Types and Sources of Air Pollution

o **Air Pollution**
  - Chemicals added to the atmosphere by natural events or human activities in high enough concentrations to be harmful

o **Two categories**
  - Primary Air Pollutant
    - Harmful substance that is emitted directly into the atmosphere
  - Secondary Air Pollutant
    - Harmful substance formed in the atmosphere when a primary air pollutant reacts with substances normally found in the atmosphere or with other air pollutants

Major Air Pollutants

Table 20.1 Major Air Pollutants

Pollutant	Composition	Primary or Secondary	Characteristics
Particulate matter			
Dust	Variable	Primary	Solid particles
Lead	Pb	Primary	Solid particles
Sulfuric acid	H_2SO_4	Secondary	Liquid droplets
Nitrogen oxides			
Nitrogen dioxide	NO_2	Primary	Reddish-brown gas
Sulfur oxides			
Sulfur dioxide	SO_2	Primary	Colorless gas with strong odor
Carbon oxides			
Carbon monoxide	CO	Primary	Colorless, odorless gas
Carbon dioxide*	CO_2	Primary	Colorless, odorless gas
Hydrocarbons			
Methane	CH_4	Primary	Colorless, odorless gas
Benzene	C_6H_6	Primary	Liquid with sweet smell
Ozone	O_3	Secondary	Pale blue gas with acrid odor
Air toxics			
Chlorine	Cl_2	Primary	Yellow-green gas

* Discussed in Chapter 21.

Source: Environmental Protection Agency.

Primary air pollutants

CO CO_2
SO_2 NO NO_2
Most hydrocarbons
Most particulates

Secondary air pollutants

HNO_2 SO_3
HNO_3 H_2SO_4
H_2O_2 O_3 PANs
Most NO_3^- and SO_4^{2-}
salts

Natural sources

Human sources
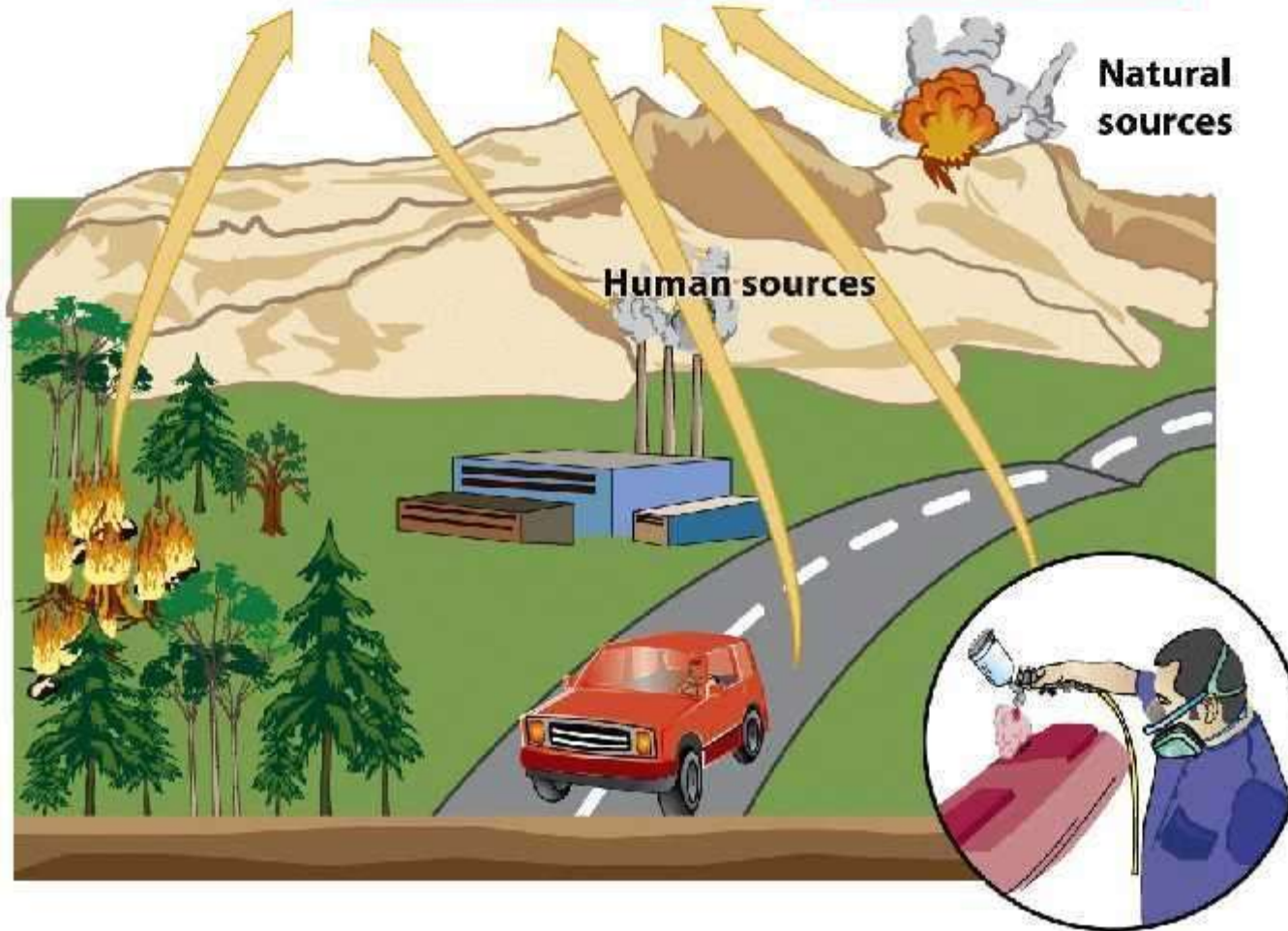
Major Classes of Air Pollutants

