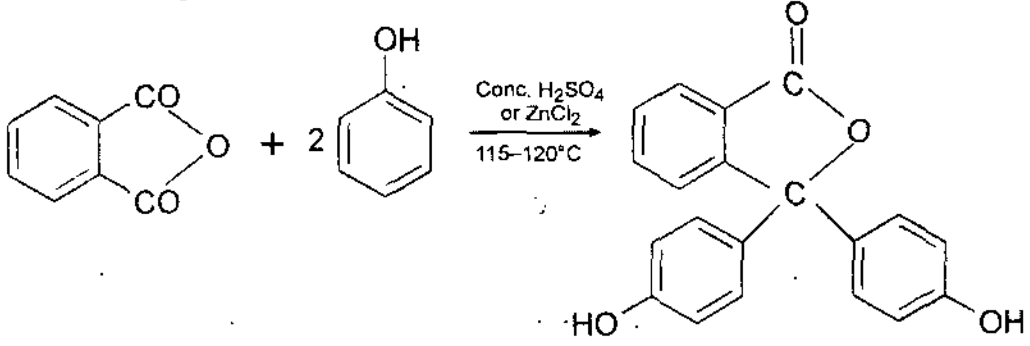
(ii)



Crystal violet

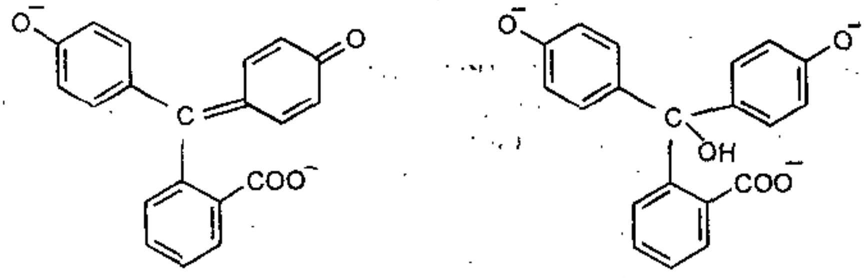
(e) Phthaleins : Phthaleins are prepared by reacting phenols with phthalic anhydride in the presence of a dehydrating agent (for example: concentrated H_2SO_4 or $ZnCl_2$ or anhydrous oxalic acid). These dyes belong to triphenylmethane derivative.

Phenolphthalein : Phenolphthalein is a triphenylmethane derivative. It is synthesized by heating phthalic anhydride (one mole) with phenol (two moles) in the presence of concentrated sulphuric acid or $ZnCl_2$.



Phenolphthalei

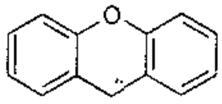
Phenolphthalein is a colourless crystalline solid having melting point 251°C. It is insoluble in water but soluble in alkali forming deep red solution. In excess of alkali, the solution again becomes colourless due to the loss of quinonoid structure and resonance.



Deep red

Colourless

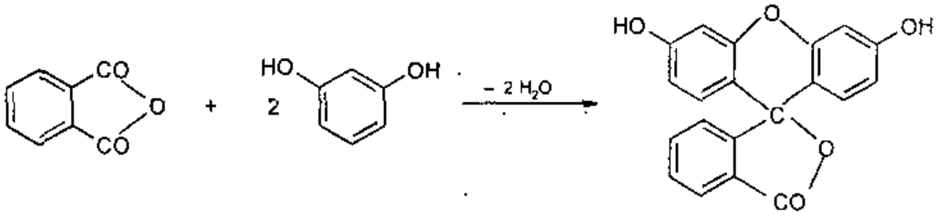
(6) Xanthen dyes : Xanthen (dibenzo-1,4-pyran) is the parent substance of this group of dyes.



Xanthen

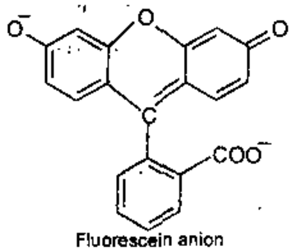
Fluorescein, eosin, mercurochrome, rhodamines etc are important examples of xanthene dyes.

(a) Fluorescein : It is a xanthen derivative. It is synthesized by heating phthalic anhydride (one mole) with resorcinol (2 moles) at 110-120°C in the presence of anhydrous oxalic acid.



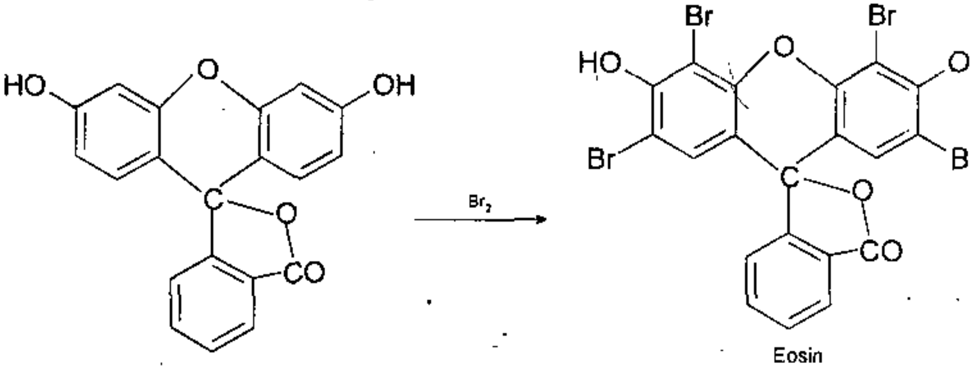
Fluorescein

Fluorescein is a red powder. It is insoluble in water. It dissolves in alkali to give a reddish brown solution and on dilution strong yellowish-green fluorescence is obtained. The structure of fluorescein anion is depicted below:



Fluorescein anion

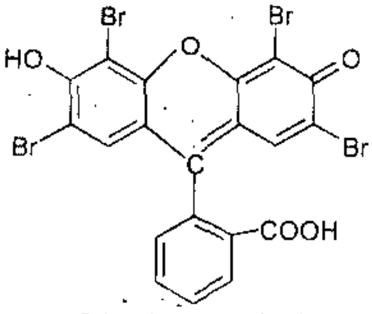
(b) Eosin : Eosin is tetrabromofluorescein. It is synthesized by the action of bromine on fluorescein in glacial acetic acid solution



Fluorescein

Eosin

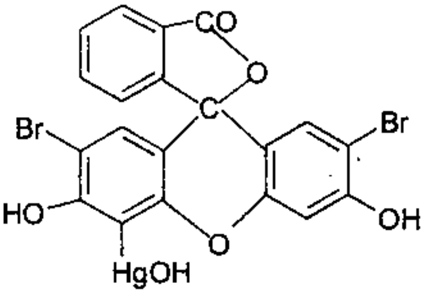
Quinonoid structure of eosin is represented below :



Quinonoid structure of eosin

Eosin is used for dyeing wool and silk. It is also useful as the lead lake (Vermilionette) for poster printing. The red inks are prepared using dilute solution of eosin.

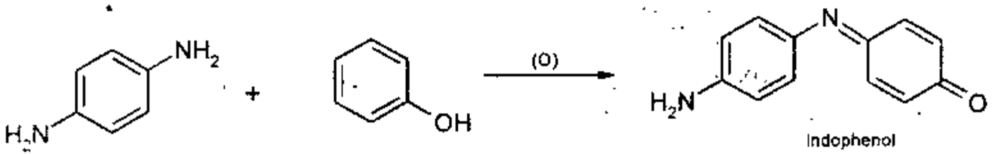
(c) Mercurochrome : Mercurochrome is a derivative of fluorescein. It has medicinal importance and is used as an antiseptic. It is an organometallic compound of mercury



Mercurochrome

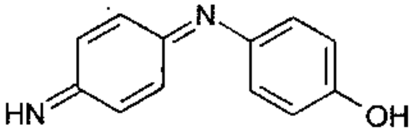
(7) Diphenylamine dyes : Indamines and indophenols are the two different groups of diphenylamine dyes. Both are sensitive to light and therefore they are not used as dyes. However, indamines are used for the manufacture of azines, thiazines and oxazines; wheras indophenols are used for preparing various sulphur dyes.

(a) Indophenol : Indophenol (Blue) is synthesised by oxidation of a mixture of *p*-phenylenediamine and phenol, in the presence of alkaline hypochlorite solution



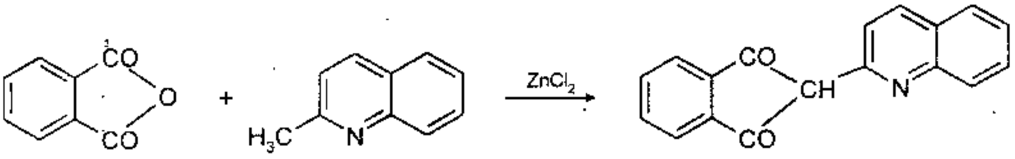
Indophenol

Indophenol is considered as the amino-structure and not the imino-structure because it is not soluble in alkali but is soluble in acids.



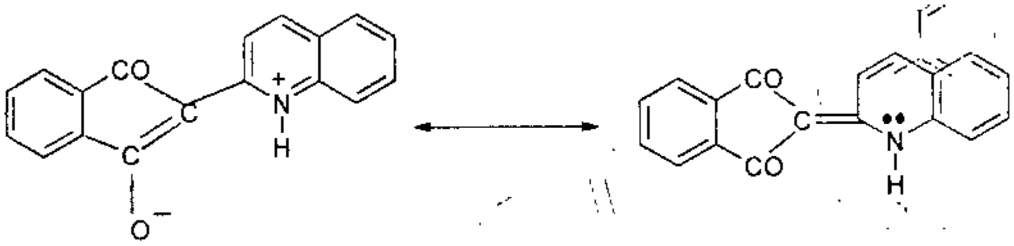
(8) Heterocyclic dyes : ***(a) Acridine dyes :*** Acridine dyes are basic dyes and all are yellow to orange and brown in colour. They are used for dyeing cotton, silk and leather, and in calico printing. These dyes possess medicinal and antiseptic properties. One of the examples of these dyes is acridine yellow.

(b) Quinoline dyes : These dyes are used as photographic sensitizers, and also for dyeing fabrics. One of the examples of these dyes is quinoline yellow. It is used for dyeing textiles, and is synthesized by reacting phthalic anhydride with quinoline in the presence of $ZnCl_2$.



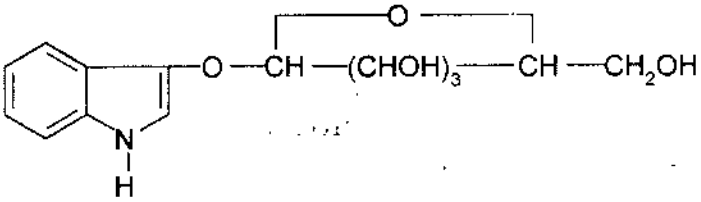
(Quinoline yellow)

Quinoline yellow is supposed to have resonance hybrid.



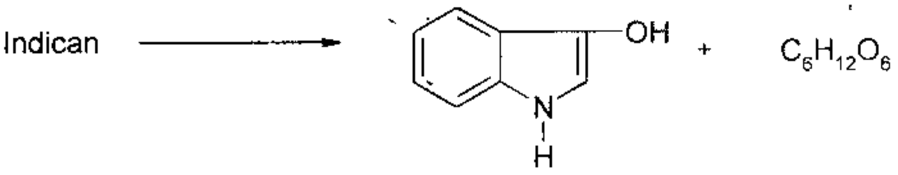
(c) ***Azine dyes :*** One of the examples of Azine dyes is **Safranine T**. Safranine *T* is a basic dye and is used for dyeing wool, silk and tanned cotton.

(9) Vat dyes : ***(a) Indigo or indigotin :*** It is one of the most important vat dyes. It is a natural dye and occurs in the leaves of indigo plant (*Indigofera tinctoria*) as well as in the leaves of Isatis tinctoria. Indigo plants grow in India, Jawa and China ,whereas Isatis tinctoria plants grow in Hungary and France. In both the plants, Indigo is present as **indican** (glucoside of indoxyl).



Indican

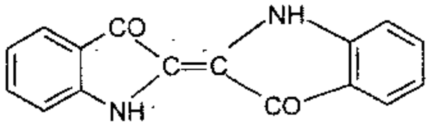
Indican is extracted from the leaves of the plants by maceration with water. The enzyme (indimulsin) occurring in the crushed leaves converts indican into indoxyl and glucose. Indoxyl on further oxidation with atmospheric oxygen gives indigotin.



Indoxyl

$$\text{Indoxyl} \xrightarrow{(O)} \text{Indigo or Indigotin}$$

Structure of indogotin is depicted as follows :

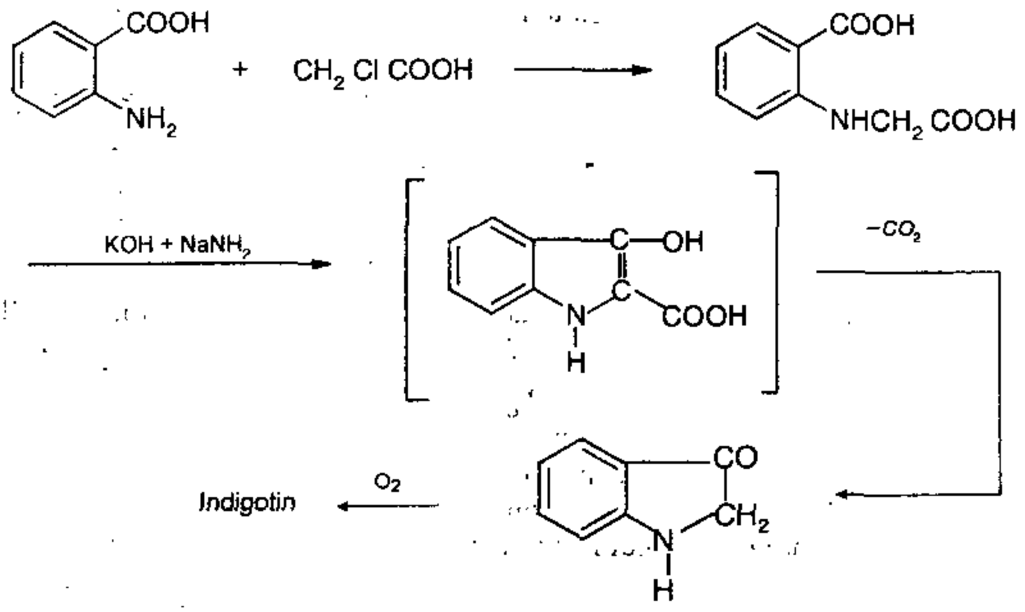


Indigotin

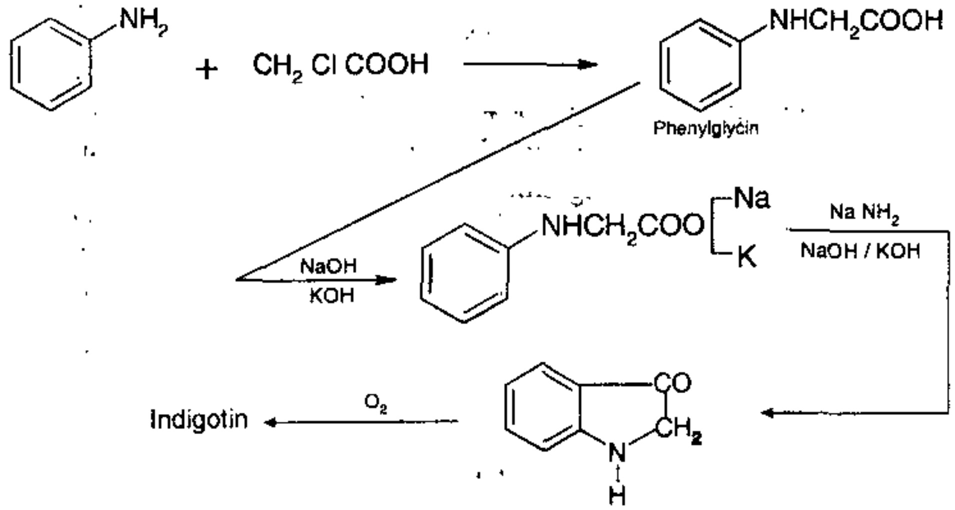
[I] Commercial Synthesis of Indigotin

Indigotin is synthesized on commercial scale by the following methods :

(i) Anthranilic acid is heated with chloroacetic acid and the product (phenylglycine–*o*-carboxylic acid) obtained is heated with a mixture (KOH+ $NaNH_2$) to get indoxylic acid. This acid further undergoes decarboxylation to give indoxyl. Indoxyl on oxidation in air produces indigotin.

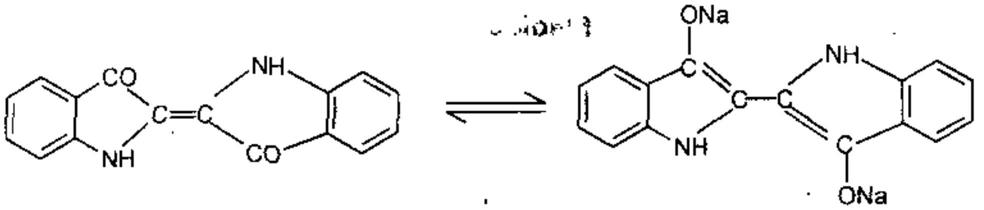


(ii) Aniline is heated with chloroacetic acid to give phenylglycine. It is then converted into a mixture of its sodium and potassium salts. The salts are then fused with $NaNH_2$ and a mixture of KOH and NaOH at 220-240°C to give indoxyl. Indoxyl thus obtained is converted into indigotin by atmospheric oxygen.



[II] Properties of Indigotin

Indigotin is a dark blue powder having a copper lustre. It is insoluble in water but when its paste is agitated with alkaline sodium hyposulphite in large vats, the insoluble indigotin gets converted into soluble lecuo compound (indigotin white).

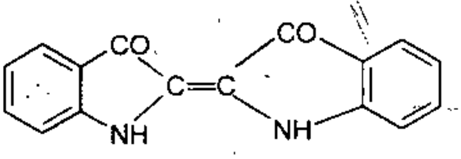


Indigotin

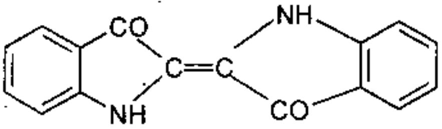
Indigotin white

For dyeing, the cloth is soaked in this alkaline solution and then it is exposed to air. The original blue dye regenerates on the cloth.

Two geometrical isomers are there for indigotin (***cis* form** and ***trans* form**). *X*-ray studies indicate that *trans* form is more stable.

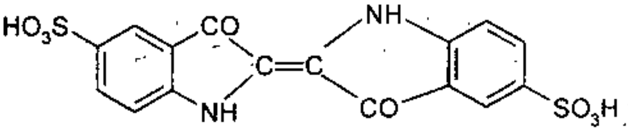


Cis-form



Trans-form

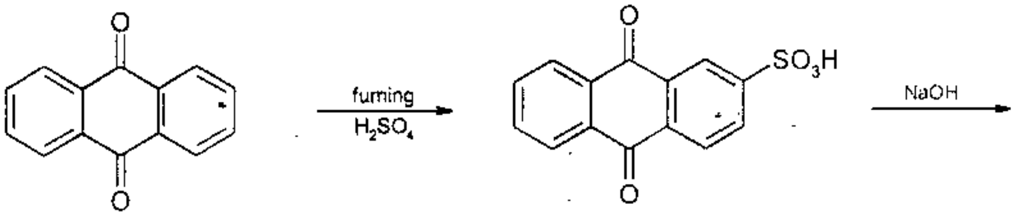
Indigo caramine (5,5' disulphonic acid derivative of indigo) is a beautiful blue dye used for dyeing wool.

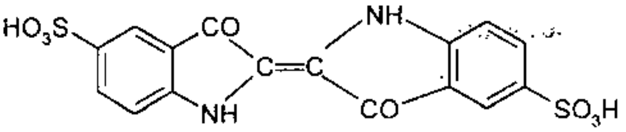


Indigo caramine

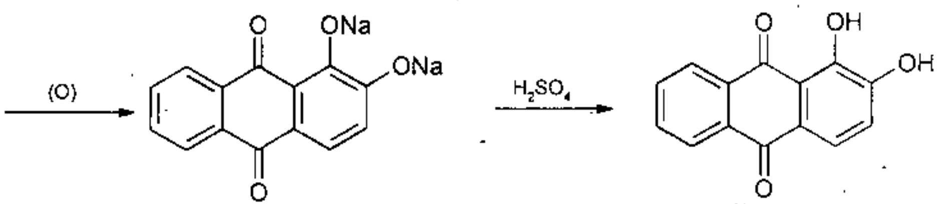
(b) Anthraquinone type of vat dyes : The examples of anthraquinone type vat dyes are indanthrone and flavanthrone :

(10) Anthraquinoid dyes : *(a) Alizarin* : It belongs to anthraquinoid dye. It occurs in the roots of **maddar plant.** It is manufactured by sulphonating anthraquinone with fuming sulphuric acid at 160°C to get anthraquinone-2-sulphonic acid. The sodium salt of this acid is then treated with NaOH and $KClO_3$ at 170°C under pressure to get sodium alizarate. This compound on further acidification with sulphuric acid gives alizarin.





Indigo caramine

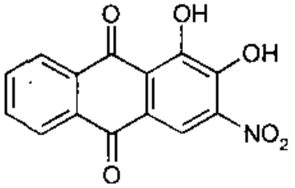


Sodium alizarate

Alizarin

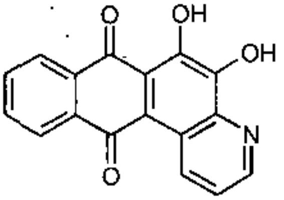
Alizarin is a crystalline compound (ruby red crystals) having melting point 290°C. It is soluble in ethanol but insoluble in water. It dissolves in alkali giving purple solution. It is a mordant dye and the colour of the lake depends upon the metal used. Aluminium forms a red lake (Turkey red), iron (ferric state) froms a violet black and chromium forms a brown violet lake. For dyeing of cotton and for printing, aluminum and iron lakes are used; whereas for dyeing wood, aluminum and chromium lakes are employed.

(i) Alizarin orange is synthesized by the nitration of alizarin in sulphuric acid solution in the presence of boric acid. With aluminum, it forms orange lakes.



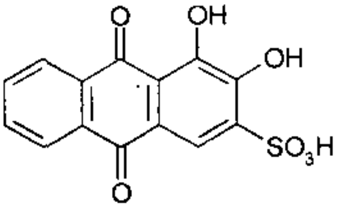
Alizarin orange

(ii) Alizarin blue is synthesized by the reduction of alizarin orange to the corresponding amino compound, followed by heating the amino compound with glycerol, sulphuric acid and nitrobenzene (Skraup synthesis). It is used for dyeing wool mordanted with chromium a blue colour.



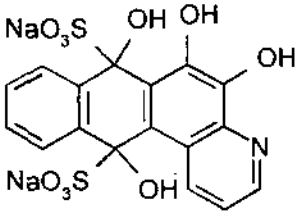
Alizarin blue

(iii) Alizarin red S is synthesized by sulphonation of alizarin with fuming H_2SO_4. It is used for dyeing wool (mordanted with aluminum) a scarlet red.



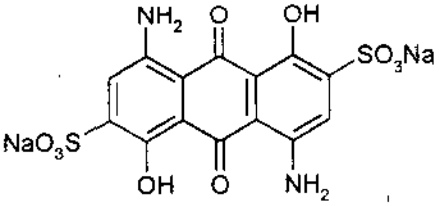
Alizarin red S

(iv) Alizarin blue S is a bisulphite compound of alizarin blue, and gives a reddish blue lake with chromium.



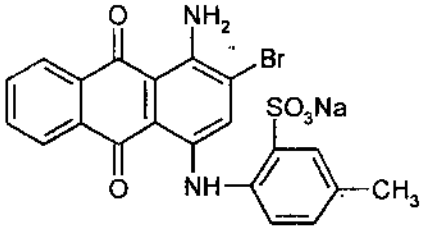
Alizarin blue S

(v) Alizarin saphirol B is used for dyeing wool.



Alizarin saphirol B

(vi) Alizarin sky blue BS is also used for dyeing wool.



Alizarin sky blue BS

(11) Sulphur dyes : These dyes are synthesized by heating various organic compounds (for example amines, aminophenols and nitrophenols) with sodium polysulphide. Sulphur dyes are coloured solids and are insoluble in water and acids. They are soluble in cold alkaline solutions of sodium sulphide giving leuco compounds. When cotton is dipped in it and then exposed to air, the leuco compound oxidizes to the dye.

A sulphur dye used on large scale for dyeing cloth khaki is prepared by heating *p*-phenylenediamine with *p*-aminoacetanilide and sulphur (with or without benzidine), followed by heating the product with sodium sulphide.

(12) Phthalocyanine dyes : One of the important classes of organic dyes and pigments is phthalocyanines. These are coloured (blue to green) compounds and are very fast to light, heat, acids and alkalies. They are used for making paints, printing inks, synthetic plastics and fibres etc.

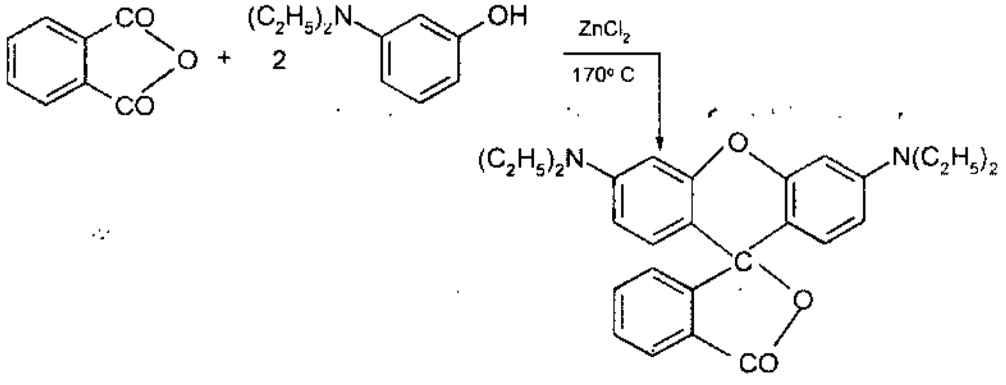
3.4. MANUFACTURE OF RHODAMINE B DYE

Rhodamine B is a red basic dye and is structurally related to xanthen. It is manufactured by reacting phthalic anhydride (one mole) and diethyl-*m*-aminophenol (2 moles) in the presence of $ZnCl_2$.

Raw materials required per ton of rhodamine B are :

Phthalic anhydride	: 1420 kg
Diethyl-*m*-aminophenol	: 1160 kg
Zinc chloride	: 1205 kg

Reaction



Rhodamine B

Manufacturing process : Diethyl-*m*-aminophenol and phthalic anhydride are delivered to the reactor and the reaction mixture is heated to 100°C. Zinc chloride is then added to the reactor and the reaction mixture is heated to 170-175°C. The temperature is maintained for 4-5 hours. The product is then cooled and powdered in ball mill. It is then extracted with boiling alcohol. The alcoholic solution is filtered and cooled in the crystallizer. The colour base crystallized is then filtered.

The base is dissolved in water and hot dil HCl. The hydrochloride is then separated by cooling the solution. The product is then filtered and dried. The flowchart is depicted in the following figure 1.

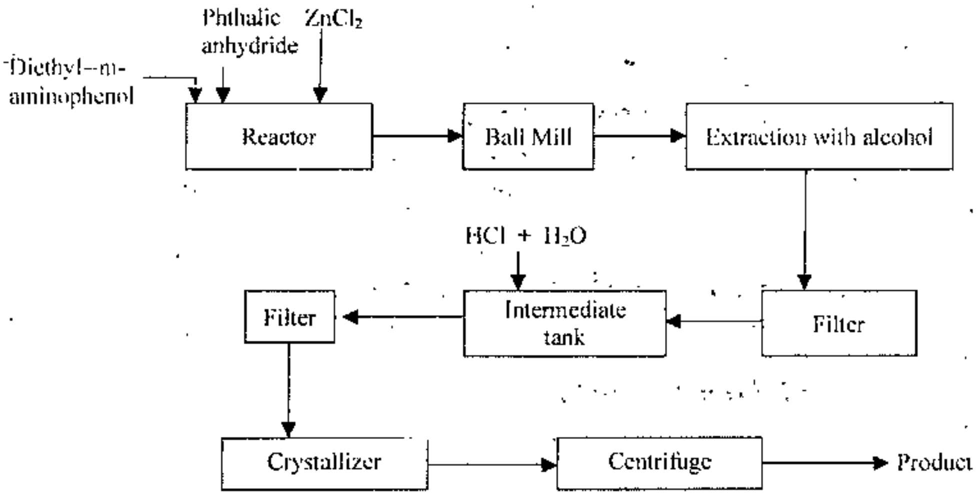


Fig. 1. Flowchart for the manufacture of Rhodamine B

Rhodamine B is used as a red dye for dyeing wool and silk. It is also employed as an analytical reagent for analysis of heavy metals.

3.5. INTRODUCTION OF DRUGS

Ehrlich (1909) introduced the term **chemotherapy,** which appears to be used for the treatment of diseases (caused due to bacterial attack) by chemical compounds that destroy only the microorganism without affecting the tissues of the host. The compounds like formaldehyde, phenol and iodine etc have capacity to destroy the bacteria. These compounds are applied externally and they tend to destroy the tissues. So, they are not considered as **therapeutic agents** but are termed as **disinfectants.**

The *compounds that show various physiological effects of therapeutic value are collectively known* as **drugs.** An ideal requirement of a drug is that on administration to the host the drug should be localised at the site where it is required. Actually in practice the drug does not behave in this way but it tends to distribute itself anywhere in the tissues of the host. One more problem is that the cells which were originally susceptible to a particular drug, may acquire a tolerance or resistance to that drug. It is also observed that the drug exhibits reverse action (that is the drug stimulates the cell instead of inhibiting it). Some other requirements of a drug are as follows :

(i) The drug should act on a system with efficiency and safety.
(ii) The drug should have minimum side effects.
(iii) The drug should not cause injury to the tissues of the host or physiological processes.

There are three ways to solve the problem of finding a drug to combat (or to struggle) with a particular disease :

(i) Trial and error method. It involves the trial of all kinds of compounds (natural and synthetic)
(ii) The method requiring knowledge of the cell system, and then synthesizing compounds that interfere with it.
(iii) The method in which one starts with a compound known to have some of the required activity and then to vary the structure of the molecule. This method is found to be most fruitful.

3.6. SULPHONAMIDES

Sulphonamides are antibacterial drugs. They are classified on the basis of their mode of action as follows

(i) Sulphonamides for general infections
(ii) Sulphonamides for urinary infections

(iii) Sulphonamides for intestinal infections

(iv) Sulphonamides for local infections

(v) Sulphonamide related compounds

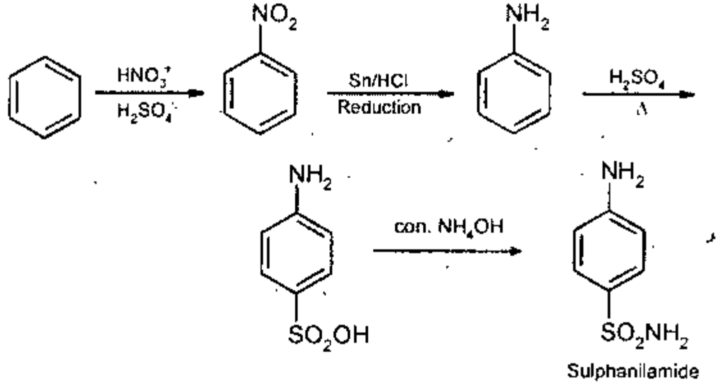
[I] Sulphonamides for General Infections

These are used against *streptococcal, meningococcal, gonococcal, staphylococcal and pneumococcal* infections. Examples of sulphonamides are: sulphanilamide, sulphapyridine, sulphathiazole, sulphadiazine, sulphamerazine, sulphamidine, sulphalene and sulphamethizole.

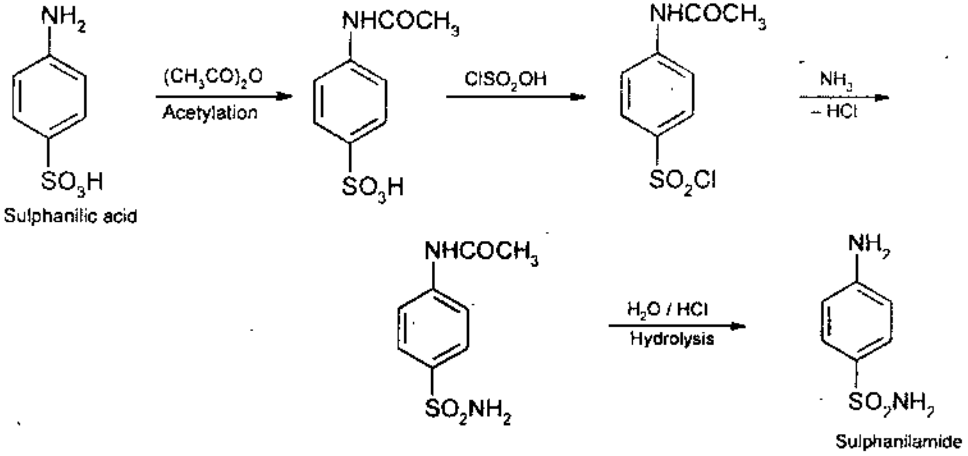
(1) Sulphanilamide, (*p*-Aminobenzenesulphonamide)

Sulphanilamide is synthesised by three different methods as summarised below :

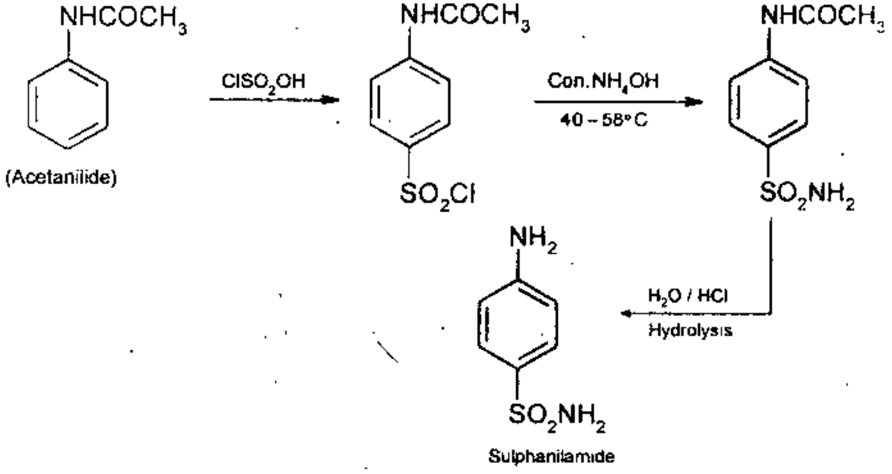
(a) ***Method I (From benzene)***



(b) ***Method II (From sulphanilic acid)***

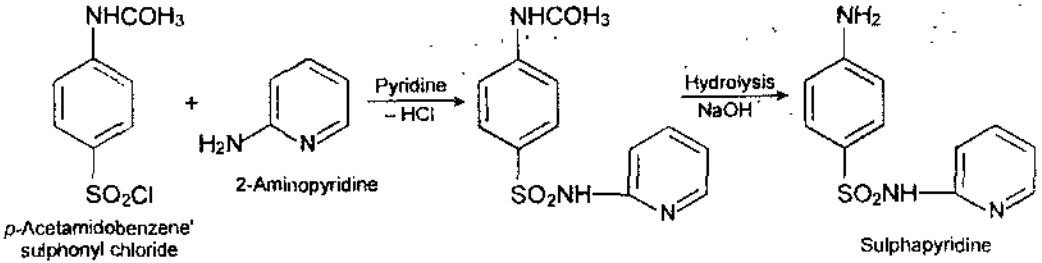


(c) ***Method III (From acetanilide)***

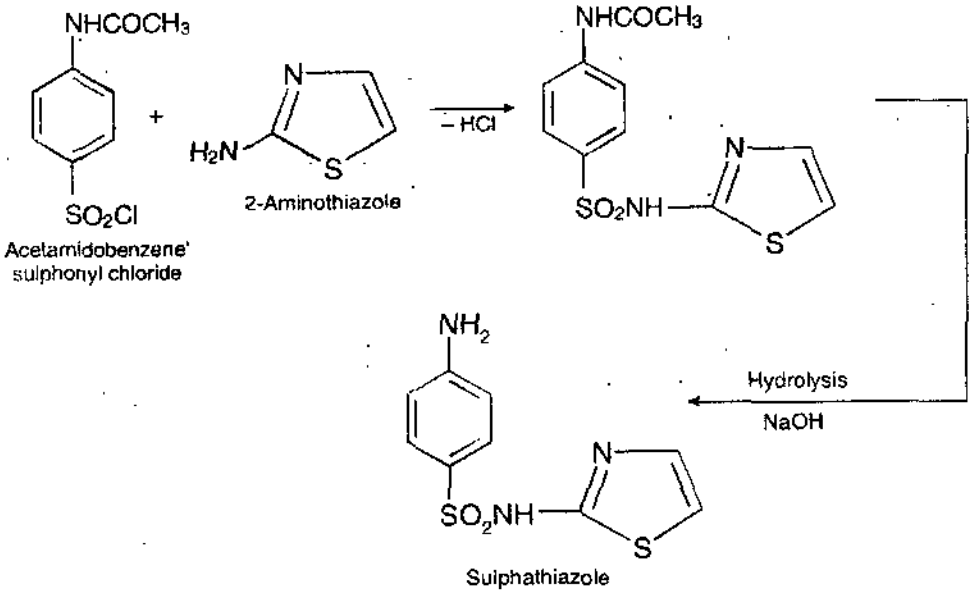


Because of high toxicity, sulphanilamide is now rarely used. It has been replaced by less toxic sulpha drugs. However, it is still used as veterinary medicine.

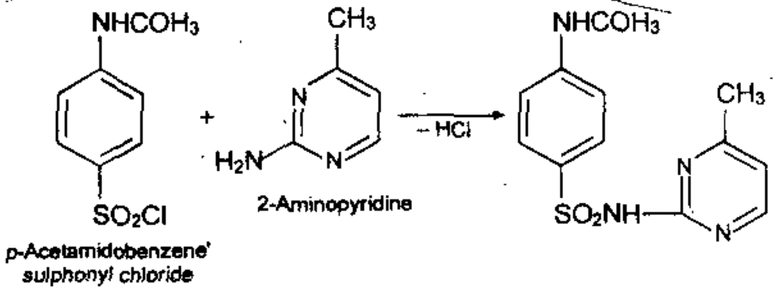
(2) Sulphapyridine, (N^1-2-pyridylsulphanilamide) : Sulphapyridine is effective against pneumonia. It is more potent than sulphanilamide. Because of its toxicity, sulphapyridine has been replaced by sulphadiazine. Sulphapyridine is synthesised as follows :

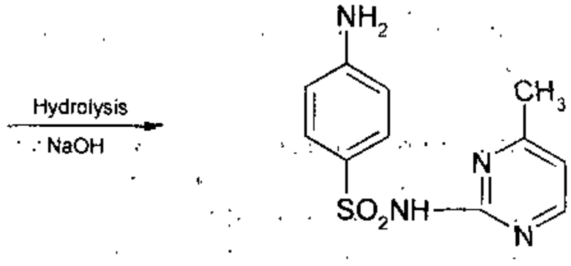


(3) Sulphathiazole (N^1-2-thiazolylsulphanilamide) : Sulphathiazole is useful against *staphylococcal* infections. It is synthesised as follows:



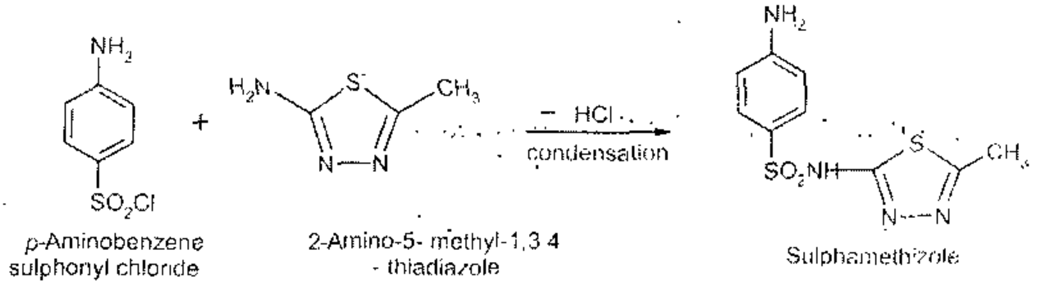
(4) Sulphamerazine [N^1-(4-Methyl-2-pyrimidinyl) sulphanilamide] : Sulphamerazine is generally used in *combination with other sulphonamides.* It is synthesized as follows :





Sulphamerazine

(5) **Sulphamethizole, [N^1-(5-methyl-1,3,4-thiadiazol-2-yl) sulphanilamide]** : Sulphamethizole is useful for the treatment of coliform infections of the urinary track. It possesses the general properties of sulphonamides. It is synthesised as follows :

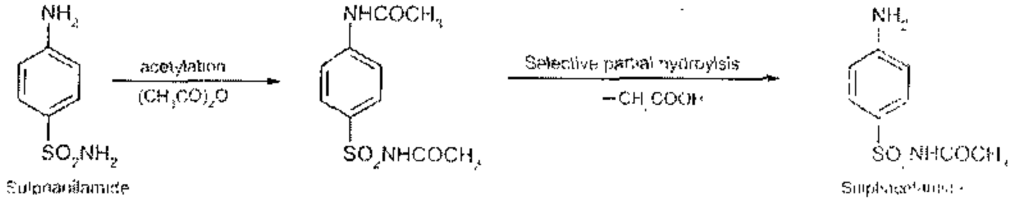


[II] Sulphonamides for Urinary Infections

A number of sulphonamides are used for the treatment of urinary track infections. Examples of such sulphonamides are sulphacetamide, sulphafurazole, sulphisoxazole acetyl, sulphacitine etc.

(A) Sulphacetamide, [N-Sulphanilylacetamide]

Sulphacetamide possesses general characteristics of a sulphonamides. It was formerly used for the treatment of bacterial infection of urinary tract. Sulphacetamide is synthesised as follows :

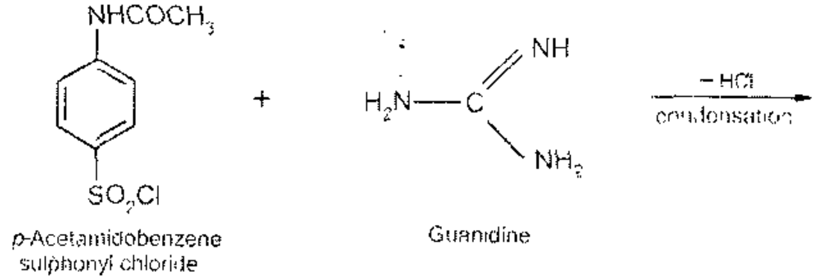


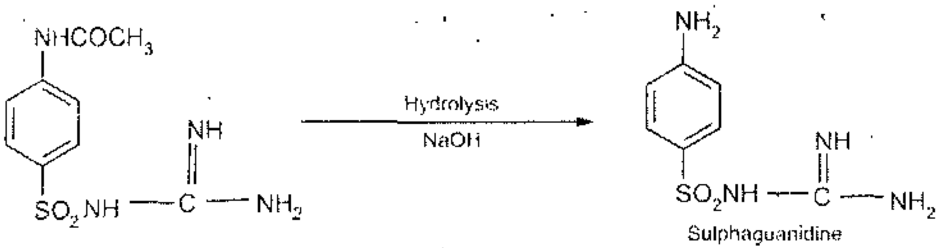
[III] Sulphonamides for Intestinal Infections

Sulphaguanidine, phthalylsulphathiazole, succinylsuphathiazole; phthalylsulphacetamide and salazosulphapyridine etc are some examples of sulphonamides useful for the treatment of intestinal infections.

(A) Sulphaguanidine, [N^1-(diaminomethylene) sulphanilamide]

Sulphaguanidine is used for the treatment of local intestinal infections particularly bacillary dysentery. It is synthesized as follows :





[IV] Sulphonamides for Local Infections

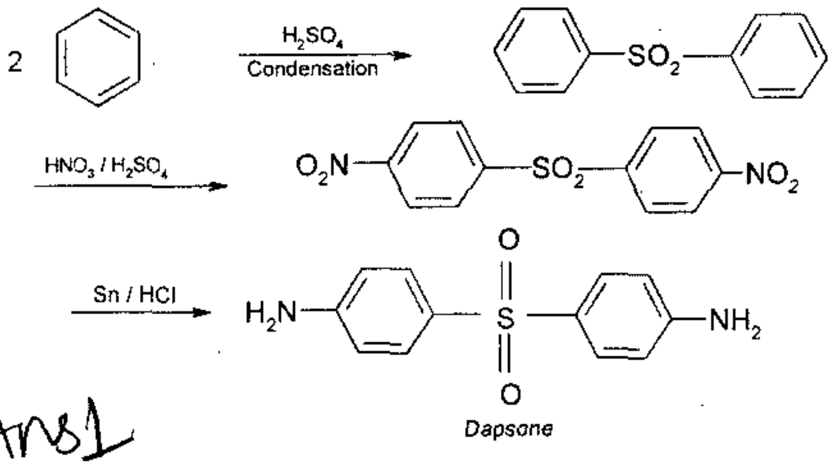
Some of the sulphonamides are useful for the treatment of local infections. Examples of such sulphonamides are sulphacetamide sodium and mafenide etc.

[V] Sulphonamide Related Compounds

These compounds differ from the basic sulphonamide nucleus and do not possess antibacterial activity. Nitrosulphathiazole, dapsone and silver sulphadiazine are some of the examples.

Dapsone, [4 ,4'-Sulphonyldianiline]

Dapsone is used for the treatment of leprosy and nocardiosis. It is also useful in the treatment of dermatitis herpetiformis. It is synthesized as follows:



Ans1

3.7. ANTIPYRETIC ANALGESICS

Antipyretic analgesics are the remedial agents, which are used to reduce the temperature of the body in case of fever condition. However, they do not reduce the normal body temperature.

Antipyretic analgesics are classified on the basis of their chemical structure :

- (i) Aniline and *p*-aminophenol analogues
- (ii) Quinoline acid derivatives
- (iii) Quinoline derivatives
- (iv) Pyrazolones and pyrazolodiones
- (v) *N*-Arylanthranilic acids

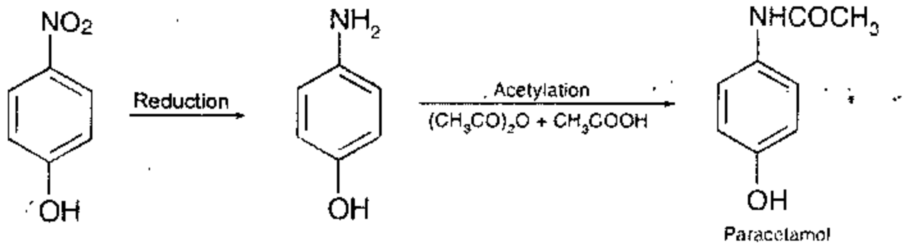
[I] Aniline and *p*-Aminophenol Analogues

Some of the examples belonging to this category of antipyretic analgesics are as follows :

(1) Paracetamol, (*p*-Hydroxyacetanilide)

Paracetamol is used effectively in the conditions linked with musculoskeletal pain, headache, and neuralgias and dysmenorrhea. It is useful for the treatment of aspirin sensitive patients.

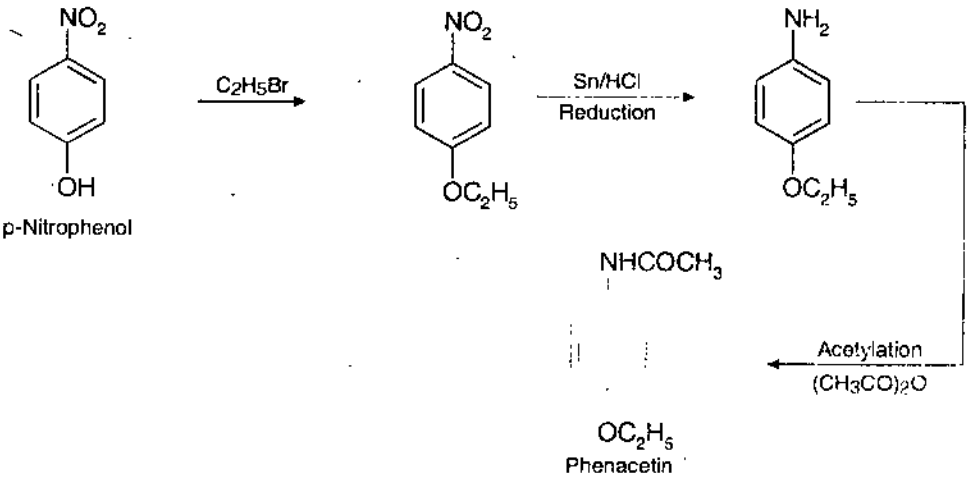
Paracetamol is synthesised as follows:



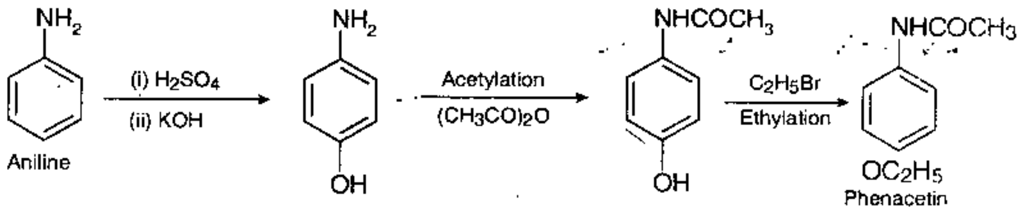
(2) Phenacetin, [*p*-Acetophenetidide]

Phenacetin may be synthesized by three different methods as given below :

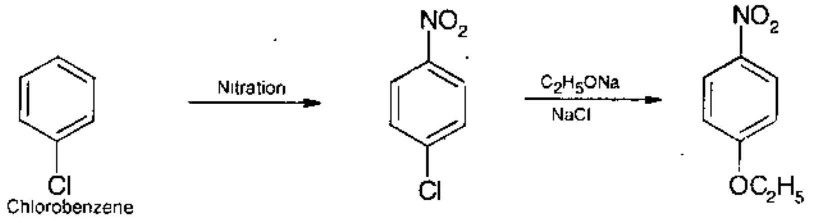
(a) *Method I (From p-nitrophenol)*

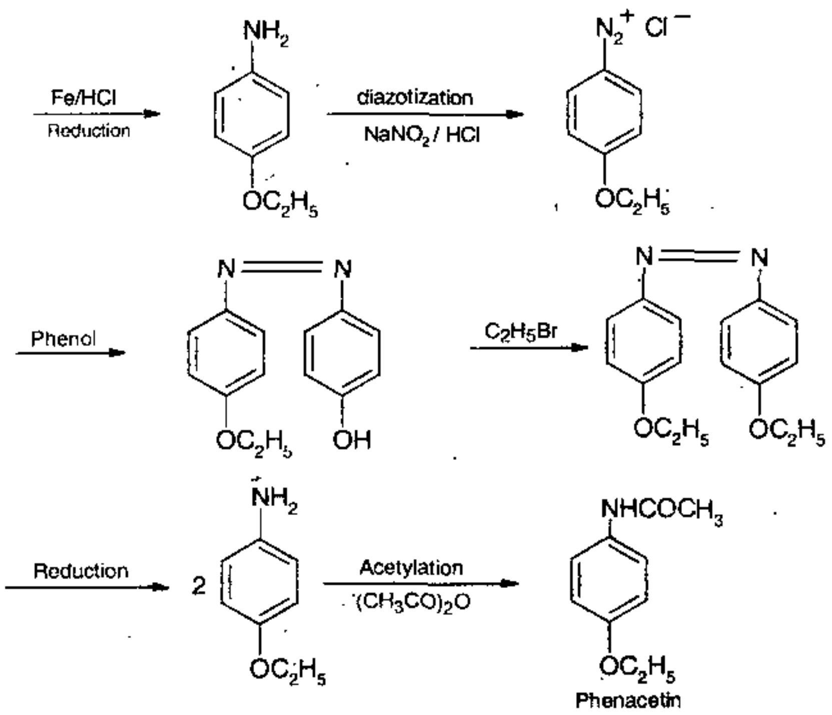


(b) *Method II (From aniline)*



(c) *Method III (From chlorobenzene)*





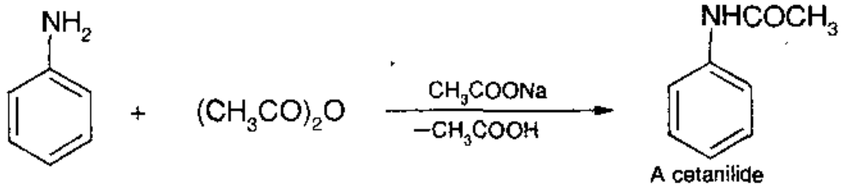
Phenacetin is used as an analgesic and as antipyretic. In many countries, phenacetin is not used as a drug because it damages the kidney.

(3) Acetanilide [*N*-Phenylacetamide]

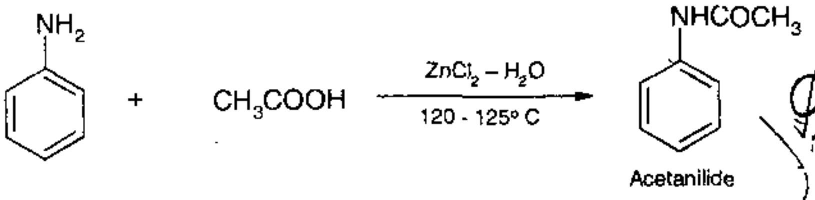
Acetanilide is very cheap antipyretic drug. It is replaced by other antipyretics because of its toxicity caused due to liberation of aniline in vivo.

It is synthesized by the following two methods :

(a) ***Method I (From aniline and acetic anhydride)***



(b) ***Method II (From aniline and acetic acid)***



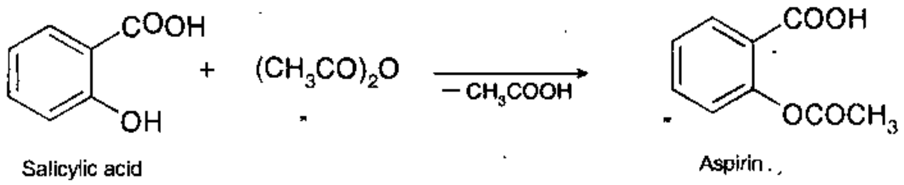
Ans

[II] Salicylic Acid Analogues

A few examples of drugs belonging to this category of antipyretic analgesics are discussed as follows :

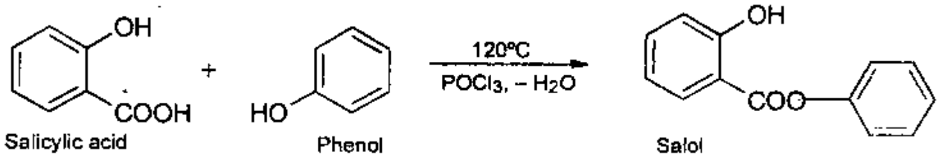
(4) Aspirin (Acetylsalicylic acid)

Aspirin is useful as an antipyretic analgesic and also as an anti-inflammatory agent for the treatment of headache, muscular pains and fever caused due to common cold. It is synthesized by reacting salicylic acid and acetic anhydride as follows :



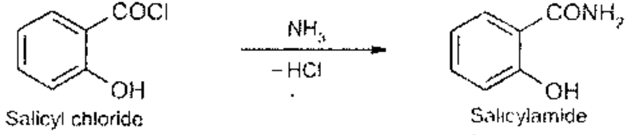
(5) Salol (Phenylsalicylate)

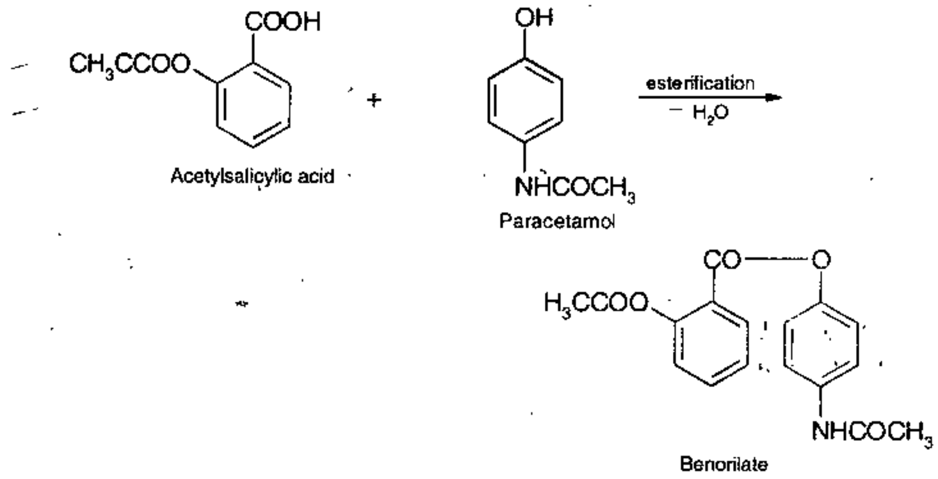
Salol is used as an antipyretic and also as internal antiseptic. In the intestine ,salol undergoes hydrolysis producing salicylic acid and phenol. The liberated phenol exerts antiseptic action without any toxic effects. It is prepared by heating salicylic acid and phenol in the presence of phosphorus oxychloride.



(6) Salicylamide (o-Hydroxybenzamide)

Salicylamide possesses antipyretic and analgesic activities. It is synthesized by the action of ammonia on salicyl chloride.





[III] Quinoline Derivatives

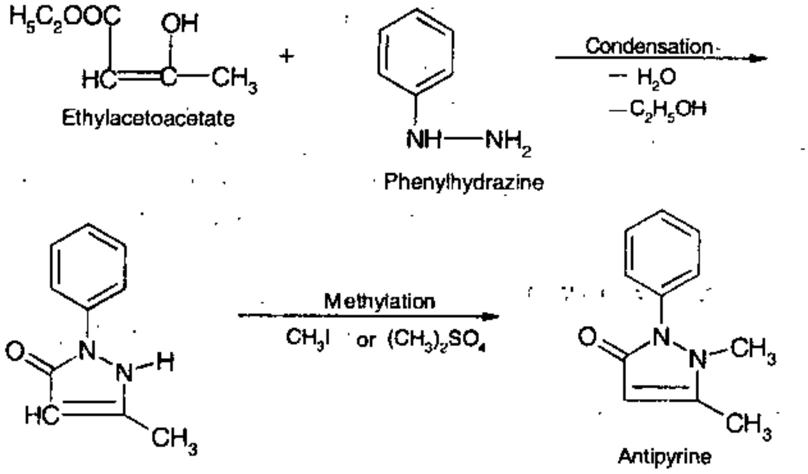
The antipyretic analgesics belonging to this category are cinchophen and neocinchophen.

[IV] Pyrazolones and Pyrazolodiones

The important antipyretic analgesics belonging to this category are described here. For example: antipyrine, aminopyrine, phenylbutazone, oxyphenbutazone and sulphinpyrazone etc.

(A) Antipyrine [2,3 Dimethyl-1-phenyl-3-pyrazolin-5-one]

Antipyrine is synthesized by condensation of ethylacetoacetate with phenylhydrazine, followed by methylation of the resulting product.



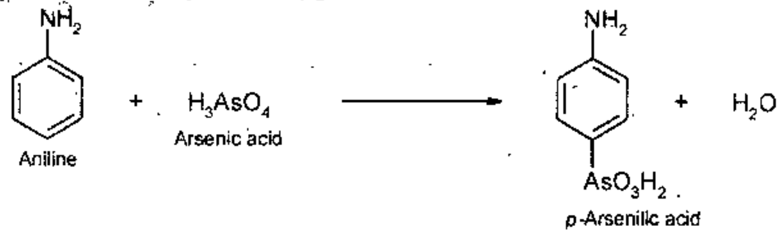
Antipyrine is used to reduce the body temperature in fever condition.

[V] *N*-Arylanthranilic Acids

Antipyretic analgesics belonging to this category are mefenamic acid and meclofenamate sodium.

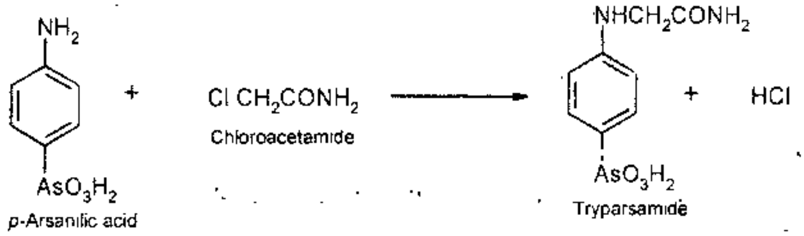
3.8. ARSENICAL DRUGS

Arsenical drugs are used in the treatment of *syphilis*. Arsphenamine, neoarsphenamine, atoxyl and tryparsamide are some of the arsenical drugs.



[I] Tryparsamide

Tryparsamide is the sodium salt of *N*-phenylglycineamide-*p*-arsonic acid; it is less toxic than atoxyl, and may be synthesixed by refluxing the latter with chloroacetamide.



3.9. ANTIMALARIALS

Antimalarials are the chemotherapeutical agents, which are useful for the treatement of **malaria.** The organisms responsible for malaria belong to the genus *plasmodium*. It is one of the classes of protozoa known as *sporozoa*. The species which are responsible for human malaria are :

- *Plasmodium malariae* (the parasite of quartan malaria)
- *Plasmodium vivax* (the parasite of tertian malaria)

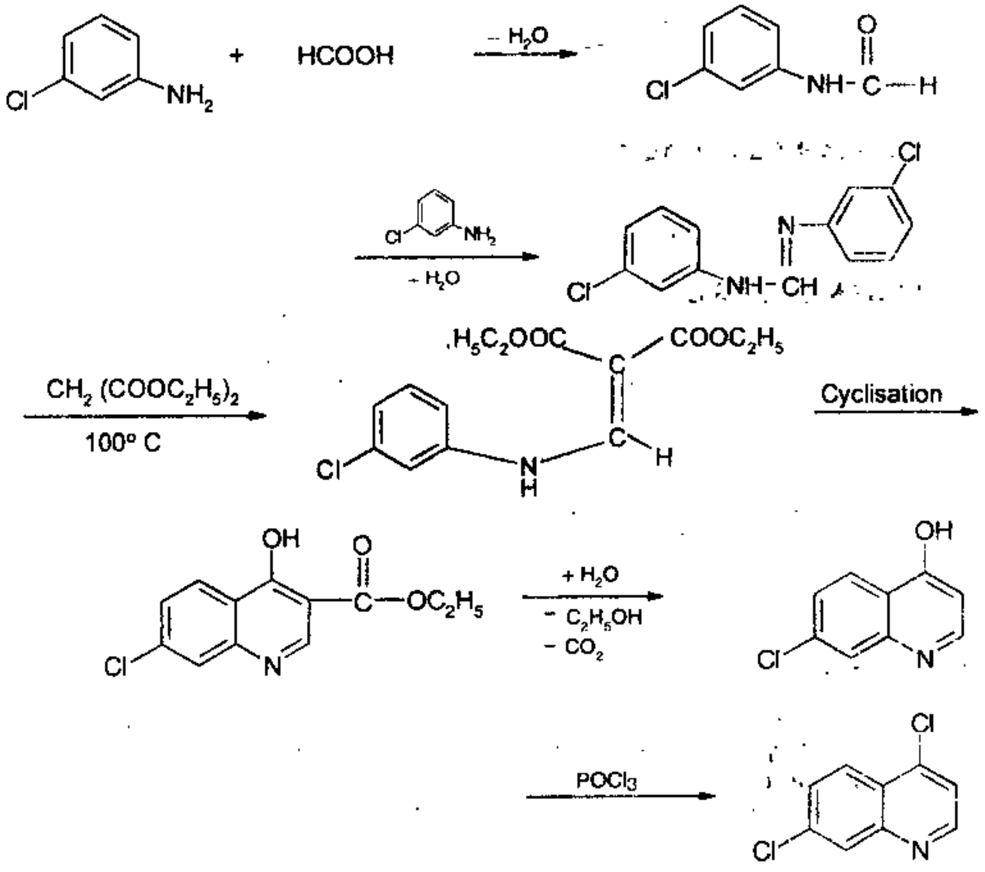
- *Plasmodium falciparum* (the parasite of malignant or subtertain malaria)
- *Plasmodium ovale* (the parasite of mild tertian malaria)

Quinine was originally the only drug known to be effective for the treatment of malaria. Now there are several synthetic compounds which are used against malaria, for example: plasmoquine, mepacrine and proguanil etc.

(1) Chloroquine (Aralen)

Chloroquine is superior to both quinine and mepacrine. Chloroquine is prepared as follows :

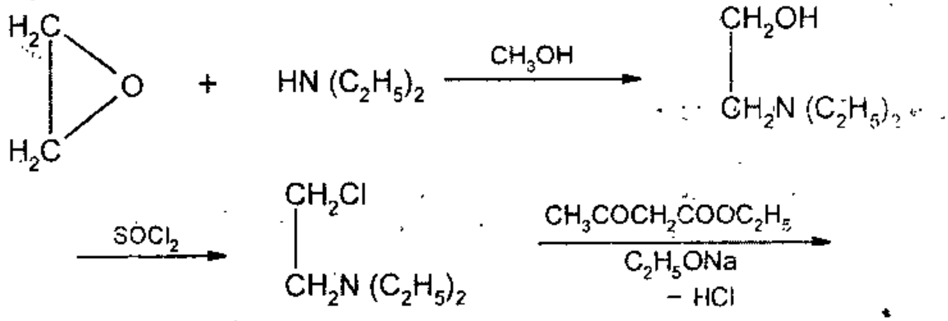
(i) Synthesis of 4, 7 dichloroquinoline (A).

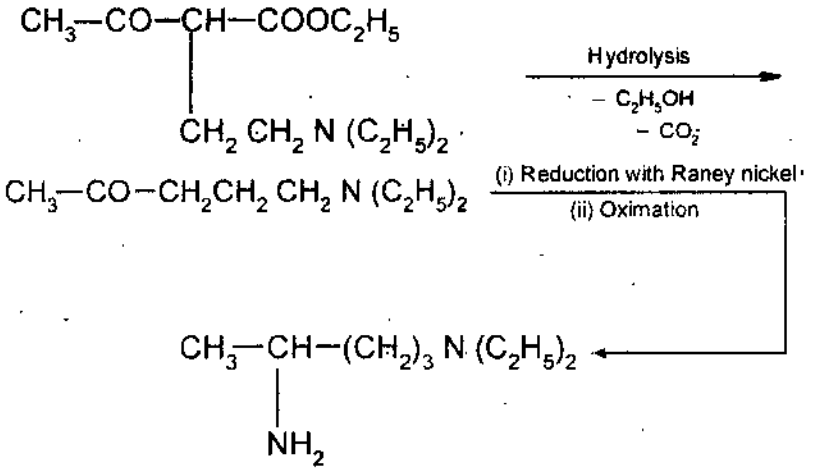


4, 7-Dichloroquinoline

(A)

(ii) Synthesis of 4-amino-1-diethylamino pentane (b).

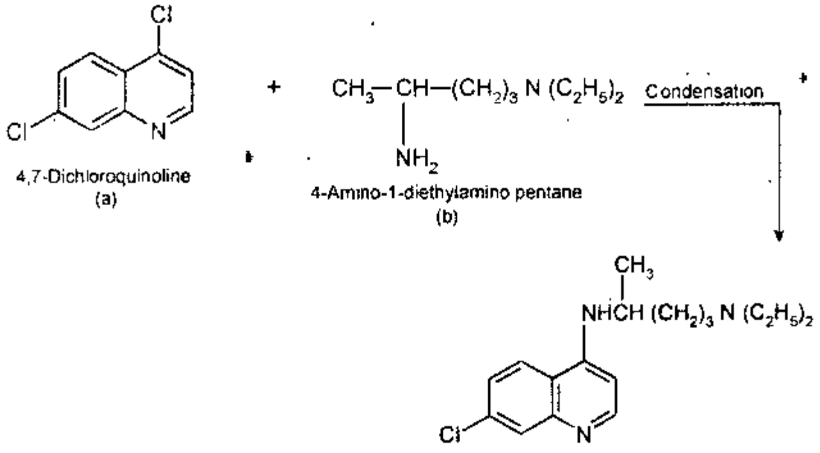




4-Amino-1-diethylamino pentane

(B)

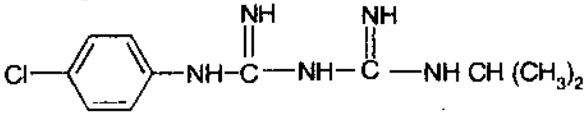
(iii) Condensation of (A) and (B) to get chloroquine.



Chloroquine

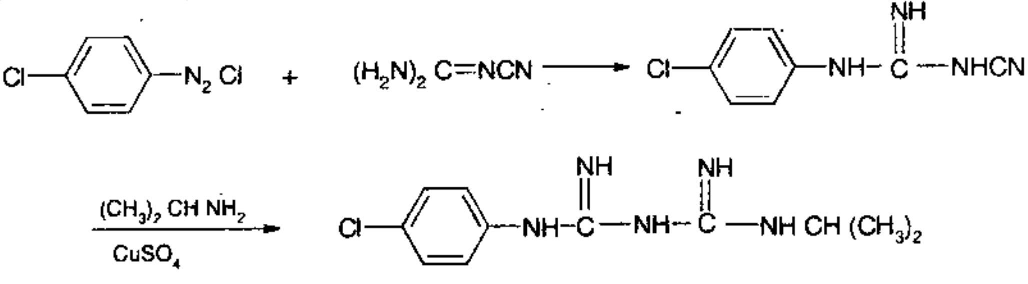
(2) Proguanil (Paludrine)

It is N^1-*p*-chlorophenyl-N^5-isopropyldiguanide. It is superior to mepacrine and chloroquine, and acts as the best antimalarial drug.



Proguanil

It is prepared by coupling p-chlorobenzenediazonium chloride with dicyanodiamide, followed by treating the product with isopropylamine in presence of copper sulphate.



Proguanil

3.10. ANTIBIOTICS

Many micro-organisms produce within themselves chemical substances which, when excreted, interfere with the growth or metabolism of other micro-organisms. Such chemical substances or compounds are called **antibiotics.** Antibiotics are the chemotherapeutic agents and in low concentration they inhibit the growth of micro-organisms.

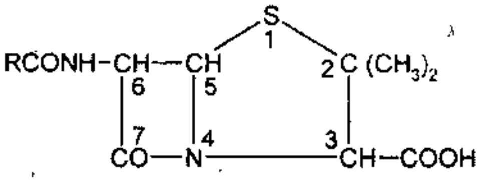
Fleming (1929) discovered a mould of **penicillium** species that inhibited the growth of certain bacteria. A number of researchers investigated this observation and culminated in the isolation of the active **penicillin.** Later on many other antibiotics were also isolated.

A wide range of compounds having different chemical structures are covered under antibiotics. A rational classification of antibiotics is very difficult. However, many schemes have been suggested for the classification, for example:

- Classification based on the chemical structure
- Classification according to the nature of activity

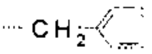
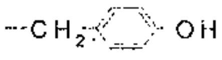
[I] The Penicillins

Penicillin is the name assigned to the mixture of naturally occurring compounds having the molecular formula **$C_9H_{11}N_2O_4SR$**. There are at least six natural penicillins as depicted in the following table 1.

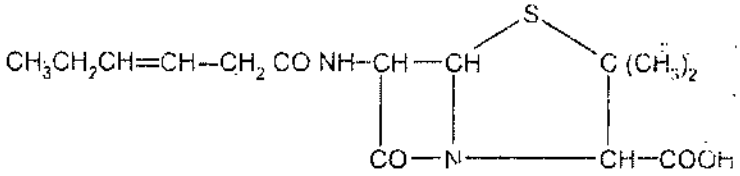


Penicillin

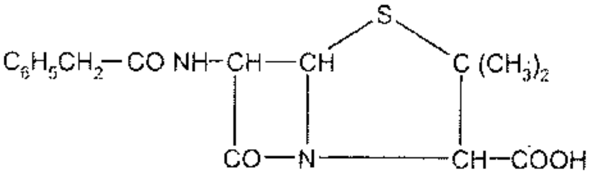
Table 1 Naturally occurring penicillins

Sr. No	Chemical name	Other names	R
1.	Pent-2-enylpenicillin	Penicillin I or F	$—CH_2CH{=}CHCH_2CH_3$
2.	Benzylpenicillin	Penicillin II or G	
3.	*p*-Hydroxybenzylpenicillin	Penicillin III or X	
4.	*n*-Heptylpenicillin	Penicillin IV or K	$(CH_2)_6\,CH_3$
5.	*n*-Amylpenicillin	Dihydro-F-penicillin	$—(CH_2)_4\,CH_3$
6.	Phenoxymethylpenicillin	Penicillin V	$—CH_2\,O\,C_6H_5$

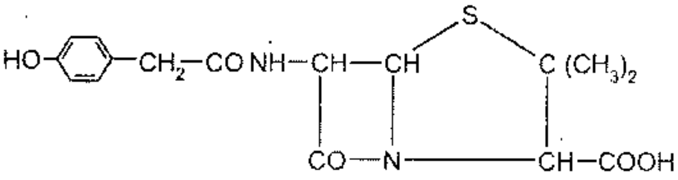
Penicillin I or F



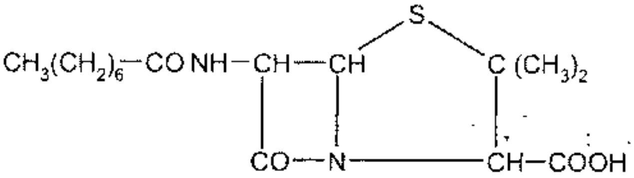
Penicillin II or G



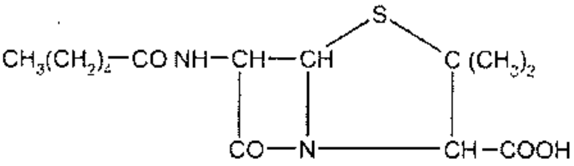
Penicillin III or X



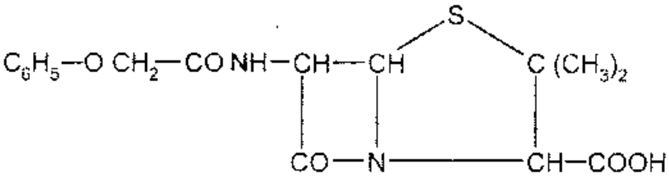
Penicillin IV or K



Dihydro–F–penicillin



Penicillin V



The commercial preparations of penicillin consist of one or more of the penicillins in varying proportions. It is observed that the addition of various compounds having a benzyl group (phenylacetic acid, phenylacetamide etc) to the culture medium enhances the total yield of penicillin and also the proportion of benzylpenicillin. In similar way, the addition of compounds possessing the p-hydroxybenzyl group to the culture medium enhances the proportion of p-hydroxybenzylpenicillin. A number of **unnatural penicillins** have been prepared by addition of various compounds to the culture medium.

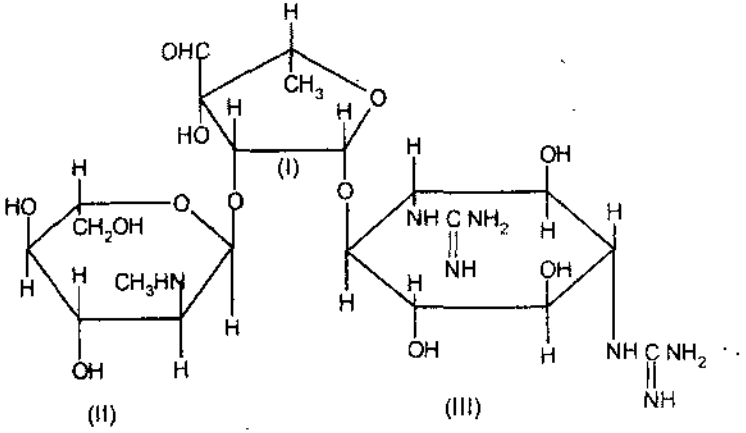
[II] Chloramphenicol (Chloromycetin)

Chloramphenicol is a laevorotatory compound. It is produced by *streptomyces venezuelae* (Carter and coworkers, 1948) and is effective for the treatment of typhoid fever.

[III] Streptomycin

Streptomycin, an antibiotic, is useful for the treatment of tuberculosis, meningitis and preumonia. Waksman and coworkers isolated streptomycin from the culture of *Streptomyces Griseus*. It is a laevorotatory solid compound. Its structure is composed of three units :

- Streptose (I)
- *N*-methyl-*L*-glucosamine (II)
- Streptidine (III)



Streptomycin

3.11. MANUFACTURE OF ASPIRIN

Aspirin is manufactured by acetylation of salicylic acid in the presence of acetic anhydride.

Flowchart for the manufacture of aspirin is depicted in figure 3. The raw materials required to produce one ton of aspirin are mentioned below :

- Salicylic acid : 860 kg
- Acetic anhydride : 640 kg

Salicylic acid and acetic anhydride are delivered to a stainless steel reactor (provided with a jacket and a stirrer). The reaction mixture is heated to 80 – 85°C for two to three hours. After completion of the reaction, the reaction mixture is filtered and the filtrate is delivered to the crystallizer. During crystallization process, the temperature is reduced to 0°C. The crystalline product (aspirin) thus obtained is centrifuged, washed and dried in dryer. The mother liquor obtained is reused for the next batch. Aspirin thus obtained is further purified by recrystallization. About 380 kg of acetic acid is recovered in the process.

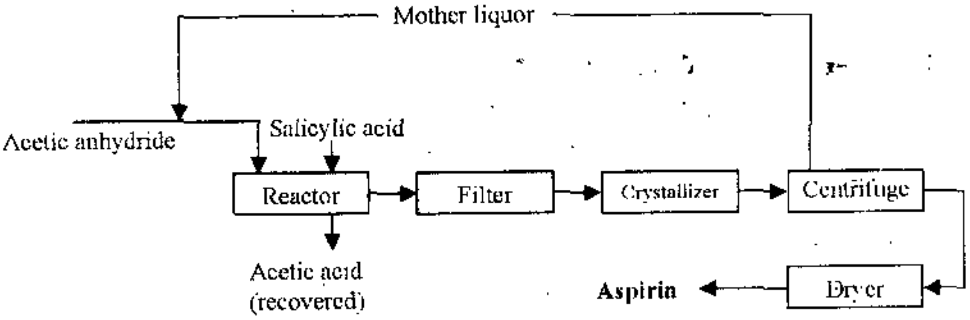


Fig. 3: Flowchart for the manufacture of aspirin

Properties of Aspirin

Aspirin is a colourless crystalline solid. It is soluble in chloroform and alcohol but very slightly soluble in water. Some of its physical properties are summarized below :

(i) Melting point : 135°C
(ii) Boiling point : Decomposes
(iii) Density : 1.40 g/cm^3

STUDENT ACTIVITY

1. What is the use of aspirin ?

2. Write the structure of phenolphthalein and quinoline.

3. What are analgesics ? Given one example.

4. Write the essentials of a dye.

5. Mention the preparation of eosin.

6. Define the terms chromophore and auxochrome.

SUMMARY

- A group with multiple bonds which give colour to a dye is known as a chromophore, *e.g.*, nitro (– NO_2), azo (—N=N–), carbonyl (>C=O) etc.
- A compound containing a chromophoric group is called chromogen.
- A group in the chromogen which deepens the colour even though these groups are chromophores are called auxochromes, *e.g.*, –NH_2, –NHR, –OH etc.
- The groups which cause deepening of the colour are called bathochromic groups.
- The groups which diminish the colour are called *hypsochromic groups*.
- Dyes are classified on the basis of their applications and their chemical constitution.
- A compound which shows different physiological effects of therapeutical value is known as a drug. It must act on a system with efficiency and safety. A drug should have minimum side effects. A drug should not cause injury to the tissues of the host.
- Sulphonamides are antibacterial drugs, *e.g.*, sulphacetamide.
- Antipyretic drug reduces the temperature of the body *e.g.*, paracetamol.
- Arsenical drugs are used in the treatment of syphilis, *e.g.*, salvarsan 606, atoxyl etc.
- Antimalarial drug is used in the treatment of malaria, *e.g.*, chloroquin.
- Many micro-organisms produce within themselves chemical substance which when exereted interfere with the growth on metabolism of other micro-organisms. These compounds are called antibiotics, *e.g.*, penicillin, streptomycin.

TEST YOURSELF

Answer the following questions :

1. *Write the essential conditions for a substance to act as a dye.*
2. Write a note on colour and constitution of dyes.
3. How are dyes classified on the basis of applications ?
4. How are dyes classified on the basis of their chemical constitution ?
5. What are mordant, vat and ingrain dyes ? Give one example of each type.
6. What are azo dyes ? How are they classified ?
7. Write the structure of a phthalein dye.
8. Describe the structure and method of preparation of the following :

(i) Methyl orange	(ii) Congo red
(iii) Malachite green	(iv) Pararosaniline
(v) Crystal violet	(vi) Rosaniline
(vii) Phenolphthalein	(viii) Fluorescein
(ix) Eosin	(x) Indigo
(xi) Alizarin	(xii) Indophenol

9. Discuss the manufacture of a dye.
10. Describe the basic requirements of a drug.
11. What are sulphonamides ? Give the preparation of any one such drug.
12. Describe the preparation and uses of the following drugs :

(i) Sulphamethizole (ii) Sulphacetamide
(iii) Sulphaguanidine (iv) Sulphanilamide
(v) Sulphathiazole (vi) Phenacetin
(vii) Acetanilide (viii) Aspirin
(ix) Streptomycetin (x) Antipyrine

13. Antipyrine is used to :
(i) Reduce the body temperature
(ii) Reduce skin diseases
(iii) Increase body weight
(iv) Act as an antimalarial

14. Eosin is a :
(i) Xanthen dye (ii) Heterocyclic dye
(iii) Vat dye (iv) Azo dye

15. Paludrine is used as an :
(i) Antipyretic (ii) Analgesic
(iii) Antibiotic (iv) Antimalarial

16. Which of the following substances is an antibiotic :
(i) Sulphathiazole (ii) Atoxyl
(iii) Streptomyctin (iv) Aspirin

17. **Fill in the blanks :**
(a) Fluorescein in is a .... type of dye.
(b) For dyeing wood, ... is used.
(c) Sulphaguanidine is used to control ....
(d) .... is used in staphylococcal infections.
(e) Phenacetin is used both as an .... and ....
(f) Acetylsalicylic acid is commonly named as ....
(g) Salol has an .... action.

ANSWERS

13. (i) **14.** (i) **15.** (iv)
16. (iii)
17. (a) xanthen (b) alizarin (c) dysentery
(d) Chloromycetin (e) analgesic, antipyretic
(f) aspirin (g) antiseptic

UNIT

4

INORGANIC CHEMICALS AND INDUSTRIAL GASES

STRUCTURE

- Inorganic Chemicals
- Inorganic Nitrogen Chemicals
- Bromine and Fluorocarbon Industries in India
- Industrial Gases
- Student Activity
- Summary
- Test Yourself

LEARNING OBJECTIVES

After studying this chapter, you will learn about the different types of inorganic chemicals including nitrogen chemicals. You will also learn about the gases which are industrially used and have wide applications.

4.1. INORGANIC : CHEMICALS

[I] Alumina, (Al_2O_3)

Alumina is required on a very large scale for the manufacture of metallic aluminum. More than 90 percent of alumina production is consumed for this purpose. Other uses of alumina are as abrasives, on manufacture of chemicals in refractories and for ceramic fibers.

Manufacturing process : The flowchart for the manufacture of alumina is shown in fig. (1). Bauxite ore containing aluminum oxide (55%) and silica (less than 7%) is crushed and well ground to 100 mesh.

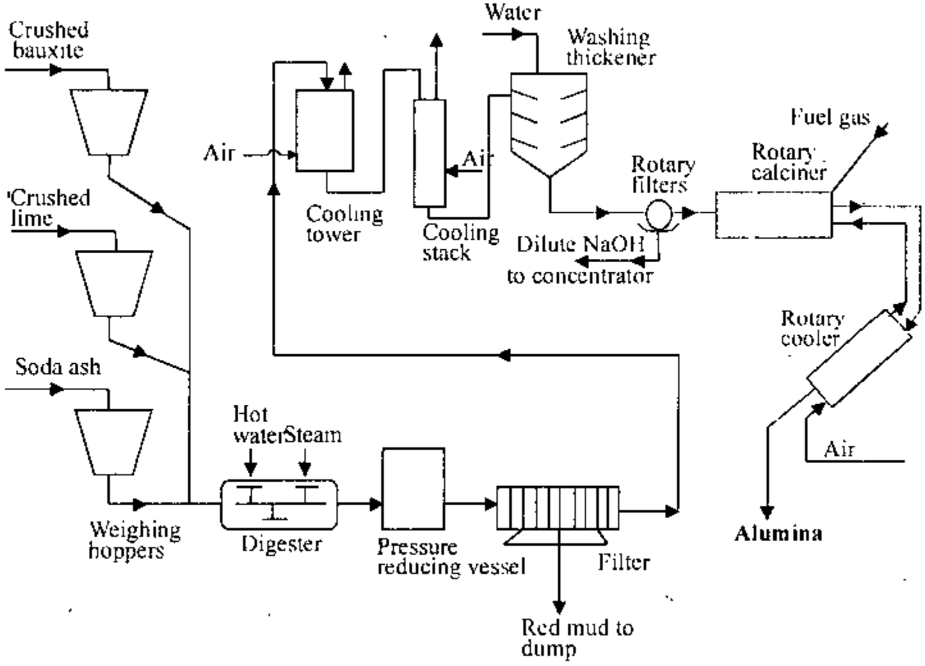


Fig. 1. Flowchart for the manufacture of alumina

The finely ground bauxite is dissolved under pressure and then heated in Bayer digesters with concentrated spent caustic soda solution (obtained from a previous cycle) and sufficient amount of lime and soda ash. Sodium aluminate is formed, and dissolved silica is precipitated as sodium aluminum silicate.

The undissolved residue (red mud) is separated from the alumina solution by filtration; it is washed and sent to recovery. Thickeners and drum filters are used.

The filtered solution of sodium aluminate is hydrolyzed to precipitate aluminum hydroxide by cooling. The precipitate of aluminum hydroxide is filtered from the liquor and washed. It is then calcined by heating at ~ 980°C in the rotary kiln. The alumina thus obtained is cooled and then transported to reduction plants.

The dilute caustic soda filtered from aluminum hydroxide is concentrated and reused for the next batch. The red mud may be used for the recovery of alumina.

[II] Aluminum Sulphate [$Al_2(SO_4)_3$]

Aluminum sulphate is an industrially important chemical. It is used in the sizing of paper. It reacts with sodium resinate giving insoluble aluminum resinate. For the sizing of paper, aluminum sulphate must be free from ferric ions; otherwise the paper will be discoloured. Aluminum sulphate is used for:

(i) Manufacturing of chemicals (ii) Concrete modifications
(iii) Preparation of pharmaceuticals (iv) Soaps and greases
(v) Fire extinguishing solutions (vi) Tanning
(vii) Cellulosic insulations.

Manufacturing process : Aluminum sulphate is manufactured using bauxite. The bauxite, after crushing and grinding, is delivered to bauxite feeder. The reaction takes place in steel tanks (provided with lead lining), where the reactants are mixed and heated with the help of agitators and live steam. The reactors are arranged in series. Barium sulphide (black ash) is added to the last reactor in order to reduce ferric sulphate to the ferrous state and to precipitate the iron. The reaction mixture is then delivered through a series of thickeners, which removes undissolved material and washes the waste so that it does not contain any alum.

The clacified aluminum sulphate solution is concentrated in an open evaporator (steam coil heated). The concentrated liquor thus obtained is then passed into flat pans for cooling and solidification. The solid cake of aluminum sulphate is broken and ground to size for transportation. The flowchart is shown in fig. (2).

The raw materials required to produce one ton of aluminum sulphate are as follows :

(i) Bauxite (55 % Al_2O_3)	: 338 kg
(ii) H_2SO_4 (60° Bè)	: 575 kg
(iii) Black ash (70 % BaS)	: 6.6 kg
(iv) Flake glue	: 0.2 kg

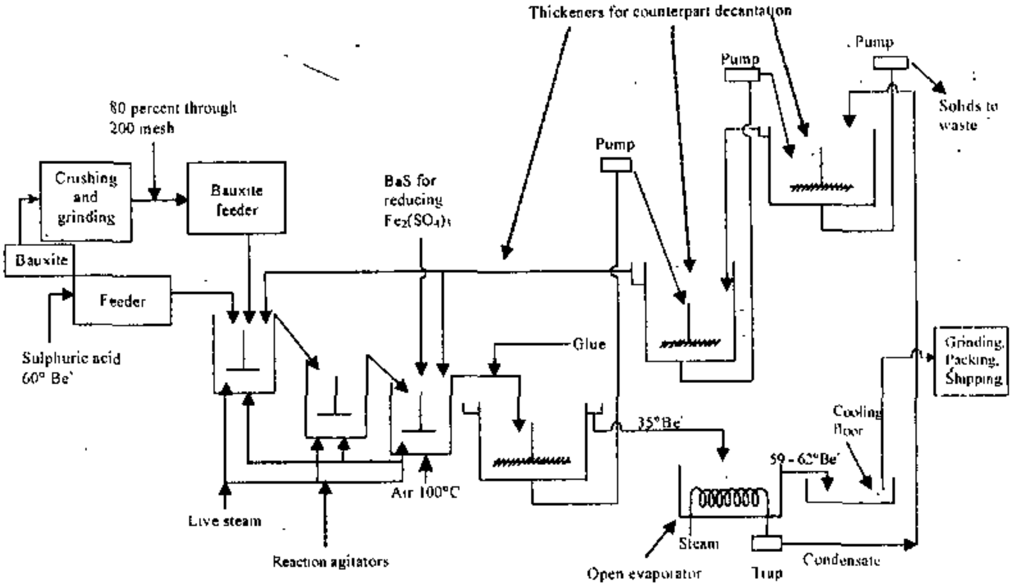


Fig. 2: Flowchart for the manufacture of aluminum sulphate

[III] Fluorocarbons

Fluorocarbons are the compounds of carbon, fluorine and chlorine with little or no hydrogen. The fluorocarbons, having two or more fluorine on a carbon atom, are chemically inert and stable. They possess higher volatility and density as compared to the corresponding hydrocarbons. The uses of fluorocarbons are mentioned below (use percentage is given in parentheses) :

(i) Refrigerants consumed (46%)
(ii) Foam blowing agents (20%)
(iii) Solvents (16%)
(iv) Fluoropolymers (7%)
(v) Aerosol propellants (less than 1%)

Manufacturing process : The fluorocarbons are manufactured by reacting chlorinated hydrocarbons with hydrogen fluoride (anhydrous), in the presence of antimony pentachloride as catalyst. The fluorocarbons viz. trichlorofluoromethane (CCl_3F), dichlorodifluoromethane (CCl_2F_2) and chlorodifluoromethane ($CHClF_2$) compose 90% of the fluorocarbon production.

$$CCl_4 + HF \xrightarrow{SbCl_5} CCl_3F + HCl$$

$$CCl_4 + 2\,HF \xrightarrow{SbCl_5} CCl_2F_2 + 2HCl$$

Chlorodifluoromethane is obtained by reacting chloroform with hydrogen fluoride (anhydrous), in the presence of antimony perntachloride as the catalyst.

$$CHCl_3 + 2\,HF \xrightarrow{SbCl_5} CHClF_2 + 2HCl$$

Flowchart for the manufacture of fluorocarbons is shown in fig. (3). Hydrogen fluoride (anhydrous) and carbon–tetrachloride or chloroform are passed through molten antimony pentachloride catalyst. These reactions are exothermic and are performed in a steam jacketed atmospheric pressure reactor at 65-95°C. The gaseous mixture of fluorocarbon and unreacted chlorocarbon is then separated by distillation, and the chlorocarbon is recycled into the reaction. Hydrogen chloride evolved in the reaction is removed by absorption in water. The last traces of hydrogen chloride and chlorine are removed by absorbing in sodium hydroxide solution in causting scrubbing tower.

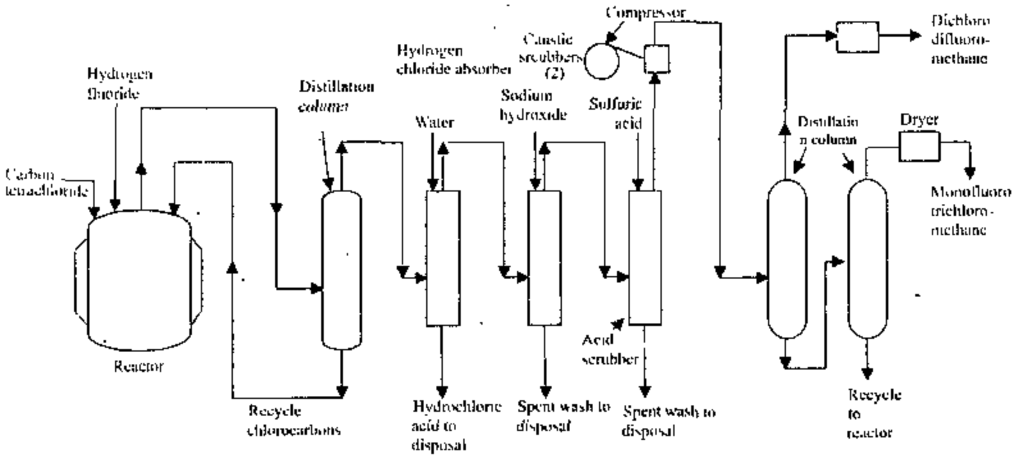


Fig. 3: Flowchart for the manufacture of fluorocarbons

[IV] Bromine

Bromine is a heavy dark-red liquid and it belongs to halogen family. It is more expensive than chlorine. The uses of bromine are summarised as follows :

(i) Around sixty percent of bromine output is utilized for the manufacture of ethylene dibromide for antiknock fluids. This compound prevents the deposition of lead oxide in engines which would otherwise result from tetraethyl lead (TEL).

(ii) It is used in organic synthesis.

(iii) It is used in swimming pools. Addition of bromine (less than one ppm) sterilizes the swimming pool water without causing irritation to eyes.

(iv) The compounds of bromine such as alkali bromides are used in photography.

Manufacturing process : A process was introduced for the removal of a small quantity of bromine by air-blowing it out of the chlorinated seawater according to the following equation :

$$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2 \uparrow$$

In ocean water (where the concentration of bromine is relatively less), air is found to be economical blowing-out agent. For the treatment of brine (a relatively rich bromine source), steaming out process is used for bromine manufacture. Flowchart for the process is shown in fig. (4).

In this process, brine is heated to 90°C in a heat exchanger and then it is passed down a chlorinator tower. After partial chlorination, the brine is delivered to a steaming-out tower. In this tower, steam is injected at the bottom and the remaining chlorine is introduced. The halogen containing vapours are condensed and then delivered to gravity separator. The top halogen layer is delivered back to the steaming-out tower. The bottom layer (crude bromine) is delivered to distilling column for getting pure bromine.

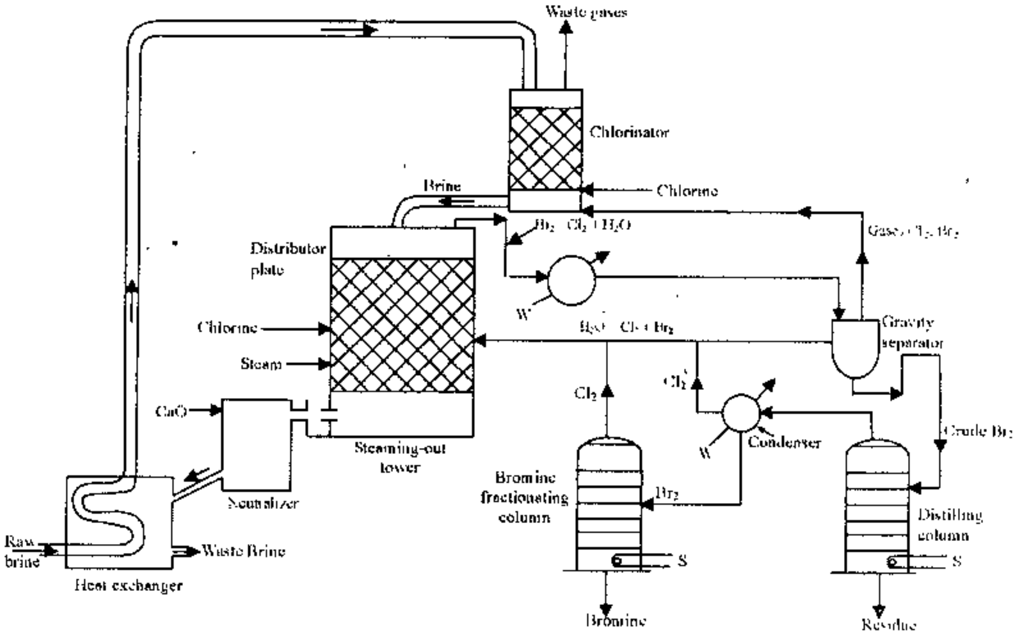


Fig. 4: Flowchart for steaming-out process for bromine manufacture

Properties of bromine : Physical properties of bromine are summarized as follows :

(i) Physical state : Dark red liquid (vapourizes rapidly)
(ii) Odour : penetrating odour
(iii) Boiling point : 58.73°C
(iv) Density : 3.21 g cm^{-3} at 20°C
(v) Freezing point : – 7.3°C
(vi) Refractive index : 1.6475 at 25°C

[V] Sodium Dichromate ($Na_2Cr_2O_7$)

Sodium dichromate is used as the starting material for making the solutions of chromium salts which are employed in chrome leather tanning, and in chrome mordant dyeing of wool. Yellow lead chromate (a pigment) is also manufactured from sodium dichromate.

Manufacturing process : Sodium dichromate is manufactured using chromite ore (composition: 50% Cr_2O_3 and the balance being FeO. Al_2O_3, SiO_2 and MgO). The chromite ore (ground to 200 – mesh) is mixed with ground limestone and soda ash. The mixture is roasted at ~1200°C in a strong oxidizing atmosphere. The sintered mass is crushed and treated with hot water in order to separate the soluble sodium chromate. The solution is then treated with enough quantity of sulphuric acid for the conversion of sodium chromate to sodium dichromate, alongwith the formation of sodium sulphate. During acidification. most of the sodium sulphate crystallizes out in anhydrous form and the remaining sodium sulphate drops out in the evaporators on concentrating the dichromate solution. The hot saturated solution of sodium dichromate is delivered from evaporator to the crystallizer, and then to the centrifuge and dryer. Flowchart for the manufacturing process is shown in fig. (5).

The raw materials required to produce one ton of sodium dichromate and 0.66 ton of anhydrous sodium sulphate are summarized as follows :

- Chromite ore : 1100 kg
- Limestone : 1650 kg .
- Soda ash : 880 kg
- Sulphuric acid (66° Be) : 500 kg

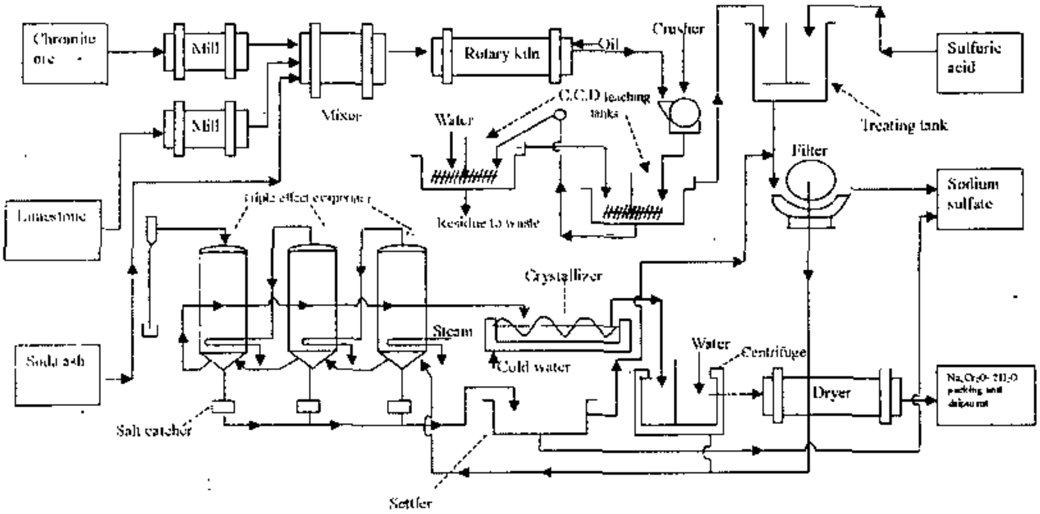


Fig. 5: Flowchart for the manufacture of sodium dichromate from chromite ore.

[VI] Sodium Silicate

More than forty varieties of sodium silicate are available. The ratio of the constitutients Na_2O and SiO_2 in sodium silicate may be varied to have desired properties. Some of the important varieties of sodium silicate are listed as follows :

(1) **Colloidal silicates** : These have a molar ratio of 1 Na_2O / 1.6 SiO_2 to 1 Na_2O/4 SiO_2.

(2) **Sodium metasilicate (Na_2SiO_3)** : It possesses the molar ratio of 1 mol of Na_2O to 1 mol of SiO_2

(3) **Sodium sesquisilicate (Na_2SiO_4. Na_2SiO_3 . $11H_2O$)** : It has molar ratio of 1.5 mol of Na_2O to 1 mol of SiO_2

(4) **Sodium orthosilicate (Na_4SiO_4)** : It possesses molar ratio of 2 mol of Na_2O to 1 mol of SiO_2.

The major uses of sodium silicates are summarised as follows :

(i) In the manufacture of silica based catalyst and silica gel.

(ii) In the production of soaps and detergents, pigments and adhesives.

(iii) For metal cleaning and for the treatment of water and paper.

(iv) Sodium metasilicate exists in hydrated form. It is used for metal cleaning and also as strongly alkaline detergent.

(v) Lower colloidal silicates (water glass), sold as 32 to 47% solutions, are useful as adhesives for making paperboard used in corrugated containers. These solutions are employed alone (or in combination with other materials) as adhesive for plywood, wall-board, flooring and metal foils.

Manufacturing process : The above silicates are manufactured by fusing sodium carbonate and silica (sand) in a furnace

$$Na_2CO_3 + n\,SiO_2 \longrightarrow Na_2O\,.\,nSiO_2 + CO_2$$

In commercial silicates the value of *n* corresponds to 2.0 or 3.2. Intermediate compositions are obtained by mixing, and more alkaline ratios by adding caustic soda or initially fusing the sand with caustic soda. The product formed upon cooling is a clear and light bluish-green glass (the colour may be due to the presence of impurities of less than one percent of iron). When the material is to be marketed in form of solution, then the product is ground and dissolved in water or by steam under pressure when the ratio of silica to alkali is above two. This process is depicted in figure 6. However, when liquids are made directly, the melt flows from furnace and without chilling goes into an open rotary dissolver where it is hydrated in steam and water not under pressure.

The resulting product obtained from both the methods is sold as much concentrated as possible.

The raw materials required to produce one tonne of 40 % water glass are as follows :

Sodium carbonate	: 156 kg
Sand	: 293 kg

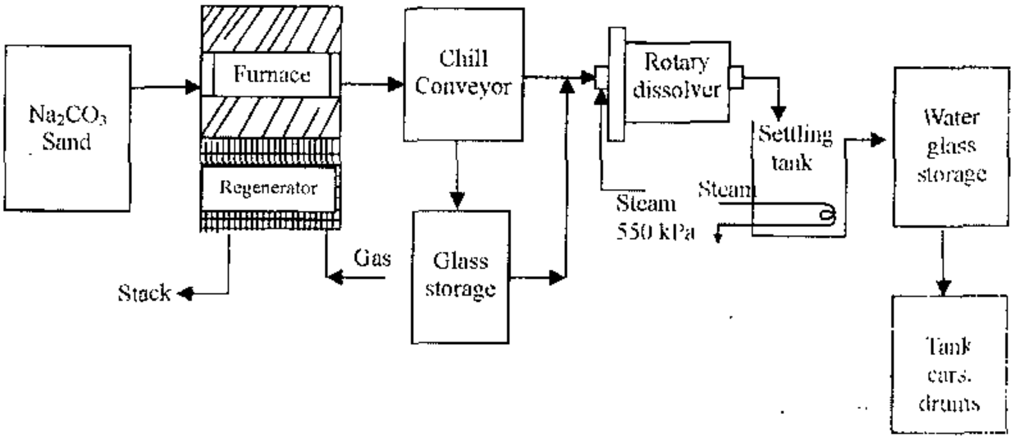


Fig. 6: Flowchart for the manufacture of sodium silicate.

[VII] Sodium Thiosulphate ($Na_2S_2O_3$)

Sodium thiosulphate is a white crystalline solid having density 1.667 g cm^{-3}. It is readily soluble in water. It has a wide range of applications. Some of the applications of sodium thiosulphate are given below :

(i) For removal of chlorine from solutions.

(ii) As fixer in photography.

(iii) As antichlor in bleaching of paper pulp.

(iv) For tanning of leather.

(v) As mordant (in dyeing and printing textiles).

(vi) As an analytical reagent.

(vii) For extraction of silver from ore.

Manufacturing process : The flowchart for the manufacture of sodium thiosulphate, using soda ash (Na_2CO_3) and sulphur dioxide, is shown in fig. (7).

The soda ash solution (26°Be') is allowed to pass down-wards through a series of absorption towers. These towers (provided with lead lining and packed with wood slats) are supported by acid proof bricks. Sulphur dioxide is introduced from the bottom of these towers.

$$Na_2CO_3 + H_2O + 2\,SO_2 \longrightarrow 2\,NaHSO_3 + CO_2$$

The solution of sodium bisulphite, from the bottom of the last absorption tower, is delivered to a cast iron kettle (provided with ceramic lining and an agitator). After addition of soda ash and sulphur, the reaction mixture is boiled in the kettle. The resulting sodium thiosulphate solution is delivered to steam heated evaporator and concentrated. The hot liquor thus obtained from the evaporator is delivered to crystalliser. The crystals of sodium thiosulphate thus obtained are collected after centrifugation. The crystals are packed in moisture-tight containers.

$$2NaHSO_3 + Na_2CO_3 + 2S \longrightarrow 2Na_2S_2O_3 + H_2O + CO_2$$

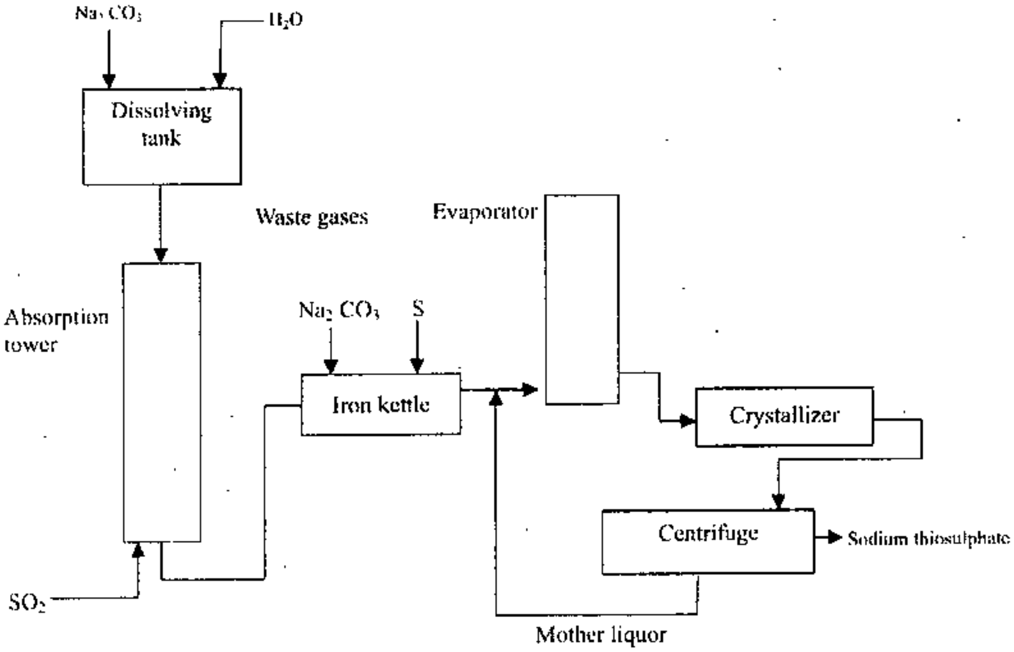


Fig. 7: Flowchart for the manufacture of sodium thiosulphate

Raw materials required to produce one tonne of sodium thiosulphate are:

- Soda ash : 400 kg
- Sulphur dioxide : 250 kg
- Sulphur : 125 kg

[VIII] Sodium Nitrite ($NaNO_2$)

Sodium nitrite is an important chemical and some of its important uses are listed as follows :

(1) It is used for diazotisation of amines in making azo dyes

(2) It is used as preservative in meat processing

(3) The mixture of sodium nitrite and sodium nitrate is employed in metal treatment.

(4) It is used in photography and in medicines.

Formerly, it was prepared by reacting lead with sodium nitrate

$$NaNO_3 + Pb \longrightarrow NaNO_2 + PbO$$

Now, sodium nitrite is manufactured by passing the oxidation product of ammonia into a soda ash solution.

$$Na_2CO_3 + 2NO + \tfrac{1}{2}O_2 \longrightarrow 2NaNO_2 + CO_2$$

[IX] Sodium Sulphide (Na_2S)

Sodium sulphide possesses an important position in the organic chemical industries. The uses of sodium sulphide are mentioned below :

(1) Sodium sulphide is used as a reducing agent in the manufacture of amino compounds.

(2) Sodium sulphide is used in the preparation of many dyes.

(3) Sodium sulphide is employed in the leather industry.

(4) Sodium sulphide is one of the reactants for making Thiokol synthetic rubber.

(5) Sodium sulphide also finds use in metallurgical, photographic and engraving fields.

Deliquescence is one of the properties of sodium sulphide. It crystallizes with nine molecules of water ($Na_2S. 9 H_2O$).

Sodium sulphide is produced by reduction of sodium sulphate with coal in reverberatory furnace, but this is the oldest method. Very drastic conditions are required for the reactions involving reduction of salt cake. The reaction must be performed above 900°C.

$$Na_2SO_4 + 4C \longrightarrow Na_2S + 4CO$$
$$Na_2SO_4 + 4CO \longrightarrow Na_2S + 4CO_2$$

Sodium sulphide is also produced by another method. The saturated solution of caustic soda is treated with hydrogen sulphide to give sodium hydrosulphide solution, which is further filtered to remove heavy metal sulphides. The filtered solution of sodium hydrosulphide is then reacted with sodium hydroxide to obtain highly pure product. Stainless steel is used as the material of construction in the production of sodium sulphide.

$$H_2S + NaOH \longrightarrow NaHS + H_2O$$
$$NaHS + NaOH \longrightarrow Na_2S + H_2O$$

[X] Sodium Bisulphite ($NaHSO_3$)

Sodium bisulphite is used in industries as a solid or in form of solution. The solid is an anhydrous form and the pure reagent has the formula $NaHSO_3$. The commercial product consists of sodium pyrosulphite ($Na_2S_2O_5$), or sodium metabisulphite, which is the dehydrated derivative of two molecules of sodium bisulphite.

Sodium bisulphite has various applications, such as

- As chemical intermediate, in pharmaceuticals, in food preservatives, as an antichlor for pulp, paper and textiles, in water treatment and pollution control, in tanning industry as a reducing agent for chrome solutions, in the manufacture of photographic and organic chemicals, as a bleaching agent in textile industry.

Manufacturing process : Sodium bisulphite is manufactured by passing sulphur dioxide through the mother liquor of previous process containing small quantity of sodium bisulphite and in suspension a considerable amount of soda ash. Sodium bisulphite is obtained as a suspension, which is removed from the solution by centrifugation.

$$2NaHSO_3 + 2Na_2CO_3 + 2H_2O + 4SO_2 \longrightarrow 6NaHSO_3 + 2CO_2$$

[XI] Sodium Bisulphate ($NaHSO_4$)

Sodium bisulphate is used in the manufacture of acid-type toilet bowl cleaners and for industrial cleaning and metal pickling. It is also useful in dye bath. carbonising-wool and in various chemical processes.

Sodium bissulphate was formerlv prepared by reacting sodium nitrate with sulphuric acid

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

Sodium bissulphate is also prepared by heating sodium chloride with sulphuric acid.

Ans3

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

[XII] Copper Sulphate ($CuSO_4$)

Copper sulphate is blue coloured crystalline solid and possseses water of crystallization ($CuSO_4.5\ H_2O$). It is soluble in water and insoluble in alcohol. It has density 2.284 g cm^{-3}.

Manufacturing process : Copper sulphate is manufactured using copper oxide ore (for example: azurite and malachite) and sulphuric acid. The raw materials required to produce one ton of copper sulphate are :

- Copper oxide ore : 325 kg ; Sulphuric acid (100%) : 400 kg.

Copper oxide ore is treated with sulphuric acid in a leaching tank (a vessel provided with lead lining and perforated coils for air blowing). The resulting solution of copper sulphate is filtered to get clear solution. The filtered solution is then concentrated in evaporator and then delivered to crystalliser. The crystals of copper sulphate pentahydrate ($CuSO_4.5\ H_2O$) are collected by centrifugation and dried. The flowchart for the process is shown in fig. (8).

$$CuO + H_2SO_4 + 4H_2O \longrightarrow CuSO_4.\ 5H_2O$$

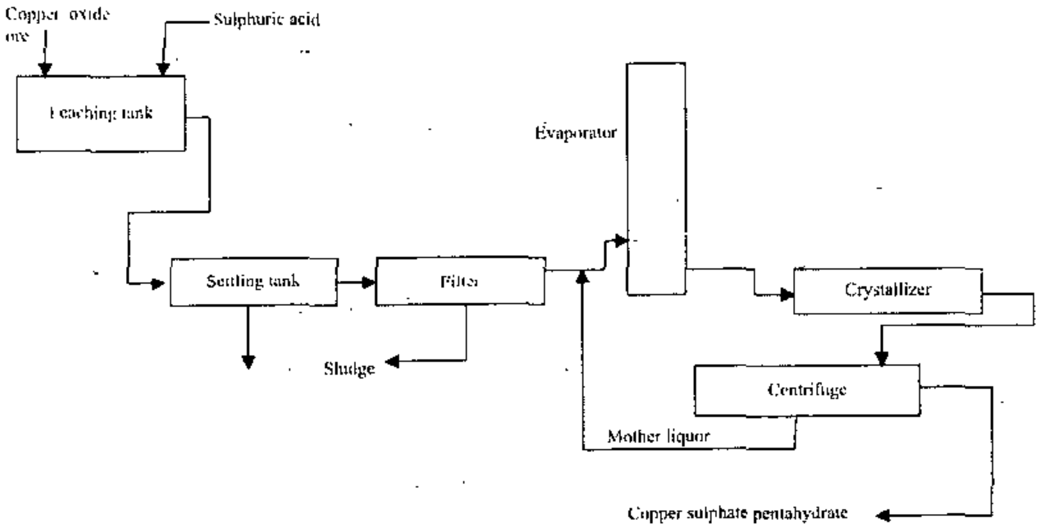


Fig. 8 : Flowchart for the manufacture of copper sulphate

Copper sulphate is an important chemical and it possesses a wide variety of applications. The uses of copper sulphate are listed as follows :

As an agricultural fungicide, as a mordant in textile dyeing, in the preparation of copper salts and azo dyes, in electroplating and leather tanning, in paints, pigments and varnishes, in petroleum refining, as additive in insecticide mixtures, as an analytical reagent, as a battery electrolyte, in metal colouring and metal marking inks, anhydrous copper sulphate ($CuSO_4$) is used for the removal of water traces from alcohols.

[XIII] Potassium Permanganate ($KMnO_4$)

Potassium permanganate is a dark purple coloured crystalline solid having metallic luster. It is soluble in water. It undergoes decomposition at ~240°C with evolution of oxygen. It has density 2.703 g cm^{-3}.

Manufacturing process : Flowchart for the manufacture of potassium permanganate is shown in fig. (9). The raw materials required to produce one ton of potassium permanganate are :

• Manganese ore (MnO_2, 88 %)	: 850 kg
• Potassium hydroxide	: 500 kg
• Carbon dioxide	: 600 kg
• Air	
• Lime (quantity required depends upon the silica content in the ore)	

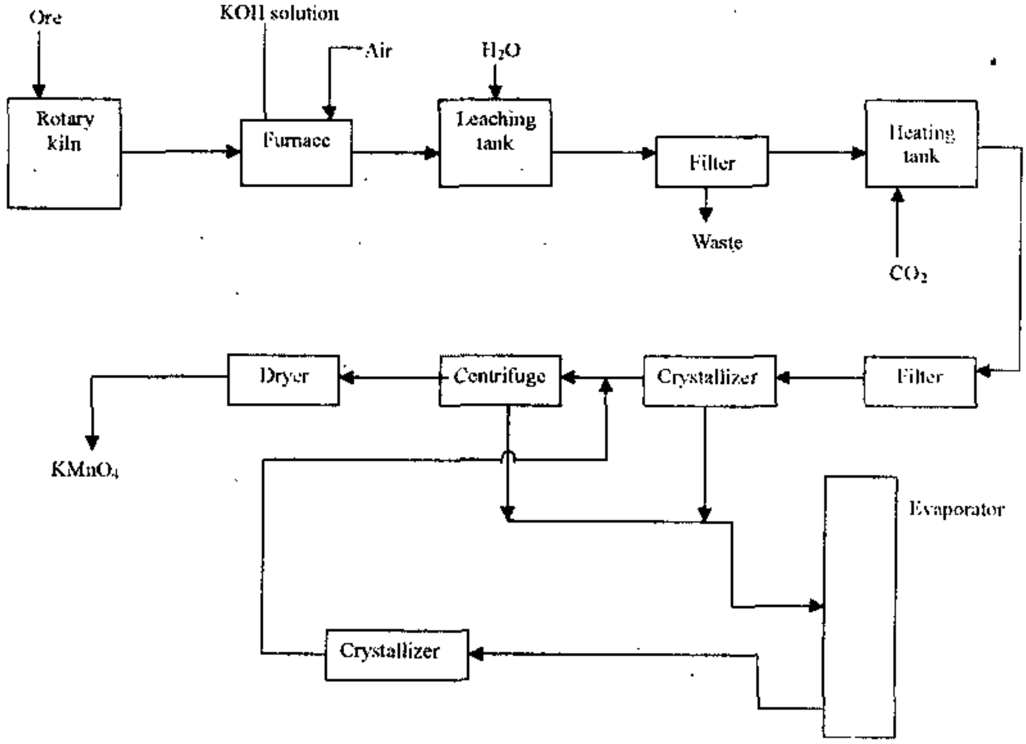


Fig. 9. Flowchart for the manufacture of potassium permanganate.

The manganese ore is calcined in a rotary kiln and then delivered to muffle furnace. In this furnace the calcined ore is reacted with caustic soda (50% solution) and air at 300°C to obtain potassium manganate (K_2MnO_4).

$$MnO_2 + 2KOH + \frac{1}{2} O_2 \longrightarrow K_2MnO_4 + H_2O$$

The product thus obtained is treated with water in leaching tank and filtered. The filtered manganate solution is heated in heating tank and treated with carbon dioxide gas, in order to convert it into permanganate solution.

$$3K_2MnO_4 + 2CO_2 \longrightarrow 2KMnO_4 + 2K_2CO_3 + MnO_2$$

The hot potassium permanganate solution is filtered to remove manganese dioxide (MnO_2). The filtered clear solution is delivered to crystalliser for cooling. The crystals of potassium permanganate thus obtained are collected by centrifugation, washed and dried. (The mother liquor alongwith centrifugal wash is concentrated by evaporation and then delivered to crystalliser for crystallization of potassium permanganate).

Uses of potassium permanganate : Potassium permanganate possesses a variety of applications. It is used :

(i) As an oxidising agent in organic synthesis
(ii) As an analytical reagent
(iii) As an antibacterial agent
(iv) For bleaching resins, waxes, cotton and silk
(v) For dyeing wool brown
(vi) For washing carbon dioxide in the manufacture of mineral water
(vii) For printing fabrics

[XIV] Potassium Bromide (KBr)

Potassium bromide is used in photographic emulsions and photoengraving. It is also used as a sedative and as an analytical reagent. Potassium bromide pallets are used in infrared spectroscopy.

It is prepared by reacting liquid bromine with scrap iron to from iron bromide (Fe_3Br_8), followed by treating the iron bromide with potassium carbonate (sometimes potassium hydroxide). The potassium bromide thus formed is filtered and recrystallied.

$$3Fe + 4Br_2 \longrightarrow Fe_3Br_8$$

$$Fe_3Br_8 + 4K_2CO_3 + 4H_2O \longrightarrow 8KBr + 2Fe(OH)_3 + Fe(OH)_2 + 4CO_2$$

[XV] Potassium Nitrate (KNO_3)

Potassium nitrate has a wide range of applications. It finds use :

(i) As a fertiliser.
(ii) In pyrotechnic mixtures.
(iii) As a heat transfer medium.
(iv) For heat treating steel.
(v) In feeds.

Potassium nitrate is prepared by double decomposition between sodium nitrate and potassium chloride

$$NaNO_3(aq) + KCl(s) \longrightarrow NaCl(s) + KNO_3(aq)$$

In a kettle, containing strong and hot solution of sodium nitrate, solid potassium chloride is added. The reaction mixture is heated when potassium chloride crystals get converted into sodium chloride crystals, and the hot potassium nitrate solution collects at the bottom of the kettle. A little quantity of water is added to prevent further decomposition of sodium chloride as the solution is cooled. Potassium nitrate is obtained in good yield.

Potassium nitrate along with chlorine is also prepared by reacting potassium chloride with nitric acid.

$$2KCl + 2HNO_3 + \tfrac{1}{2}O_2 \longrightarrow 2KNO_3 + Cl_2 + H_2O$$

The reaction is completed in three steps:

(i) $3KCl + 4HNO_3 \xrightarrow{100°C} 3KNO_3 + NOCl + Cl_2 + 2H_2O$

(ii) $NOCl + 2HNO_3 \longrightarrow 3NO_2 + \tfrac{1}{2}Cl_2 + H_2O$

(iii) $2NO_2 + H_2 + \tfrac{1}{2}O_2 \longrightarrow 2HNO_3$

Potassium nitrate is one of the constituents of black powder. Black powder is no longer a military propellant but is useful as an igniter for smokeless powder and in slow burning combustible fuels.

[XVI] Potassium Dichromate ($K_2Cr_2O_7$)

Potassium dichromate is used as an oxidizing agent as well as an analytical reagent. It is prepared by roasting caustic potash, quick lime and chrome-iron ore

$$4Fe(CrO_2)_2 + 8K_2CO_3 + 7O_2 \longrightarrow 8K_2Cr_2O_7 + 2Fe_2O_3 + 8\,CO_2$$

The quicklime is used to keep the melt porous so that air can enter and react quickly.

Potassium dichromate is also prepared by reacting sodium dichromate with potassium chloride.

4.2. INORGANIC NITROGEN CHEMICALS

[I]. Ammonium Nitrate (NH_4NO_3)

Ammonium nitrate is manufactured by reacting nitric acid with ammonia

$$NH_3\,(g) + NHO_3(aq) \longrightarrow NH_4NO_3(aq)$$

The reaction produces molten ammonium nitrate, containing 1 to 05% water, which can be formed into pills (small spheres) by dropping the reaction product through a tower or into flakes by cooling it on belts or drums. Dry granular material as the product may be obtained by fluidized treatment. Batch process is used. The flowchart of the process is shown in fig. (10).

Ammonium nitrate is nitrogeneous fertilizer because of high nitrogen content (33%). Military explosives contain ammonium nitrate as the major explosive ingredient. **Amatol** is a mixture of trinitro toluene (TNT) and granular ammonium nitrate (AN). This is the conventional military explosive. On explosive decomposition, ammonium nitrate decomposes rapidly to form elemental nitrogen

$$NH_4NO_3 \longrightarrow 2N_2 + 4H_2O + O_2$$

Ammonium nitrate decomposes at 200 to 260°C to form nitrous oxide.

$$NH_4NO_3 \xrightarrow{200-260°C} N_2O + 2H_2O$$

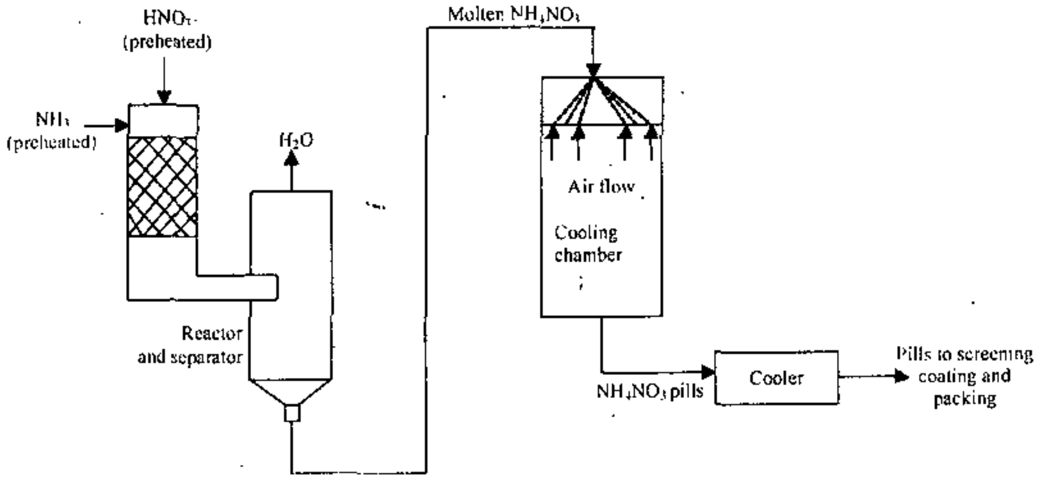


Fig. 10 : Flowchart for the manufacture of ammonium nitrate.

[II] Urea ($H_2N\ CONH_2$)

Urea is manufactured easily by reacting ammonia and carbon dioxide.

$$2NH_3 + CO_2 \longrightarrow \underset{\text{Ammonium carbamate}}{NH_2COONH_4^+} \longrightarrow \underset{\substack{\text{Urea}\\ \text{(Yield 80\%)}}}{NH_2CONH_2} + H_2O$$

Ammonia and carbon dioxide (2 : 1 mole ratio) are heated in the autoclave for two hours at 190°C and 1500-3000 psi. The mixture formed contains urea (35%), ammonium carbamate (8%), water (10%) and ammonia (47%). It is then cooled and ammonia is distilled at 60°. The residue from ammonia still is delivered to crystallizer at 15°C. More ammonia is removed under vacuum. The resulting slurry is centrifuged to obtain solid urea. All excess nitrogenous materials from the liquid are collected and processed further into liquid fertilizer.

Properties of urea : Urea is a white crystalline solid, melting point 132°C, soluble in water and ethanol but insoluble in ether.

(1) Urea reacts with alkaline sodium hypochlorite to give hydrazine.

$$NH_2CONH_2 + NaOCl + 2\,NaOH \longrightarrow N_2H_4 + NaCl + Na_2CO_3 + H_2O$$

(2) Urea behaves as a monoacidic base. When urea nitrate is added to cold concentrated H_2SO_4, nitrourea is formed

$$NH_2CONH_2.NHO_3 \xrightarrow{H_2SO_4} \underset{\text{Nitrourea}}{NH_2CONH\,.\,NO_2} + H_2O$$

(3) Urea undergoes hydrolysis on boiling with acids and alkalies

$$CO(NH_2)_2 + H_2O \longrightarrow CO_2 + 2NH_3$$

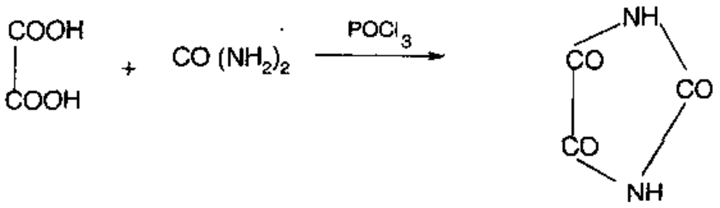
(4) On slow heating, urea loses ammonia to form biuret

$$2NH_2CONH_2 \longrightarrow NH_2CONHCONH_2 + NH_3$$

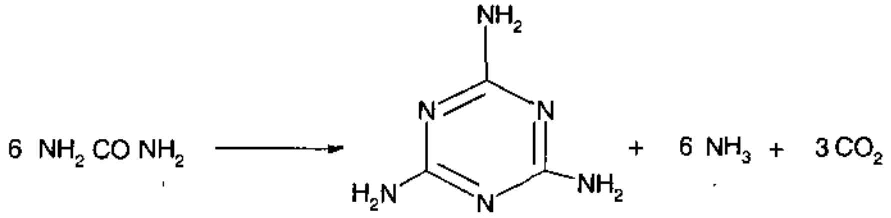
(5) Urea reacts with nitrous acid with liberation of nitrogen.

$$CO\,(NH_2)_2 + 2HNO_2 \longrightarrow CO_2 + 3H_2O + 2N_2$$

(6) Urea reacts with oxalic acid in the presence of $POCl_3$, as follows :



Melamine is synthesised by condensation of urea molecules



Melamine

Uses of urea : Urea has a variety of applications. The uses of urea are summarized as follows (percentage use is given in parentheses) :

(i) Solid fertilizers (54%)
(ii) Liquid fertilizers (32%)
(iii) Livestock feed (7%)
(iv) Urea-formaldehyde resin (5%)
(v) Melamine (1%)
(vi) Miscellaneous applications (1%)

[III] Ammonium Sulphate [$(NH_4)_2SO_4$]

Ammonium sulphate is important in the fertilizer industry. It is manufactured by reacting ammonia with sulphuric acid. Water is removed by evaporation and the product obtained is recrystallized to get white uniform crystals of ammonium sulphate

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2\ SO_4$$

Ammonium sulphate is also obtained as a by-product of caprolactam (for nylon–6) manufacture.

Ammonium sulphate (melting point 513°C, dec.) is used to the extent of 97%, in fertilizers. It is also used in water treatment, fermentation processes and leather tanning.

4.3. BROMINE AND FLUOROCARBON INDUSTRIES IN INDIA

1. DCW Ltd. Nirmal, 3rd floor, Nariman Point, Mumbai 400021 (Bromine Plant).
2. Sree Rayalaseema Petrochemicals Ltd. 1-1-290, First Floor, A Block, Ashoknagar, Hyderabad 500020 (Bromine Plant).
3. Hindustan Fluorocarbons Ltd., 1401 Bakukhan Est. Basheerbagh, Hyderabad 500001 (Fluorocarbon Plant).
4. SRF Ltd., Express building, 9-10 Bahadur Shah Zafar Marg, New Delhi 110002 (Fluorocarbon Plant).

4.4. INDUSTRIAL GASES

[I] Introduction to Industrial Gses

Nitrogen, oxygen and carbondioxide gases are included in the top fifty chemicals. Hydrogen gas is also one of the important gases and is used on a very large scale for the manufacture of ammonia (Haber-Bosch process). Fritz

Haber obtained Nobel Prize in 1918 for making ammonia from nitrogen and hydrogen in laboratory.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Carl Bosch was a chemical engineer. He also received Nobel Prize in 1931 for setting up a chemical plant for the manufacture of ammonia using Haber process.

Nitrogen and oxygen are produced by liquefaction of air. Carbondioxide and hydrogen gases are manufactured by the process of steam-reforming of hydrocarbons.

[II] Nitrogen

Nitrogen, oxygen and argan are made available on large scale from the process of liquefaction of air. Air contains nitrogen (78%), oxygen (21%) and argon (0.9%). About 90% recovery of these three major components from air is now feasible. Two major processes are used for this purpose. These two processes differ only in the way in which the expansion of air takes place.

- The Linde-Frankl cycle
- Claude process

The Linde-Frankl cycle is based on the classic Joule-Thomson effect of a gas, which states that there is a tremendous cooling effect of a gas when it is allowed to expand rapidly, even though no external work is performed on the system. Alternately, the Claude process employs an expansion engine performing useful work on the gas. The temperature decreases due to the removal of energy. This process is more effective than the Joule-Thompson effect.

Flowchart for the liquefaction of air is shown in fig. (11). Air is filtered (in order to remove particulates) and then compressed to 77 psi. In the oxidation chamber, the traces of hydrocarbons are converted into carbon dioxide and water. The air is then passed through the water separator, which gets some of the water out. The heat exchanger cools the sample to very low temperature. The solid water and carbon dioxide formed are separated from the main components.

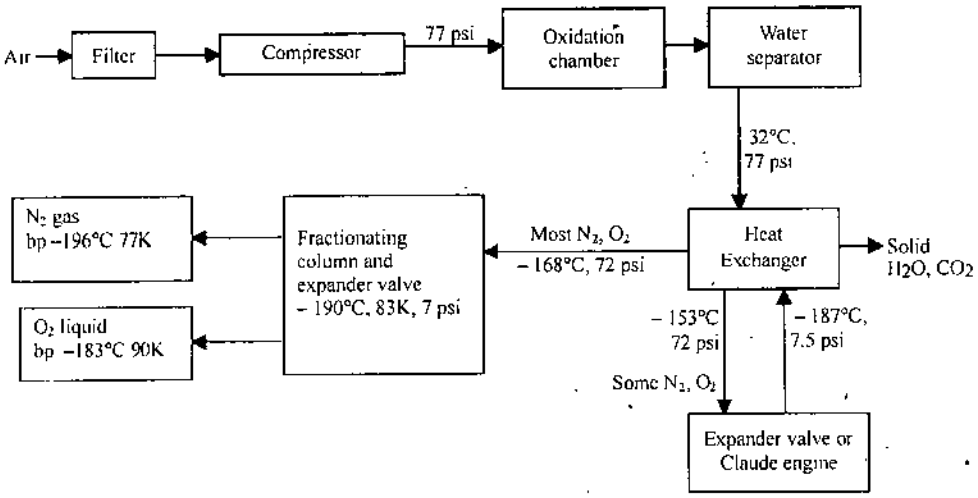


Fig. 11 : Flowchart for liquefaction of air

Nitrogen-oxygen mixture (at – 168°C and 72 psi) is delivered to the bottom of the fractionating column. Further cooling occurs because of an expansion valve at this point. Nitrogen is more volatile and it rises to the top of the column. Since, nitrogen (boiling point –196°C or 77K) has a lower boiling point as compared to oxygen (boiling point –183°C or 90K) and therefore the column (at – 190°C, 83K) is able to separate nitrogen and oxygen from each other. Oxygen is less volatile, therefore, it remains as a liquid at the bottom of the column.

A small quantity of nitrogen-oxygen mixture after being recooled in the heat exchanger is shunted to the main expander valve or Claude engine. The extremely cold gas is recycled into the heat exchanger in order to keep system cold. Some argon remains in the oxygen fraction. This mixture can be sold as 90-95% oxygen. When more pure oxygen is needed, then a more elaborate fractionating column with more number of plates is used to give an oxygen-argon separation. In this way, oxygen with high purity (99.5%) is obtained.

Argon is obtained from the midway fraction of nitrogen and oxygen and then redistilled. A small quantity of hydrogen may be added to react with any remaining oxygen to obtain argon free oxygen. Other rare gases (neon, krypton, and xenon) can also be obtained in separation. (Helium is not obtained from liquefaction of air. Helium exists in much higher concentration, 2%, in natural gas wells and it is isolated in petroleum refineries).

Nitrogen fixation : Chemical processes involving fixation of atmospheric nitrogen include,

(a) Haber-Bosch process for the manufacture of ammonia.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

(b) Cyanamide process

$$CaC_2 + N_2 \xrightarrow{1100^\circ C} CaNCN + C$$

$$CaNCN + 5H_2O \longrightarrow CaCO_3 + 2NH_4OH$$

Calcium cyanamide is used as a nitrogeneous fertilizer.

Uses of nitrogen : The uses of nitrogen are summarized in the following table 1;

Table 1: Uses of nitrogen

	% Use
Chemicals	33
Oil and gas extraction	14
Electronics	13
Primary metals	11
Petroleum refining	10
Food industries	5
Glass	2
Rubber and plastics	1
Miscellaneous	11

[III] Oxygen

Oxygen is produced by liquefaction of air, along with nitrogen, as described above. Oxygen gas is colourless, odourless and tasteless. It is slightly blue in liquid state. Highly pure oxygen (99.995% purity) is available commercially. It is stored in seamless steel cylinders under pressure (2000 *psi*).

Oxygen finds a wide range of applications. Its important uses are mentioned below (use percentage is given in parenthesis) :

(i) Primary metal protection (49%)
(ii) Chemicals and gasification (25%)
(iii) Clay, glass and concrete products (6%)
(iv) Petroleum refineries (6%)
(v) Welding and cutting (6%)
(vi) Health sciences (4%)
(vii) Paper and pulp (2%)
(viii) Water treatment (1%)
(ix) Miscellaneous (1%)

Steel industries prefer oxygen rather than air in processing iron. Oxygen reacts with carbon to form carbon monoxide. Carbon monoxide is processed with iron oxide in order to incorporate carbon into iron metal. The material thus obtained is called pig iron. **Pig iron** contains 4.3% carbon and it melts at 1130°C (pure iron has melting point 1539°C). The *reactions involved are* represented as follows :

$$2C + O_2 \longrightarrow 2CO$$

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

$$2CO \longrightarrow C\,(\text{in iron}) + CO_2$$

Oxygen also removes sulphur, phosphorus, *silicon* and other *impurities* from iron.

Gasification involves partial oxidation of hydrocarbons to produce *synthesis gas*. Chemicals like ethylene oxide, propylene oxide and titanium dioxide are manufactured using oxygen. In metal industries, **oxygen-acetylene flame** is used for welding and cutting purposes. The temperature of the flame is as high as 3300°C.

$$2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O + \text{Heat}$$

Oxy-hydrogen flame is also used for heating purposes.

$$2H_2 + O_2 \longrightarrow 2H_2O + \text{Heat}$$

In hospitals, oxygen is required for the patients suffering from respiratory diseases. Oxygen is also used in pulp and paper bleaching and for the *treatment of sewage*. Oxygen *is* used at the time of high altitude flying.

[IV] Hydrogen

Hydrogen is used on a very large scale for the manufacture of ammonia, hydrogen chloride and methanol. It is manufactured by steam-reforming of natural gas or hydrocarbons.

In steam-reforming process, low molecular weight hydrocarbons are used *as feedstock (for example methane and propane)*. The reaction takes place in two separate steps (reforming and shift conversion).

Methane : Reforming step $CH_4 + H_2O \longrightarrow CO + 3H_2$

Shift conversion step $CO + H_2O \longrightarrow CO_2 + H_2$

Propane : Reforming step $C_3H_8 + 3H_2O \longrightarrow 3CO + 7H_2$

Shift conversion step $3CO + 3H_2O \longrightarrow 3CO_2 + 3H_2$

The reforming step produces a mixture **hydrogen:carbon monoxide (synthesis gas)**. Synthesis gas is used in the manufacture of a variety of chemicals. The old method of producing synthesis gas was from coke, but this method gave low percentage of hydrogen in the mixture **(water gas)**.

$$C + H_2O \longrightarrow CO + H_2$$

Newer hydrocarbon feedstock are now used for getting higher hydrogen: carbon monoxide ratio in the mixture, as represented below :

Feedstock	**H_2 : CO ratio**
Coal	1 : 1
Oil	2 : 1
Gasoline	2.4 : 1
Methane	4 : 1

In the shift conversion step, more hydrogen is formed along with carbon dioxide. This step is one of the important methods for making carbon dioxide.

The flowchart for the steam-reforming process is shown in fig. (12). The hydrocarbon feedstock (contaminated with traces of organosulphur) is heated (370°C) and delivered to the desulphurizer. The desulphurizer contains metallic oxide catalyst, which converts organosulphur compounds into hydrogen sulphide. Elemental sulphur can be removed with activated carbon absorption. The hydrogen sulphide is removed by salt formation in the caustic soda scrubber.

$$H_2S + 2NaOH \longrightarrow Na_2S + 2H_2O$$

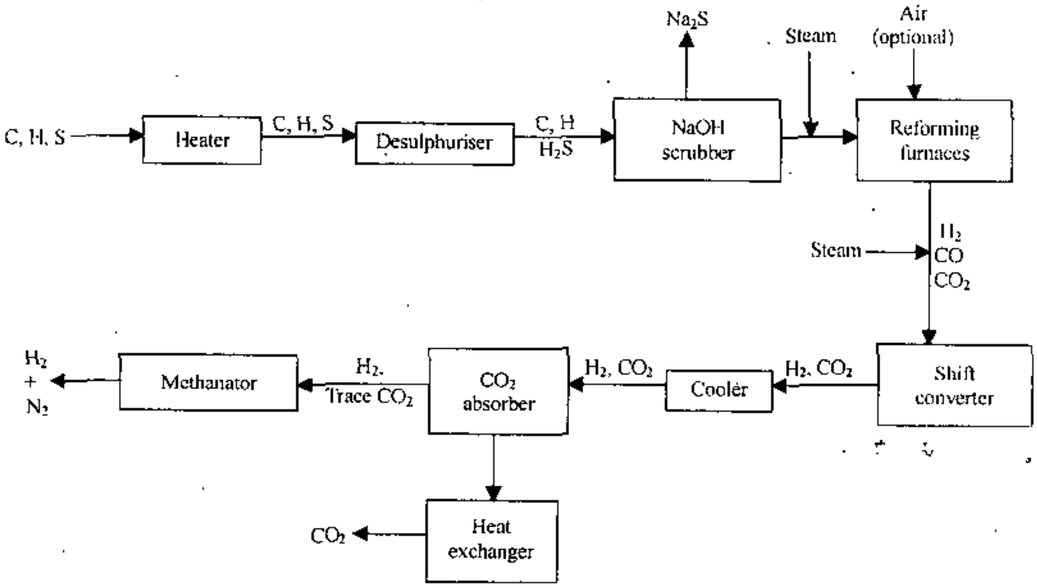


Fig. 12 : Flowchart for the steam-reforming process

Steam is added and the mixture is heated in the furnace at 760-980°C and 600 psi over a nickel catalyst. In some plants there are primary and secondary furnaces. Air can be added to the secondary reformers. Oxygen reacts with some of hydrocarbon feedstock to maintain high temperature. The nitrogen of the air is used when it (along with the hydrogen formed) reacts in the ammonia synthesizers. More steam is introduced and the mixture is delivered to shift converter, where iron or chromic oxide catalysts at 425°C further react the gas to hydrogen and carbon dioxide. Some shift converters possess high and low temperature sections. The high temperature section converts carbon monoxide to carbon dioxide relatively faster and the low temperature section completes the process and takes advantage of a more favourable equilibrium towards carbon dioxide at low temperature in the exothermic reaction. Cooling to 38°C is followed by carbon dioxide absorption with monoethanolamine. Carbon dioxide is desorbed by heating the monoethanolamine and reversing this reaction. Carbon dioxide is an important by-product. Alternately, hot carbonate solutions can replace the monoethanolamine.

$$HO-CH_2-CH_2-NH_2 + H_2O + CO_2 \rightleftharpoons HO-CH_2-CH_2-NH_3^+ + HCO_3^-$$

The methanator converts the last traces of carbon dioxide into methane.

Uses of hydrogen : The uses of hydrogen are summarized as follows (use percentage is given in parentheses)

Ammonia production (40%), methanol production (10%), other chemicals production (6%), in petroleum refining (4%), miscellaneous uses (40%).

The miscellaneous uses include hydrogenation of fats and oils, reduction of the metal oxides to obtain free metals, manufacture of pure hydrogen chloride, and use of liquid hydrogen as rocket fuel.

[V] Carbon Dioxide

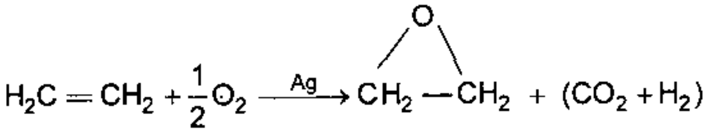
More than 90% of carbon dioxide is produced by steam reforming of hydrocarbons, and generally natural gas is the feedstock. Carbon dioxide is also obtained as an important by-product of hydrogen and ammonia manufacture.

$$CH_4 + 2H_2O \longrightarrow 4H_2 + CO_2 \uparrow$$

A small amount of carbon dioxide (1%) is also obtained as a by-product in the fermentation of molasses for manufacturing ethanol.

$$C_6H_{12}O_6 \xrightarrow{\text{Yeast}} 2C_2H_5OH + 2CO_2 \uparrow$$

A small quantity of carbon dioxide (1%) is obtained as a by-product during the manufacturing process of ethylene oxide from ethylene and oxygen.



Carbon dioxide is also obtained in small amounts from the following processes.

(i) Burning of coke : $C\text{ (coke)} + O_2 \longrightarrow CO_2$

(ii) Calcination of lime : $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

(iii) Manufacture of sodium phosphate from soda ash and phosphoric acid.

$$Na_2CO_3 + H_3PO_4 \longrightarrow Na_2HPO_4 + CO_2 + H_2O$$

Properties of Carbon Dioxide

(i) Carbon dioxide is a gas at room temperature..

(ii) It is solid at temperature below – 78°C. The solid carbon dioxide is referred as **dry ice.** At this temperature it sublimes and changes directly from solid to a vapor. Because of this unique property and its non-combustible nature, it is used as **refrigerant** and as **inert blanket.**

Uses of Carbon Dioxide

The principal uses of carbon dioxide are summarised as follows (percentage uses are given in parentheses) :

(i) Carbon dioxide (in liquid and solid state) uses

Food industry (51%)
Beverage carbonation (18%)
Oil and gas recovery (11%)
Manufacture of chemicals (10%)
Metal working (4%)
Miscellaneous (6)

(ii) Carbon dioxide (in gas state) uses

Oil and gas recovery (83 %)
Manufacture of chemicals (17%)

STUDENT ACTIVITY

1. Write two uses of copper sulphate ?

2. Name two fluorocarbon industries in India.

3. What happens when molasses is fermented ? Write reaction also.

4. What happens when a drop of water is added to anhydrous copper sulphate ?

SUMMARY

- Aluminium sulphate is used in the sizing of paper. For sizing of paper, the salt must be free from ferric ions, otherwise the paper will be discoloured.
- Fluorocarbons are compounds of carbon, fluorine and chlorine with little or no hydrogen. They are used as refrigerants, arosol propellants etc.
- Bromine is used in swimming pools. An amount of less than one ppm sterilises swimming pool without causing irritation to the eyes. Alkali bromide is also used in photography.
- Yellow sodium chromate (pigment) is manufactured from sodium dichromate.
- Sodium silicate is used in the production of soaps, detergents, pigments, adhesives etc. It is also used for metal cleaning and for the treatment of water and paper.
- Sodium thiosulphate is used as a fixer in photography. It is also used as an antichlor in the bleaching of paper pulp.
- Sodium nitrite is used in the diazotisation of amines in the making of azo dyes, as a preservative in meat processing, in photography and in medicines.
- Sodium sulphide is used in leather industry and in the manufacture of thiokol synthetic rubber.
- Sodium bisulphate is used as a food preservative, an antichlor in paper, pulp and textiles, in water treatment and pollution control, as a bleaching agent in textile industry.
- Sodium bisulphate is used in the manufacture of acid type toilet bowl cleaners and metal pickling. It is also used in dye bath, carbonising wool and in other chemical processes.
- Copper sulphate is used as an agricultural fungicide, as mordant in textile dyeing, petroleum refining, as a battery electrolyte, in metal colouring and metal making inks, in electroplating and leather tanning.
- Anhydrous copper sulphate is white. When a drop of water is added to it, the anhydrous salt becomes blue.
- Potassium permanganate is used as an antibacterial agent, for dyeing wool brown, for bleaching resins, waxes, cotton and silk, for printing fabrics, as an oxidising agent.
- Potassium bromide pellets are used in infrared spectroscopy.
- Potassium nitrate is used as a fertiliser for heat treatment of steel, in pyrotechnic mixtures.
- Potassium dichromate is used as an oxidising agent and as an analytical reagent.
- Ammonium nitrate, urea and ammonium sulphate are used as fertilisers.
- On slow heating, urea loses ammonia to form biuret.

$$NH_2CO\boxed{NH_2 + H}NHCONH_2 \xrightarrow[-NH_3]{\Delta} \underset{\text{Biuret}}{NH_2CONHCONH_2}$$

- Nitrogen gas is used in oil and gas extraction, food industries, rubber and plastic industries, petroleum refining.

- The uses of oxygen are in welding and cutting, health sciences, paper and pulp, water treatment, petroleum refinery, gasification.
- Hydrogen is used for the manufacture of ammonia, hydrogen chloride and methanol. It is also used as a fuel.
- Carbon dioxide is used in food industry, beverages carbonation, oil and gas recovery and manufacture of several chemicals.

TEST YOURSELF

Answer the following questions :

1. How will you manufacture the following compounds ? Describe any four uses also.
   (i) Alumina (ii) Fluorocarbons
   (iii) Sodium dichromate (iv) Copper sulphate
   (v) Sodium nitrite (vi) Bromine
   (vii) Potassium bromide (viii) Potassium nitrate.
   (ix) Potassium dichromate (x) Sodium silicate
   (xi) Sodium thiosulphate (xii) Sodium bisulphate
2. Describe the methods of preparation and properties of urea.
3. How are ammonium nitrate and ammonium sulphate manufactured ?
4. Describe the manufacture of oxygen and hydrogen.
5. What are the important uses of the following ?
   (i) Nitrogen (ii) Hydrogen
   (iii) Oxygen (iv) Carbon dioxide
6. Malachite is an ore of :
   (i) Lead (ii) Zinc
   (iii) Copper (iv) Silver
7. Azurite is :
   (i) Ore (ii) Mineral
   (iii) Flux (iv) Salt
8. Water gas is a mixture of :
   (i) CO, H_2 (ii) CO_2, N_2
   (iii) CO, N_2 (iv) N_2, H_2O
9. Urea reacts with nitrous acid to form :
   (i) CO, N_2 (ii) CO_2, NH_3
   (iii) CO, H_2 (iv) CO_2, N_2
10. Ammonia reacts with carbon dioxide to give :
    (i) Ammonium carbonate (ii) Ammonium sulphate
    (iii) Urea (iv) Carbon monoxide
11. **Fill in the blanks :**
    (a) Urea reacts with alkaline sodium hypochlorite to give ..... .
    (b) Urea reacts with .... to give bakelite.
    (c) Ammonium nitrate on heating at 260°C gives ..... .
    (d) Sodium thiosulphate is used as a .... in photography.
    (e) .... is used as a sedative.
    (f) For sterilising swimming pools, we generally use ....

(g) Fluorocarbons are compounds of fluorine, chlorine and .... with little or no hydrogen.

ANSWERS

6. (iii) **7.** (i) **8.** (i)

9. (iv) **10.** (iii)

11. (a) hydrazine (b) formaldehyde (c) nitrous oxide
(d) fixer (e) potassium bromide (f) bromine
(g) carbon

❑

UNIT 5

PIGMENTS, CEMENT AND LIME

STRUCTURE

- Introduction of Pigments
- Scenario of Dyes and Pigment Industries in India
- Introduction of Cement and Lime
- Cement
- Lime
- Cement and Lime Industries in India
- Student Activity
- Summary
- Test Yourself

LEARNING OBJECTIVES

After studying this chapter, you will learn about different types of pigments and their uses in industry. You will also learn about the manufacture of cement, different types of cement and their wide uses, as well as the manufacture of lime and its uses.

5.1. INTRODUCTION OF PIGMENTS

Pigments are coloured, *organic and inorganic insoluble substances*. They have a wide range of applications as follows :

(i) They are used in surface coating

(ii) They are used in inks, plastics, rubber, ceramics, paper and linoleus industries for imparting colour

(iii) They are consumed to a large extent because different products require a particular choice of material to give durability, colour, opacity and desired reflectance.

A pigment should possess properties such as *opacity and good covering power, wettability by oil, chemical inertness, non-toxicity or low toxicity and reasonable cost.* Pigments are available in the following different types :

(i) **White pigments**: Titanium dioxide, zinc oxide, lithopone, zinc sulphide, antimony oxide.

(ii) **Black pigments:** Carbon black, lampblack, graphite, iron black.

(iii) **Blue pigments:** Ultramarine, copper phthalocyanine, iron blues.

(iv) **Red pigments:** Red lead, iron oxides, cadmium red, toners and lakes.

(v) **Yellow pigments:** Litharge, ocher, lead and zinc chromate, hansa yellows, ferrite yellows and cadmium lithopone.

(vi) **Orange pigments:** Basic lead chromate, cadmium orange, molybdenum orange.

(vii) **Green pigments:** Chromium oxide, chrome green, hydrated chromium oxide, phthalocyanine green, permansa green (pthalocyanine blue plus zinc chromate).

(viii) **Brown pigments:** Burnt sienna, burnt umber, vanadyke brown.

(ix) **Metal protective pigments**: Red lead, blue lead, basic lead, and barium potassium chromates.

(x) **Metallics**: Aluminum, zinc dust, and bronze powder.

[I] White Pigments

White lead is one of the oldest and most important white pigments but it is no longer permitted as a constituent of paints. Zinc oxide is another example of white pigments but now it is also of minor importance. Titanium dioxide is the most widely used white pigment.

(1) Lithopone : It is a mixed zinc sulphide-barium sulphate pigment. It contains about 30 percent zinc sulphide. It is a brilliant white pigment and is used for interior coatings. Lithopone is manufactured as described below.

The barium sulphide solution is prepared by reducing barite ore ($BaSO_4$) with carbon and leaching the resulting mass

$$BaSO_4 + 4C \longrightarrow BaS + 4CO$$

Concentrated zinc ore or scrap zinc is dissolved in sulphuric acid, and then it is purified. The solutions of barium sulphide (BaS) and zinc sulphate ($ZnSO_4$) are then reacted to obtain heavy precipitate containing 28 to 30 per cent barium sulphide and 70 to 72 percent zinc sulphate.

$$ZnSO_4 + BaS \longrightarrow ZnS + BaSO_4$$

The precipitate is filtered, dried crushed, heated to high temperature and then quenched in cold water. It is again heated in a muffle furnace (at 725°C) to get crystals of the pigment. The raw materials required to produce one ton of lithopone are as follows :

(i) Barites	: 850 kg.
(ii) Zinc ore (60 % zinc)	: 400 kg.
(iii) Coal (half for steam)	: 1100 kg.
(iv) Sulphuric acid (50% Bè)	: 500 kg.

Lithopones are used in water based paints because they possess high alkali resistance. They are used as whitener for rubber and paper.

(2) Titanium dioxide (TiO_2) : Titanium dioxide is an important white pigment. It is available in two crystalline forms: **anatase** and **rutile**. Rutile is more stable. Anatase form can be converted into rutile form by heating to 700-950°C. Rutile form is almost used in paints. Titanium dioxide finds use in exterior paints, enamels and lacquers. The exterior white paint contains about 20% titanium dioxide, 60% talc and 20% mica. Such composition provides a longer life because a layer of loose pigment powder on the surface of the paint film acts as a self cleaner for the paint and also presents a good surface for subsequent repainting. About 50 percent of pigment is employed in paints, varnishes and lacquers, and in paper industry. It is also used in colouring of plastics.

Some of the important properties of the two crystalline forms (anatase and rutile) of TiO_2 are summarised in table 1.

Table 1: Properties of titanium dioxide

Property	TiO_2	
	Anatase	Rutile
Refractive index	2.55	2.70
Average particle size (μ m)	0.2	0.2 – 0.3
Density (g cm^{-3})	3.8 – 4.1	3.9 – 4.2
Oil absorption (gram of oil per 100 gram pigment)	18 – 30	16 – 48
Relative hiding powder	100	125 – 135
Hardness (Mohs scale)	5 – 6	6 – 7
Dielectric constant	48	114

(a) Manufacture of titanium dioxide : Titanium dioxide is manufactured by two methods, viz., chloride process and sulphate process.

(i) ***Chloride process*** *:* In this process, rutile (synthetic or natural) is treated with chlorine gas and coke to produce titanium tetrachloride ($TiCl_4$). $TiCl_4$ is distilled for the removal of impurities and then reacted with oxygen or air in a flame (at ~ 1500°C) to get fine particles of titanium dioxide and chlorine, which is recycled. The flowchart for the manufacturing process is shown in fig. (1).

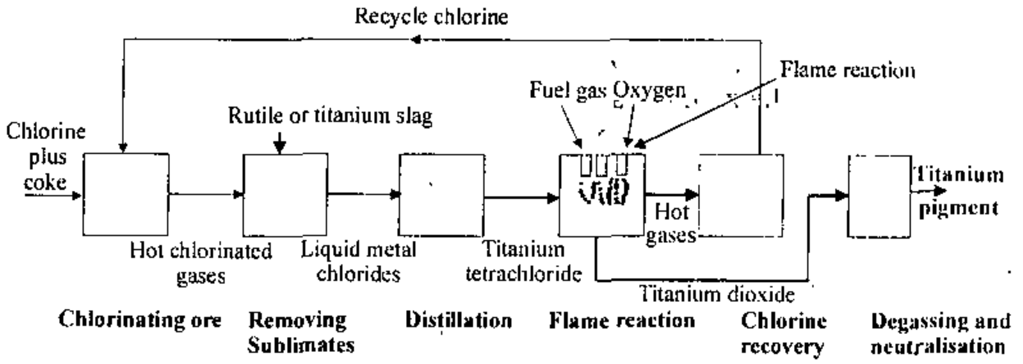


Fig. 1. Flowchart for the manufacture of TiO_2 by chloride process

(ii) ***Sulphate process*** : In this process, ilmenite ore is used as a raw material. There are two types of processes :

Batch process: The sulphate process has used batch ore digestion in which concentrated sulphuric acid is reacted with the ilmenite ore. The reaction involved in the process is very violent and it causes entrainment of SO_X and H_2SO_4 in large amount of water vapour, which is emitted in the atmosphere. In order to reduce the particulate emission, scrubbers are installed in most of the plants.

Continuous process: In this continuous process, dilute sulphuric acid (25 to 60 %) is used to temper the violent reaction and to reduce the amount of water vapour entrained particulates. In this process more dilute sulphuric acid is used as compared to batch process and therefore more of the spent acid can be recycled.

Flowchart, for both batch process and continuous process, is shown in fig. (2). The reactions involved are represented as follows:

$$\underset{\text{Ore}}{TiO_2} + H_2SO_4 \longrightarrow TiOSO_4 + FeSO_4 . H_2O$$

$$TiOSO_2 + H_2O \longrightarrow TiO_2 \times H_2O$$

$$TiO_2 . xH_2O \xrightarrow{800\text{–}1000°C} TiO_2$$

(3) Zinc oxide (ZnO) : Zinc oxide is mainly used as a paint pigment. It is produced by two different methods, *e.g.*, franch (or indirect) process and from zinc sulphide ore.

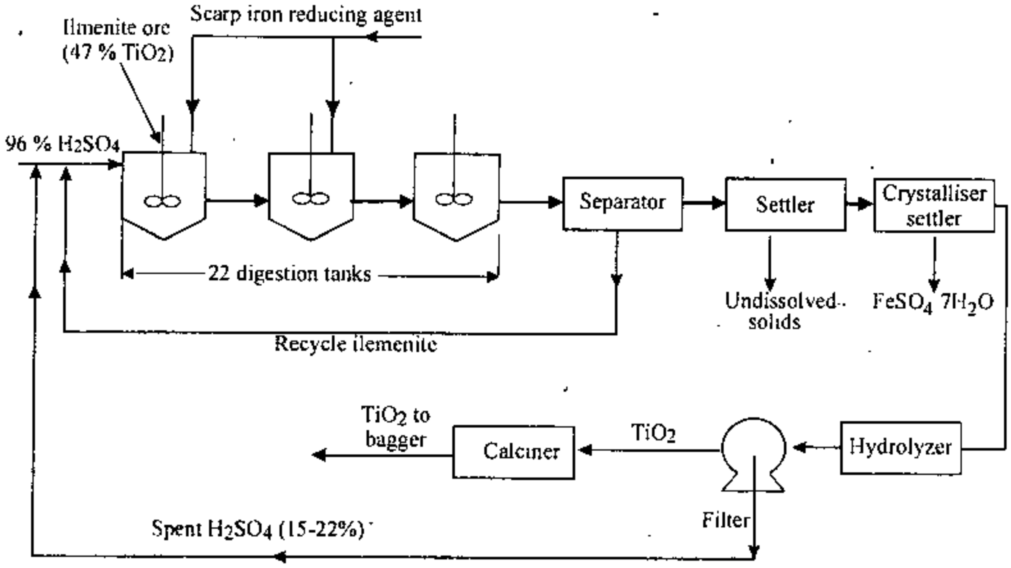


Fig. 2: Flowchart for the manufacture of TiO_2 by two types of sulphuric acid processes

(i) *French or indirect process* : In this process, zinc oxide is produced from zinc metal. The zinc metal is first vapourized and then zinc vapours are oxidized to obtain finely divided zinc oxide.

$$Zn + \frac{1}{2} O_2 \longrightarrow ZnO$$

Spelter (metallic Zinc) is charged to a retort. It is melted and vapourized by indirect heating and current of carbon monoxide gas. The preheated air is passed to the furnace for the oxidation of zinc vapours to zinc oxide and carbon monoxide to carbon dioxide. If any lead is present in the furnace, it gets converted into lead carbonate.

The vapours from the furnace are delivered to settling chamber where coarser particles settle down. The desired fine particles of zinc oxide are collected in a bag house and then packed. The coarse particles from settling chamber are fed to the reheating furnace and revolatized.

The raw materials required to produce one ton of zinc oxide are as follows :

Spelter (metallic zinc) : 850 kg, Coal (anthracite) : 660 kg

The flowchart of the process is shown in the fig. (3).

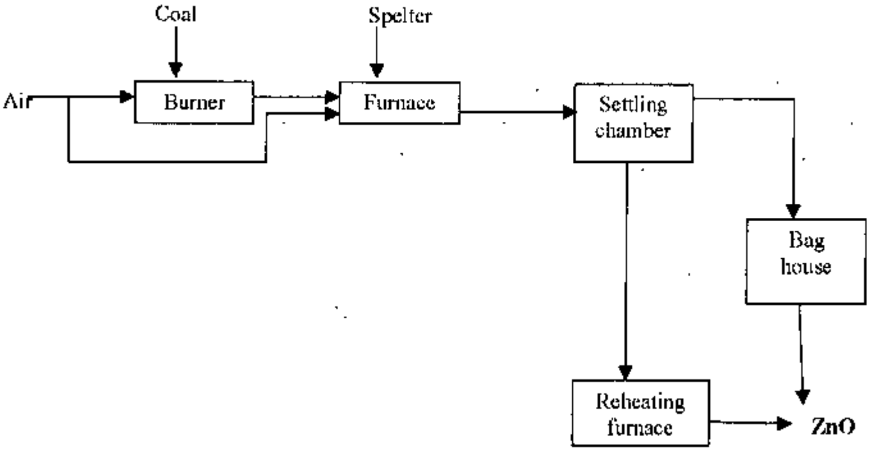


Fig. 3 Flowchart for the manufacture of zinc oxide

(ii) ***From zinc sulphide ore :*** The zinc sulphide concentrate is roasted in a roaster. The sulphur dioxide evolved during roasting is used for the manufacture of sulphuric acid. The roasted product is then mixed with coke and fluxes in a mixer. The mixture is then delivered to sintering machine and heated to 1600°C. The sintered product is crushed followed by screening. The product is then preheated and delivered to electric furnace. It is heated to 1200°C when zinc vapourizes from the mass. The zinc vapours and carbon monoxide are oxidized by adding air to obtain zinc oxide and carbon dioxide. The Zinc oxide is then collected and sent to bagging and packing section. Flowchart of the process is depicted in figure 4. The reactions involved in the process are as follows :

$$ZnS + \frac{1}{2}O_2 \longrightarrow ZnO + SO_2$$

$$ZnS + CO \longrightarrow Zn + CO_2$$

$$Zn + \frac{1}{2}O_2 \longrightarrow ZnO$$

The raw materials required to produce one ton of zinc oxide are as follows :

Zinc sulphide (100%) : 1000 kg; Coke : 840 kg ; Fluxes : variable

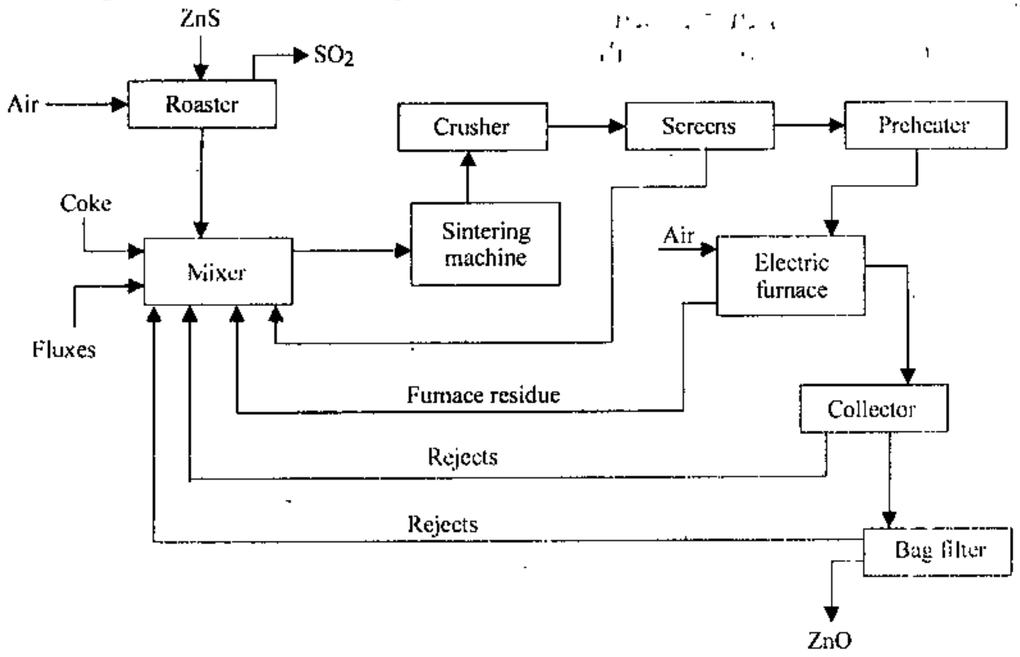


Fig. 4: Flowchart for the manufacture of ZnO from zinc sulphide

Zinc oxide is used as a pigment in white paint. It is also used in the manufacture of opaque glass, enamel, white glue, matches and white printing ink. It is also useful as a reagent in analytical chemistry.

Properties of zinc oxide : Zinc oxide is a white or yellowish powder. It is odourless. It is almost insoluble in water, dilute acetic acid, dilute mineral acids and ammonia. Some of the important physical properties are as follows:

(i) Melting point : Above 1800°C (sublimes)
(ii) Density : 5.6 g cm^{-3}
(iii) Refractive index : 2.08
(iv) Oil absorption : 10-25 (g of oil/g of pigment)

(v) Average particle size (μm) : 2.08

(vi) Hardness (Moh's scale) : 4 plus

[II] Black Pigments

Ans 7 (a)

Black pigments include carbon black, lampblack, graphite and iron black. Carbon black is the major black pigment.

Lampblack *has larger particle size* and is useful for tinging to produce shades of gray. It is prepared by restricted combustion of resins, petroleum or coal-tar by-products. In the United States, tar oils or petroleum oils are burnt with a restricted amount of air to produce soot or lampblack. The soot is *collected in large chambers from which the raw lampblack is removed*, mixed with tar, molded into bricks (or pugs) and then subjected to calcination at 1000°C in order to destroy bulkiness. The calcined mass is ground to obtain fine powder. Lampblack has been replaced in the pigment trade by carbon black because it possesses *superior tinting strength and coloring quantities* over lampblack. Lampblack is still an important constituent in the manufacture of carbon brushes for electrical equipments.

Carbon black is a finely divided, non-porous type of carbonaceous material which is produced in a controlled pyrolytic petrochemical process. Carbon black is widely consumed in rubber products especially tyres. The rubber compounds in modern tyres contain about 35 percent carbon black and this indicates that the rubber industries are the leading consumers of carbon black. It is also employed as a pigment in black plastics, paints, lacquers, and enamels. It also finds use in making type writter ribbons and carbon paper. Carbon black is manufactured by the furnace, channel and thermal process.

(1) Furnace process (From oil or natural gas) : Flowchart for the manufacture of carbon black is shown in fig. (5). Raw materials required to produce one ton of carbon black are mentioned below :

Natural gas : *8000 to 10,000 cu* m^3

Or Oil : 3000 litre; Air : 40,000 – 50,000 cu m^3

Natural gas or vaporised oil, after passing through gasoline absorbers, is delivered along with a regulated amount of air to the horizontal or vertical furnace. In the furnace, it is partially burnt in multiple free flames to get carbon black and gaseous products. The gaseous stream is passed through an aircooled flume into a spray cooler. The carbon black is then separated from the combustion gases by an electrostatic precipitator and a battery of cyclone collectors. The spent gases free from carbon black are expelled into air.

The fluffy carbon black is then transported by a screw conveyer to a blower and further transported to the pelleting equipment. Here the carbon *black is pelleted dry* by rotating drums. The reactions involved in the process are represented as follows:

For natural gas :

$$CH_4 \longrightarrow \underset{\text{Amorphous}}{C} + 2H_2$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

For oil :

$$(\overset{|}{\underset{|}{C}}H_2) \longrightarrow \underset{\text{Amorphous}}{C} + H_2$$

$$(\overset{|}{\underset{|}{C}}H_2) + 1.5\,O_2 \longrightarrow CO_2 + H_2O$$

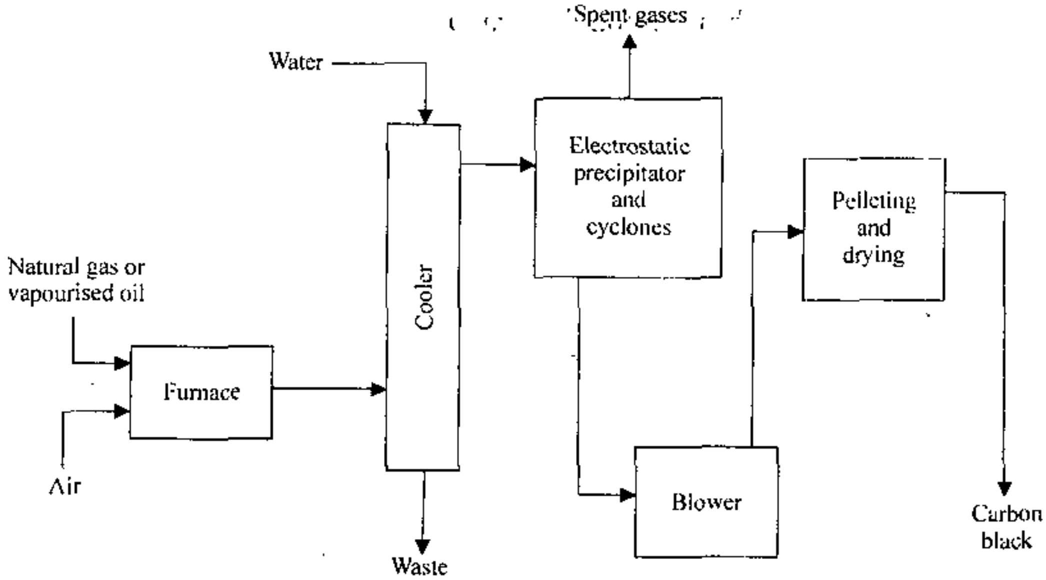


Fig. 5 : Flowchart for the manufacture of carbon black (furnace process)

(2) Channel process (from natural gas) : Carbon black is produced when underventilated natural gas flames impinge upon 20 to 25 cm **channel irons**, which are slowly reciprocated over scrapers to remove soot deposits. The type of carbon black produced is controlled by burner-tip design; burner-to-channel distance and air supply *i.e.* degree of partial combustion. The yield of carbon black thus produced is very low and they vary 5 percent (rubber grade) to only 1 percent (for high colour ink grade). This process is not of importance because it requires high steel and high capital investment, and also it causes severe pollution problems.

(3) Thermal process : In this process, natural gas is cracked to carbon black and hydrogen at high temperature (1100 to 1650°C) in a refractory lined furnace in a two-cycle (heating and making or decomposition) operation. The reaction involved in the process is as follows :

$$CH_4 \longrightarrow C_{(\text{amorphous})} + 2H_2$$

The thermal black is mainly used in special rubber applications. The yield obtained is about 30 to 45 percent.

Properties of carbon black : Carbon black is fluffy, black and amorphous powder. It is insoluble in water (cold and hot), acids and alkalies. Some of the important properties are given below :

(i) Melting point : Above 3500°C
(ii) Boiling point : 4200°C
(iii) Specific gravity : 1.8 – 2.1

The carbon blacks are very opaque and possess high durability and resistance to all types of chemicals. They should not be used in direct contact with iron and steel in primer coating because they stimulate metal corrosion.

[III] Blue Pigments

Ultramarines, copper phthalocyanine, iron blues etc are included in blue pigments.

(1) Ultramarine blue : It is a complex sodium aluminum silicate and sulphide made synthetically. It should not be used on iron or mixed with lead pigments because it has a sulphide composition. Ultramarine blue is used as bluing material in laundering in order to neutralize the yellowish tone in cotton and linen fabrics. It is also used for whitening paper and other products. Special grades (low in free sulphur) of ultramarine blue are useful in inks.

(2) Phthalocyanine blues : Phthalocyanine blues are used for nitrocellulose lacquers in low concentration as a pigment highly resistant to alkalies, acids and colour change. These are most stable pigments and possess high resistance to crystallization in organic solvents. They also possess high tinting power and therefore find use in latex paints and in printing inks as well as all types of interior and exterior coatings. They are synthesized by reacting phthalic anhydride with copper salt with or without ammonia.

(3) Ferrocyanide blues : These blues are known as prussian blue, chineses blue, milori blue, bronz blue, antwerp blue and turnbull blue. In general, these are termed as **iron blues**.

These pigments are synthesised by the precipitation of ferrous sulphate solution (preferably in the presence of ammonium sulphate) with sodium ferrocyanide to give a white ferrous ferrocyanide. It is then oxidized to ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$ or to $Fe(NH_4)[Fe(CN)_6]$, by different reagents such as potassium chorate, bleaching powder and potassium dichromate. The pigment thus formed is washed and allowed to settle.

The iron blues have high tinting strength and good colour performance. They are used in latex paints, printing inks and in tip coating for foils and bright metal objects. They have poor alkali resistance and therefore are not used in water-based paints.

[IV] Red Pigments

Ans 7 (b)

Red lead and ferric oxide are the important red pigments.

(1) Red lead (Pb_3O_4) : Red lead is brilliant red-orange in colour and possesses resistance to light. Because of the corrosion inhibiting properties, it is used as a primer for structural steels. It is manufactured by two processes viz. **regular process** and **fumed process.** In regular process, lead is oxidized to litharge (PbO) in air, which is further oxidized to red lead (Pb_3O_4).

$$Pb \xrightarrow{\text{Oxidation}} \underset{\text{Litharge}}{PbO} \xrightarrow{\text{Oxidation}} \underset{\text{Red lead}}{Pb_3O_4}$$

In the fume process, molten lead is atomized by compressed air and then forced through the centre of a gas flame. Lead gets converted into litharge (PbO) as a fume, which is collected in filter bags. The litharge is then oxidized to red lead by roasting in air.

(2) Ferric oxide (Fe_2O_3) : Ferric oxide is widely used in paints and primers, and in rubber formulation. A wide range of natural red oxide pigments is available and on account of the durability they are useful in barns and freight car paints. Synthetic pigment is prepared by heating iron sulphate.

Ventian red is a mixture of ferric oxide and calcium sulphate. It is manufactured by heating ferrous sulphate and quicklime in a furnace. Ventian red is an inert pigment. Due to the presence of corrosion stimulating sulphate ions (furnished by calcium sulphate content), this pigment is not used on iron.

Indian red is naturally occurring mineral and contains ferric oxide (80 to 95%), clay and silica.

Magnetic iron oxides are of great use in the production of magnetic tapes (for computers, and audio and video recorders) and as pigment. Forty eight percent production of magnetic iron oxide is utilized by pigment and colorant market, and eleven percent production utilized in magnetic and electronic applications.

(3) Other reds : Some examples are basic lead carbonate, cadmium red, tuscan red.

(i) *Basic lead carbonate* $[PbCrO_4 . Pb(OH)_2]$: It is used as an orange red pigment and also acts as corrosion inhibitor. It is manufactured by boiling white lead with a solution of sodium dichromate.

(ii) *Cadmium reds* : These are prepared by roasting the precipitate obtained by the mixing of cadmium sulphate, sodium sulphite and sodium selenide. Cadmium colours range from light yellow to maroon.

(iii) *Tuscan red* : Tuscan red is a name applied to combinations of red iron oxide pigment and a light-fast organic red pigment. It is used when bright colours are required for exterior paints.

Ans 7(b)

[V] Yellow Pigments

Ocher, chrome yellow and zinc yellow etc belong to this category.

(1) Ocher : Ocher is a naturally occurring pigment. It consists of clay coloured with ferric hydroxide (10 to 30%). Ochers are weak tinting colours and they are replaced by synthetic hydrated yellow iron oxides in order to have brighter colour and better uniformity.

(2) Chrome yellow : Chrome yellows include yellow pigments having a wide variety of shades. On account of high opacity, brilliance and light fastness these pigments have become very popular. They are prepared by mixing a solution of lead nitrate or lead acetate with a solution of sodium dichromate.

$$2Pb(NO_3)_2 + Na_2Cr_2O_7 + H_2O \longrightarrow 2PbCrO_4 + 2NaNO_3 + 2HNO_3$$

The precipitation is performed in wooden tanks provided with agitation system. The precipitate of lead chromate is washed in order to remove impurities, filter pressed and dried at ~90°C. The product thus obtained is pulverized and packed.

These pigments are used to a limited extent because of their toxicity.

(3) Zinc yellow : Zinc yellow has a poor tinting power. It is used in mixed paint and as a primer for steel and aluminum because of its corrosion inhibiting property. Its composition is $4ZnO. K_2O. 4CrO_3. 3H_2O$.

The yellow chromate pigments (strontium chromate and barium chromate) are also used as corrosion inhibitors.

[VI] Green Pigments

Phthalocyanine green, chromium oxide green, Guignet's green and chrome green are some examples of green pigments.

(1) Phthalocyanine green : It is one of the major green pigments. It is a complex copper compound. It possesses high opacity, light fastness and *chemical resistance*. It is used in solvent based and water based paints.

(2) Chromium oxide green (Cr_2O_3) : It is one of the oldest green pigments. It is prepared by calcination of sodium dichromate or potassium dichromate with sulphur in a reverberatory furnace.

$$Na_2Cr_2O_7 + S \longrightarrow Cr_2O_3 + Na_2SO_4$$

This pigment is very costly and possesses lack of brilliance and opacity.

(3) Guignet's green (Emerald green) : *It is a hydrated chromic oxide* $Cr_2O(OH)_4$. It has a brilliant green colour and possesses good permanence. It is prepared by roasting a mixture of sodium dichromate and boric acid for several hours at a dull red heat. The fused mass obtained is then hydrolyzed to obtain the product. The boric acid recovered is again used for the reaction.

$$Na_2Cr_2O_7 + 16H_3BO_3 \longrightarrow Cr_2(B_4O_7)_3 + Na_3B_4O_7 + 24H_2O + 3\,(O)$$

$$Cr_2(B_4O_7)_3 + 20H_2O \longrightarrow Cr_2O(OH)_4 + 12H_3BO_3$$

(4) Chrome green : This pigment is a mixture or co-precipitation of chrome yellow and Prussian blue. For marking paints, inert fillers are used with this pigment. It has poor alkali resistance and has gone out of use because of lead content. It is not used in latex paints also.

[VII] Brown Pigments

The various naturally occurring iron containing clays on carefully controlled heating give brown pigments known as burnt sienna, burnt umber and burnt ocher. Iron hydroxides are converted to oxides. *The umbers consist* of brown manganic oxide and iron oxides. These are all permanent pigments, which are suitable for wood and iron.

Vandyke brown is a native earth pigment, which contains oxide of iron and organic matter.

[VIII] Toners and Lakes

Toners are insoluble organic dyes. Because of their durability and colouring power they are directly used as pigments. Para red, Hansa yellow G (lemon yellow), Hansa yellow 10 G (Primrose yellow), toluidine toner etc are various dyes, which are used as toners in pigment industries.

Para red: It is formed by diazotizing *p*-nitroaniline and then coupling it with β-naphthol.

Hansa yellow G (lemon yellow) : It is manufactured by diazotizing *m-nitro-p-toluidine and then coupling it with acetoacetanilide.*

Hansa yellow 10 G (Primrose yellow) : It is prepared by coupling orthochloroacetanilide with diazotized 4-chloro-2-nitroaniline.

Toluidine toner : It is a red pigment and is obtained by coupling the diazotized *m*-nitro-*p*-toluidine with β-naphthol.

Lakes are the dyed inorganic pigments. The inorganic part or base contains an extender such as clay, barite, or blanc fixe and aluminum hydroxide. The organic dye may be precipitated onto an already existing base (for example: clay or barite suspended in solution) or both the dye and the base may be coprecipitated *e.g.* onto blanc fixe or aluminum hydroxide. The toners and lakes are ground in oil or applied like any other pigment.

[IX] Metallic Powders as Pigments

Metal powders and alloys are used as pigments. Fine powders of aluminum and bronze are used as pigments in lacquers. Powdered zinc (zinc dust) is used in primers and in paints for galvanized iron. Lead powders and pastes are used in primers.

5.2. SCENARIO OF DYES AND PIGMENT INDUSTRIES IN INDIA

1. Aakash Pigments Ltd., Unit 216,Mahavir Industrial Estate, Mumbai-32, Maharashtra.
2. Asiatic Colour Chem Ind. Ltd., Plot No. 1503/1504, Gidc, Phase 1, Narod, Ahmedabad, Gujarat.
3. Advaitya Dye Chem., 7, Swagat Complex, 2nd Floor, Pushpkunj, Kankaria Ahmedabad, Gujarat.
4. Aline Industries, Box. No- 71/A, Karimabad Soc., Near Ram Chawk, Ghod Dod Road, Surat, Gujarat.
5. Bhatia Colour Co./ Polychem, U-3227, Surat Textile Market, Ring Road, Surat.
6. Benzo Chem Industries Pvt. Ltd., Madhu Kunj, S.g. Marg, Prabhadevi, Mumbai, Maharashtra.
7. Best India Printers, Ramsingpura, Shikarpura Road, Gullar Ka Bandhe Se Aage, Opp. Kohinoor Print, Sanganer, Jaipur, Rajasthan.
8. Clariant Chemicals India Ltd., Ravindra Annexe, 194, Church Gate Reclamation, Mumbai Maharashtra.
9. Chemie Range, 1, Railway Station Road, Samaipur, New Delhi.
10. Color Chem. Ltd., Ravindra Annexe, 194, Churchgate Reclamation, Mumabi-400020.
11. Disha Dye Chem Private Limited, D-65, Jhandewalan Flatted Factory Complex, New Delhi.
12. Excel Industries Ltd., 184-87, S.Y. Road, Jogeshwari (W), Mumbai-400102.
13. Eastern Chemicals, H. No. 48-12-7/28, Manasa Apts., Srinagar, Visakhapatnam-530016, Andhra Pradesh.
14. Hariram Industries, Plot 318/4, 40 Shed Area, Nr.v-trans Ltd, G.I.D.C, Vapi, Gujarat.
15. Hollindia International BV, B1, Brahmakumari CHS, LJ road, Mahim, Mumbai, Maharashtra
16. Hindustan Rang Rasayan Udyog, Plot No. 36-37, Hsidc, Kundli, Sonepat, Haryana.
17. Hind Dyes & Chemicals, Dada Manzil, 67/69, 2nd Floor, Mohamedali Road, Mumbai, Maharashtra.
18. Insilco Ltd., Plot No. A-21/2 & 3, P.O. PATALGANGA, Maharashtra.
19. Kerela Minerals and Metals Ltd., Chavara, Dist. Quilon-691583, Kerala.
20. Krima Sil Pvt. Ltd., 3613, GIDC Estate, Ankleshwar, Gujarat.
21. Mallak Pigments Ltd., Unit 216, Mahavir Industrial Estate, Mumbai-32, Maharashtra.
22. Mayur Dye Chem, Plot No. 4705/2/2, New Telephone Exec. Road, G.I.D.C., Ankleshwar-393002, Gujarat.
23. Nirvip Dyes & Chemicals Pvt. Ltd., 23L, Laxmi Industrial Estate, New Link Road, Andheri (West), Mumbai, Maharashtra.
24. Nylo Speciality Colours, A-702, Rustomjee Residency J. S. Road. Dahisar West, Mumbai - 400068, Maharashtra.
25. Parshwanath Dyes, 6,Gurusadan Bldg, 76/78 Issaji Street 2nd floor, Masjid Bunder, Mumbai, Maharashtra.
26. Raja Imports & Exports Pvt. Ltd., RAJA DYE CHEM, 2285/52, 3rd floor, Hinga Beg Street, Tilak Bazar, New Delhi.
27. Ronak Orgo Chemi, 321, Super Diamond Market, Varachha Road, Surat, Gujarat.
28. Sapphire Chemicals, C-41, Jivabhai Park-i, Near Narmada Nagari, Opp. Iti, Gorwa, Gujarat.

29. S. M. Dye chem Ltd., S.M. Centre, Maro-naka, Andheri (E), Mumbai-400059.
30. Shramik Chemicals, 6904.Gidc Estate, Ankleshwar, Gujarat.
31. Shrihari Dyes Works; Plot No. 439/1. GIDC Estate, Phase-II, Vatva, Ahmedabad, Gujarat.
32. Shree Orabhadevi Dyes & Chemical Co. Pvt., 4, Nahavir Chambers, 333/337, Samuel Str, Mumbai, Maharashtra.
33. Synthetic Dyes & Chemicals, W-86, Midc, Phase II, Dombiville (e), Thane, Maharashtra.
34. *Shril International, 23, Suryoday, Stdium Road, Ahmedabad, Gujarat.*
35. Sun Bright Industries, 174/3, Gidc Estate, Phase 1, Naroda, Gujarat.
36. Tech (India) Limited, 7B, Bata compound, Near Flower Valley, Khopoli, Maharashtra.
37. Ultra Marines Blues Pvt. Ltd., 306, Sagar Plaza-II, Commercial Complex, Rani Bagh, New Delhi.
38. Ultramarine & Pigments Ltd., Mittal Tower, Nariman Point, Mumbai-400021.
39. Vindya Dye Chem., 5, Pokar Palace, Pokar Colony, Dindori Road. Nashik 422004, Maharashtra.

5.3. INTRODUCTION OF CEMENT AND LIME

The introduction of natural cement and lime mortars has created huge interest among the chemists and chemical engineers for industrial applications of cement and limestone. The construction of dams, tunnels, roads, water tanks and multistoreyed buildings has shown the importance of these products in the progress of mankind all over the world. The strength, cheapness, adaptability and durability of cement and lime have provided a strong foundation for these applications. Particularly, the construction of dams has made revolution in the growth of agricultural products and setting up of hydro-electric projects for the generation of electricity.

5.4. CEMENT

Cement is a powdered substance which, when mixed with water or liquid, has plastic flow and forms a hard solid structure in several hours with varying degree of strength and bonding properties. The construction of modern cement roads, multistoreyed buildings and dams etc has shown tremendous increase in the production of cement.

[I] Portland Cement

Egyptians used cement for the construction of pyramids. The Greeks and Romans utilized volcanic tuff mixed with lime for cement, which was used for construction of huge structures. Joseph Aspdin (an Englishman), in 1824, introduced a patent of an artificial cement prepared by calcination of an argillaceous limestone. He named it as Portland cement because the concrete made from it resembled a very famous building stone obtained from the Isle of Portland near England.

Portland cement is defined as a *finely ground mixture of calcium aluminate and silicates of different composition which hydrate on mixing with water to form a solid rigid structure having good compressive strength.* Concrete was relatively less used for construction before 1900 because the manufacture of Portland cement was very expensive. But now the situation is totally changed. Cement is now low in cost and is used everywhere for the construction of houses, multistoreyed buildings, roads, industries, dams, bridges and many other structures. The constituents of Portland cement are given in table 2.

Table 2 : Constituents of Portland cement

Chemical formula	Name	Abbreviation
$2CaO.\ SiO_2$	Dicalcium silicate	C_2S
$3CaO.\ SiO_2$	Tricalcium silicate	C_3S
$3CaO.\ Al_2O_3$	Tricalcium aluminate	C_3A
$4CaO.\ Al_2O_3.Fe_2O_3$	Tetracalcium alumino ferrite	C_4AF
MgO	Magnesium oxide	M
CaO	Calcium oxide	—

India, China, Japan and United States are the largest producers of cement in the world. In 1980 there were 142 Portland cement producing industries in the United States. India is the next largest manufacturer of cement in the world. Cement industries in India are located in Madhya Pradesh, Tamil Nadu, Andhra Pradesh, Rajasthan, Gujarat, Bihar, Maharashtra and Karnataka.

[II] Types of Portland Cement

On account of rate of setting, heat evolution and strength characteristics, Portland Cement has five different types as follows

(1) Type I (Regular portland cement) : Type I cements are used for general constructions. This type of cement includes other cements like **white cement** (possesses less ferric oxide), **oil-well-cement** and **quick-setting cements** etc

(2) Type II (Moderate-heat-of-hardening and sulphate resisting portland cement) : Type II cements are used where moderate heat of hydration is essential or for general concrete construction is exposed to moderate sulphate action. The heat evolved from this type of cements should not exceed 295 J/g (after seven days) and 235 J/g (after 28 days).

(3) Type III (High-early-strength portland cement). (HES portland cement) : Type III cements are prepared from raw materials having a lime-to-silica ratio greater than that for Type I cements. This type of cements is ground finer than Type I cements and the proportion of $\mathbf{C_3S}$ in these cements is hegher than that for regular Portland cements. This, therefore, causes quicker hardening of Type III cements and a faster evolution of heat. The roads constructed using Type III cements are brought into utilization sooner than the roads constructed using regular cements.

(4) Type IV (Low-heat portland cement) : Type IV cements contain lower percentage of C_3S (tricalcium silicate) and C_3A (tricalcium aluminate), thus lowering of heat evolution occurs. The percentage of C_4AF (Tetracalcium alumino ferrite) is increased by addition of Fe_2O_3 to reduce the amount of C_3A. The heat evolved should not be more than 250 J/g (after seven days) and 295 J/g (after twenty-eight days). The heat of evolution is 15 – 35 % less than the heat of hydration of regular or HES cements.

(5) Type V (Sulphate resisting portland cement) : Type V cement possesses better resistance to sulphates as compared to the other four types of portland cements (Type I, II, III and IV) Type V cements contain lower percentage of $\mathbf{C_3A}$ (tricalcium aluminate) compared to that of regular cements. Because of this the percentage of $\mathbf{C_4AF}$ (tetracalcium alumino ferrite) in theses cements is higher. Type V cements are used when it is essential to have high sulphate resistance.

[iii] Production of Portland Cement

The processes are classified as cement rock *benification and Portland* cement production.

(1) Cement rock benification : The limestone, which is available locally, contains high percentage of silica and iron. Therefore, it is essential to remove the undesirable constituents from limestone before its utilization for the manufacture of cement. The undesirable constituents from the limestone are removed by using **ore dressing** or **benification method,** which are based on fluid mechanics and adsorption. The flowchart for cement rock (limestone) benification is shown in fig. (6).

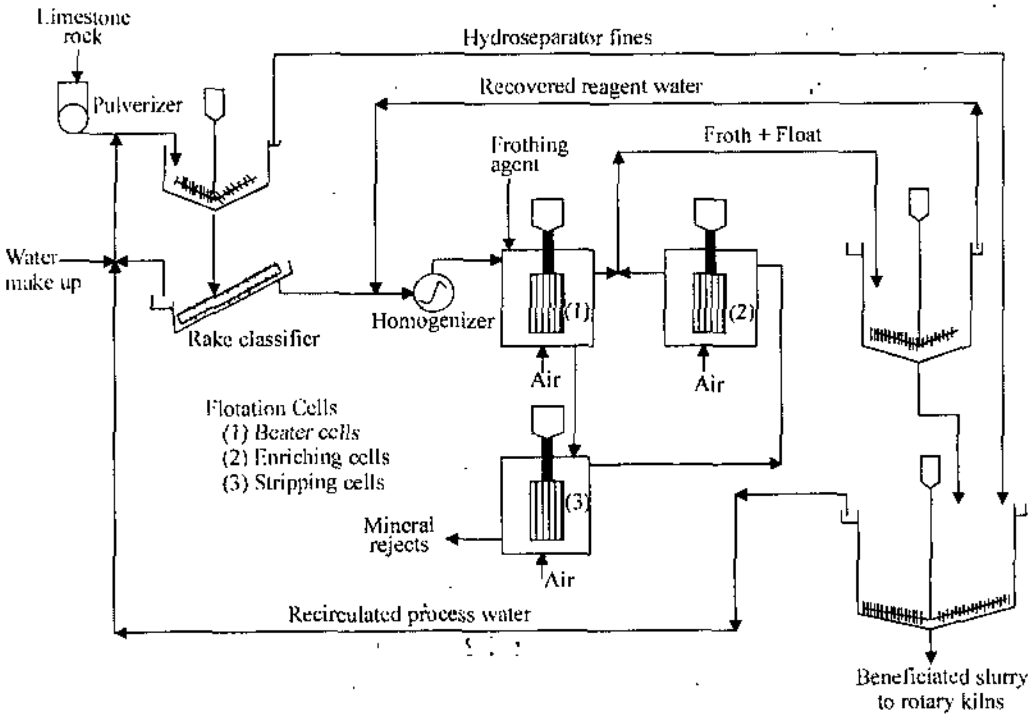


Fig. 6. Flowchart of limestone benification

The quantitiative requirements (basis : one ton of low-grade limestone) are :

Water : 2 to 3 ton ; Reagents : 50 – 200 g ; Electricity : 2.5 kWH

The benification process involves operations like grinding, classification, floatation and thickening. The limestone (rock) is wet ground and then it is delivered into a hydroseparator and the overflow is allowed to pass directly to the final thickener. The rock limestone may also be subjected to floatation separation as well as the coarse material, which must be floated for the removal of silica, mica and talc.

Floatation depends on the ability of the collecting agent to wet certain minerals causing these to be entrained in an air froth, which rises to the surface and overflows the floatation cell into the thickener. The floatation liquor is recycled and the beneficiated cement rock slurry is delivered to the cement kilns. Oleic acid (200 g per ton of lime stone) is used as the floatation agent.

***(2) Portland cement production** : The flowchart for the manufacture of* portland cement is shown in fig. (7). The chemical reactions occurring as follows :

$$CaCO_3 \xrightarrow{1100°C} CaO + CO_2$$

$$CaC + Al_2O_3 + SiO_2 \longrightarrow \text{Mixture of } C_3S, C_2S, C_3A$$

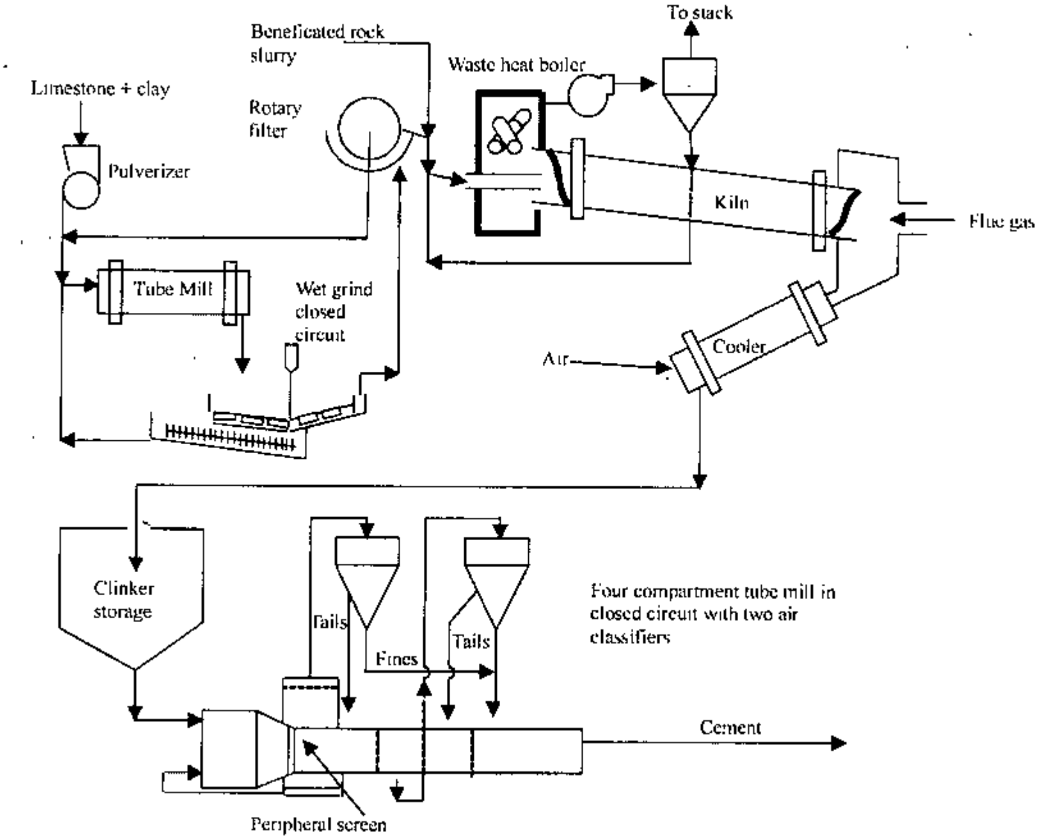


Fig. 7. Flowchart for the manufacture of portland cement

The raw materials required for the production of one ton of Type I cement are given below :

Clay : 100 – 300 kg; Limestone : 1200 – 1300 kg;
Gypsum : 30 – 50 kg; Coal : 250 – 400 kg

The limestone (cement grade), clay, sand, iron containing material (blast furnace slag), gypsum and coal are ground thoroughly together. The grinding may be performed by **wet process** or **dry process.** The dry process is preferred because of heat saving and accurate control is also possible. The sequence of operation includes rough crushing, followed by gyratory and hammer mills, then drying and fine grinding in tube mills followed by air separation and pneumatic blending.

The dry powdered feed or slurry is delivered into a direct-fire counter-current rotary kiln. The residence time is one to three hours. The mixture is decarbonated and fused to form cement **(C_2S, C_3S, C_3A).** The hot clinker (3-10 mm size) is dropped into a rotary cooler from where it is delivered to four compartment tube mill provided with two air classifiers. The cement thus obtained is sent for bagging and transportation.

[IV] Other Cements

Portland cement is not suitable for corrosive conditions. Therefore, many special types of cement are prepared which are gaining industrial importance. Some of the important types of cements are as follows :

(1) Pozzolan cement : Italians successfully used pozzolan cement since the beginning of the Christian era. It was prepared by grinding pozzolan, (2 – 4 parts) with hydrated lime (1 part). The pozzolan is a material, which is not cementitious but becomes cementitious on mixing with lime. The strength of pozzolan cement is less than the strength of Portland cement, but within a year the strength becomes equal. The pozzolan cement possesses higher resistance to the corrosive action of sea water as compared to that of portland cement.

(2) High alumina cement : High alumina cement is generally calcium aluminate cement. It is manufactured by fusing a mixture of limestone and bauxite (containing iron oxide, silica, magnesia and other impurities). This cement has a very rapid rate of development strength and superior resistance to sea water and sulphate containing waters. The constituents of high alumina cement are given in table 3.

Table 3 : Constituents of high alumina cement

Chemical formula	Name	Abbreviation
$3\,CaO.\,SiO_2$	Tricalcium silicate	C_3S
$2\,CaO.\,SiO_2$	Dicalcium silicate	C_2S
$2\,CaO.\,Al_2O_3.\,SiO_2$	Dicalcium aluminate	C_2AS

(3) Silicate cement : Silicate cement withstands all concentrations of inorganic acids (except hydrofluoric acid). These cements are not suitable in conditions having pH above seven or in the presence of crystal forming systems. Silicate cements are prepared by mixing finely divided silica powder (two parts by weight) with one part of sodium silicate (35 – 40% Bè). These cements are used for the joining of bricks in chromic acid reactions tanks and in alum tanks.

(4) Sulphur cements : Sulphur cements are commercially available :

(i) As simple mixtures of fillers (since 1900).

(ii) As homogeneous plasticized filled sulphur ingots having low coefficient of expansion (since 1930).

These cements have resistance to non-oxidizing acids and salts but are not used in the presence of alkalies, oils, greases or solvents. On account of the crystalline change in structure of sulphur occurring at 93°C, there are limitations for the use of sulphur cements. Thiokol–plasticized-silica filled sulphur cements are used as a standard material for joining bricks, tiles and cast iron pipes.

(5) Polymer concretes : Polymer concretes are polymer bonded concretes containing no portland cements. They consist of resins such as epoxy, methyl methacrylate or polyester. Each resin imparts specific properties to the concrete (for example: rapid curing, corrosion resistance or high compressive strength). Polymer concretes are more expensive than the portland cement concretes.

(6) Magnesium oxychloride cement : This cement was discovered by the French chemist Sorel and therefore it is also called as Sorel's cement. It is prepared by the action of magnesium chloride (20 % solution) on a blend of magnesia (obtained by calcinations of magnesite) and magnesia (obtained from brine).

$$3MgO + MgCl_2 + 11H_2O \longrightarrow 3MgO.MgCl_2.11H_2O$$

The product obtained is hard and strong but leaches out magnesium chloride when attacked by water. It is used as a flooring cement with inert fillers and a colouring pigment. It has corrosive action on iron pipes in contact with it.

The magnesia used for the production of this cement may contain small quantities of calcium oxide, calcium hydroxide or calcium silicate which increase the volume change during the settling process. This leads to decrease in strength and durability of this cement. To avoid this effect, hydrated magnesium sulphate ($MgSO_4 . 7H_2O$) or ten percent finely divided metallic copper is added to the mixture. The use of copper powder prevents excessive expansion and also increases water resistance, adhesion and strength over that of ordinary magnesium oxychloride cement.

5.5. LIME

Lime is used in medicines, insecticides, plant and animal food, gas adsorption, precipitation and causticising. It is also useful as a reagent in the sulphite process for paper making, and softening of water. It is used in the manufacture of soaps, rubber, varnishes, refractories and sand-lime bricks. Lime is used as a basic raw material in the production of calcium salts and for the improvement of quality of soil.

Lime acts as a basic flux in the manufacture of steel. Iron ore contains silicon dioxide (SiO_2) as an impurity. SiO_2 is a Lewis acid and it reacts with lime, which is a Lewis base. The molten silicate slag ($CaSiO_3$) is less dense as compared to the molten iron and therefore $CaSiO_3$ collects at the top of the reactor from where it is drawn off. For the manufacture of one ton of steel about one hundred pounds of lime is necessary. The reaction involved in the formation of calcium silicate slag is represented as follows :

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

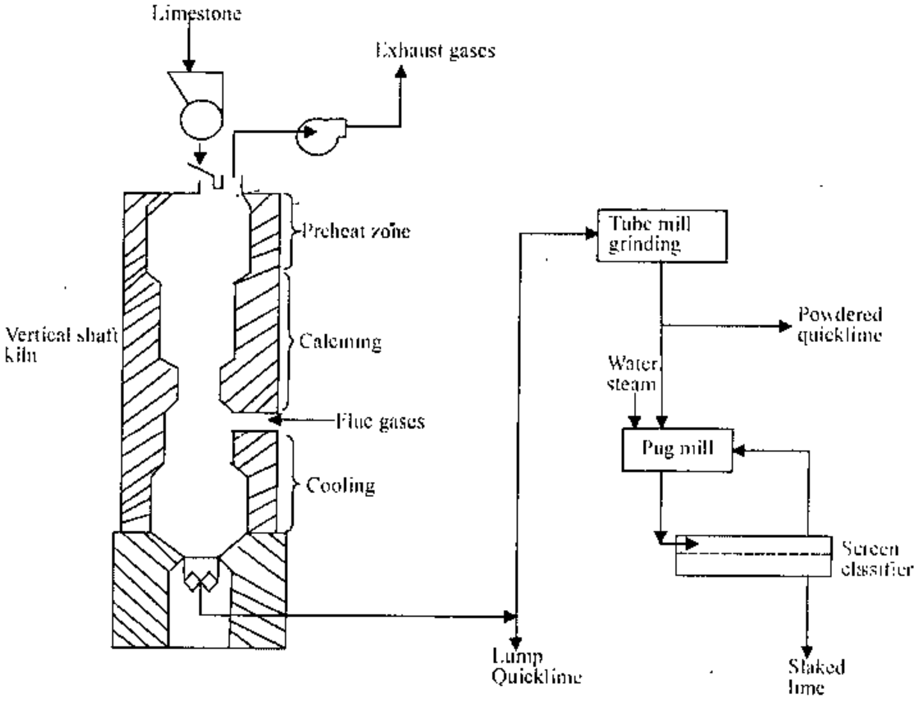


Fig. 8 : Flowchart for the manufacture of lime

Lime and limestone are used on large scale in industries much more than any other natural substance. Lime is sold as high-calcium quicklime containing CaO (not less than 90%), magnesia (0 to 5%) ; small amounts of calcium carbonate, silica, alumina and ferric oxide are present as impurities.

There are several types of lime. Hydraulic lime is prepared by burning limestone containing clay, and the nature of the product obtained after contact with water varies from putty to set cement. High-calcium content limes becomes very hard by absorbing CO_2 from air. Hydraulic lime also becomes hard slowly, but it can be used under water. High-calcium lime is preferred in building industry for the manufacture of mortar lime plaster; there are places where limestone containing magnesium is burned or where dolomitic stone is calcined. Compositions of such stones are CaO (35-45%) and MgO (10-25%). These products are known as Magnesian limes or dolimes. In metallurgy, refractory lime is used as a refractory patching material in open-hearth furnace. **Hydrated lime** is preferred in the building trade over less stable quicklime. **Quick lime** is slaked or hydrated before use.

The physical properties of quick lime and hydrated lime are as follows :

(a) Quick lime (CaO)

Molecular weight : 56.08
Melting point : 2570°C
Boiling point : 2850°C
Density : 3.32 g/ml
Solubility : soluble in water and acids

(b) Hydrated lime [$Ca(OH)_2$]

Molecular weight : 74.1
Density : 2.2 g/ml
Decomposes forming CaO at 580°C
Solubility : Slightly soluble in water

[I] Methods of Production

The processes are classified as calcination of limestone to yield quicklime and hydration of quick lime.

(a) Calcinations of limestone to yield quick lime: Flowchart of the *process is depicted in figure (8). The reaction occurring in the process is as* follows:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

The quantitative raw materials required to produce one ton of quicklime are limestone (pure) : 1870 kg and coal : 300 kg.

The limestone is quarried or mixed and then taken to the conveyors feeding the mill crushing unit. Limestone of variable size is obtained. The size depends upon type of calciner used: vertical shaft (size : 10-20 cm), moving bed (1-10 cm), rotary kiln (0.5-5 cm), fluidized bed (0.5-0.05 cm). Generally vertical shaft or rotary kilns are used.

The vertical shaft kiln is three to eight meter in diameter and ten to twenty five meter in height. It is lined with refractory bricks and covered with sheet steel outside for strength and to avoid gas leakage.

The limestone is fed from the top of the furnace. The combustion gas preheats the limestone as it goes down gradually in the calcining zone, operating at 1000 – 1100°C. The limestone ($CaCO_3$) decomposes to CaO (lime) at 898°C. The lime lumps move to cooling section (heat exchange occurs between secondary air and hot lime particles). The lime is then packed as lump lime or crushed and screened to get pulverized lime.

(b) Hydration of quick lime : Flowchart of the processes is shown in fig. (3). The chemical reaction involved is the process is as follows

$$CaO\,(s) + H_2O\,(\text{liq. or vapour}) \longrightarrow Ca(OH)_2\,(s)$$

The raw materials required for the manufacture of one ton of hydrated lime are quicklime (pure) : 790 kg and water : 245 kg.

The quick lime lumps are crushed (size 2 cm or less) and then delivered along with water or steam into a vertical cylindrical pug mill, which contains eighteen to twenty four extended horizontal arms. The product obtained is light and dry slaked lime. It is then calcified by screen calcified to remove unreacted lime. The finely divided product is sent to packing and transportation section.

5.6. CEMENT AND LIME INDUSTRIES IN INDIA

1. Associated Cement Company, Cement House, 121, Maharshi Karve Road, Mumbai (Maharashtra).
2. Birla Jute and Industries Ltd., Birla Building, 9/1 R.N. Mukherjee Road, Kolkata (West Bengal).
3. Chettinad Cement Corporation Ltd., Rani Seethai Hall Building, 601 Anna Salai, Chennai (Tamilnadu).
4. Century Textiles and Industries, Century Bhavan, Dr. Annie Basant Road, Mumbai (Maharashtra).
5. Dalmia Cement (Bharat) Ltd, Hansaaya Building, 15, Barakhamba Road, New Delhi.
6. Gujarat Sidhee Cement Ltd., Sidheegram, Dist. Junagadh (Gujarat).
7. Gujarat Ambuja Cements Ltd., 122, Maker Chamber III, Nariman Point, Mumbai (Maharashtra).
8. India Cements Ltd., Dhun Building, 827, Anna Salai, Chennai (Tamilnadu).
9. Jaiprakash Industries Ltd., JA House, 63, Basant Lok, Vasant Vihar, New Delhi.
10. Larsen and Tourbo Ltd., L and T House, Ballard Estate, Mumbai (Maharashtra).
11. Madras Cements Ltd., 98-A, Dr. Radhakrishanan Sali, Mylapore, Chennai (Tamil Nadu).
12. Modi Cements Ltd., 32, Community Centre, New Friends Colony, New Delhi.
13. Mysore Cements Ltd., Industry House, 4, Race Course Road, Bangalore (Karnataka).
14. Narmada Cement Company Ltd., 2-C, Phoenix Mill Compound, 462, Senapati Bapat Marg, Lower Parel, Mumbai (Maharashtra).
15. Orissa Cement Ltd., B-47, Cannaught Place, New Delhi.
16. Panyam Cement and Mineral Industries Ltd., Cement Nagar, Karnool (Andhra Pradesh).
17. Rassi Cement Ltd., Minerva House, 94-Sarojini Devi Road, Secunderabad (Andhra Pradesh).
18. Shree Cement Ltd., 21, Strand Road, Kolkata (West Bengal).
19. Shree Digvijay Cement Company Ltd., Digvijay Gram (Gujarat).

STUDENT ACTIVITY

1. Mention the properties that a pigment should possess.

2. Write the formula of lithopone and titanium dioxide.

3. What is lampblack ?

4. What is a toner ?

5. Write the constituents of portland cement.

6. Write three uses of lime.

7. What is dolime ?

SUMMARY

- A pigment is coloured, organic or inorganic soluble substance.
- A pigment should possess properties like opacity, good covering power, wettability by oil, chemical inertness, non-toxicity or low toxicity and reasonable cost.
- Lithopone is used in water based paints. It is used as a whitener for rubber and paper.
- Lampblack is a black pigment. It is used in paints, lacquers and enamels. It is used in making writer ribbons and carbon paper.
- Red lead is used in paints and primers and in rubber formulation.
- Ocher is a naturally occurring pigment.
- Toners are insoluble organic dyes. Because of their durability and colouring power they are directly used as pigments, *e.g.*, para red etc.
- Lakes are dyed inorganic pigments. These are ground in oil and applied like any other pigment.

- Cement is a powered substance which when mixed with water or liquid has plastic flow and forms a hard solid structure in several hours with varying degree of strength and bonding properties.
- Portland cement is a finely ground mixture of calcium aluminate and silicates of different composition which hydrate on mixing with water to form a solid rigid structure having good compressive strength.
- Lime is used in medicines, insecticides, plant and animal food, gas adsorption and causticising etc. It is also used as a reagent for paper making and softening of water. It is used in the manufacture of soaps, rubbers, varnishes, refractories and sand lime bricks.
- Lime is used as a basic flux in the manufacture of steel.
- Quick lime is calcium oxide (CaO), while hydrated lime is calcium hydroxide [$Ca(OH)_2$].

TEST YOURSELF

Answer the following questions :

1. Define a pigment.
2. How many types of pigments do you know ?
3. Name two white pigments and black pigments.
4. How is lithopone manufactured ?
5. Define portland cement. Name the constituents present in it.
6. What is the difference between quick lime and slaked lime ?
7. How is lime manufactured ?
8. Name five cement industries in India.
9. Lamp black is a :
   (i) White pigment (ii) Black pigment
   (iii) Green pigment (iv) Red pigment
10. Titanium dioxide is a :
    (i) Black pigment (ii) Red pigment
    (iii) White pigment (iv) Blue pigment
11. Dyed inorganic pigments are called :
    (i) Toners (ii) Lacquers
    (iii) Varnishes (iv) Lakes
12. The pigment used as a primer is :
    (i) White lead (ii) Green paint
    (iii) Red lead (iv) Carbon black

13. Fill in the blanks :

(a) Ultramarine is a .... pigment.
(b) $PbCrO_4.Pb(OH)_2$ is known as ....
(c) Para red acts as a ....
(d) .... acts as a basic flux in steel manufacture.
(e) The raw materials required for the manufacture of portland cement are clay, coal, limestone and ....

ANSWERS

9. (i) **10.** (iii) **11.** (iv) **12.** (i), (iii)
13. (a) blue (b) basic lead carbonate (c) toner
(d) lime (e) gypsum

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