o Particulate Material

o Nitrogen Oxides

o Sulfur Oxides

o Carbon Oxides

o Hydrocarbons

o Ozone
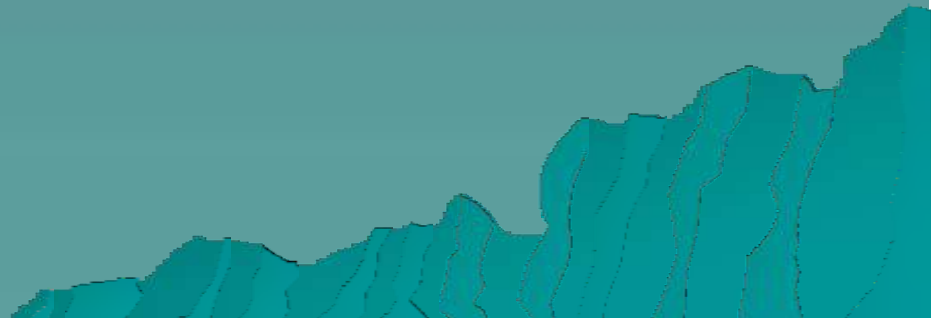
Particulate Material

o Thousands of different solid or liquid particles suspended in air

- Includes: soil particles, soot, lead, asbestos, sea salt, and sulfuric acid droplets

o Dangerous for 2 reasons

- May contain materials with toxic or carcinogenic effects
- Extremely small particles can become lodged in lungs

Nitrogen and Sulfur Oxides

- Nitrogen Oxides
  - Gases produced by the chemical interactions between atmospheric nitrogen and oxygen at high temperature
  - Problems
    - Greenhouse gases
    - Cause difficulty breathing
- Sulfur Oxides
  - Gases produced by the chemical interactions between sulfur and oxygen
  - Causes acid precipitation

Carbon Oxides and Hydrocarbons

o Carbon Oxides
  - Gases carbon monoxide (CO) and carbon dioxide (CO_2)
  - Greenhouse gases

o Hydrocarbons
  - Diverse group of organic compounds that contain only hydrogen and carbon (ex: CH_4- methane)
 - Some are related to photochemical smog and greenhouse gases

Ozone

- o Tropospheric Ozone
  - Man- made pollutant in the lower atmosphere
  - Secondary air pollutant
  - Component of photochemical smog
- o Stratospheric Ozone
  - Essential component that screens out UV radiation in the upper atmosphere
  - Man- made pollutants (ex: CFCs) can destroy it

Sources of Outdoor Air Pollution

o Two main sources
  - Transportation
  - Industry
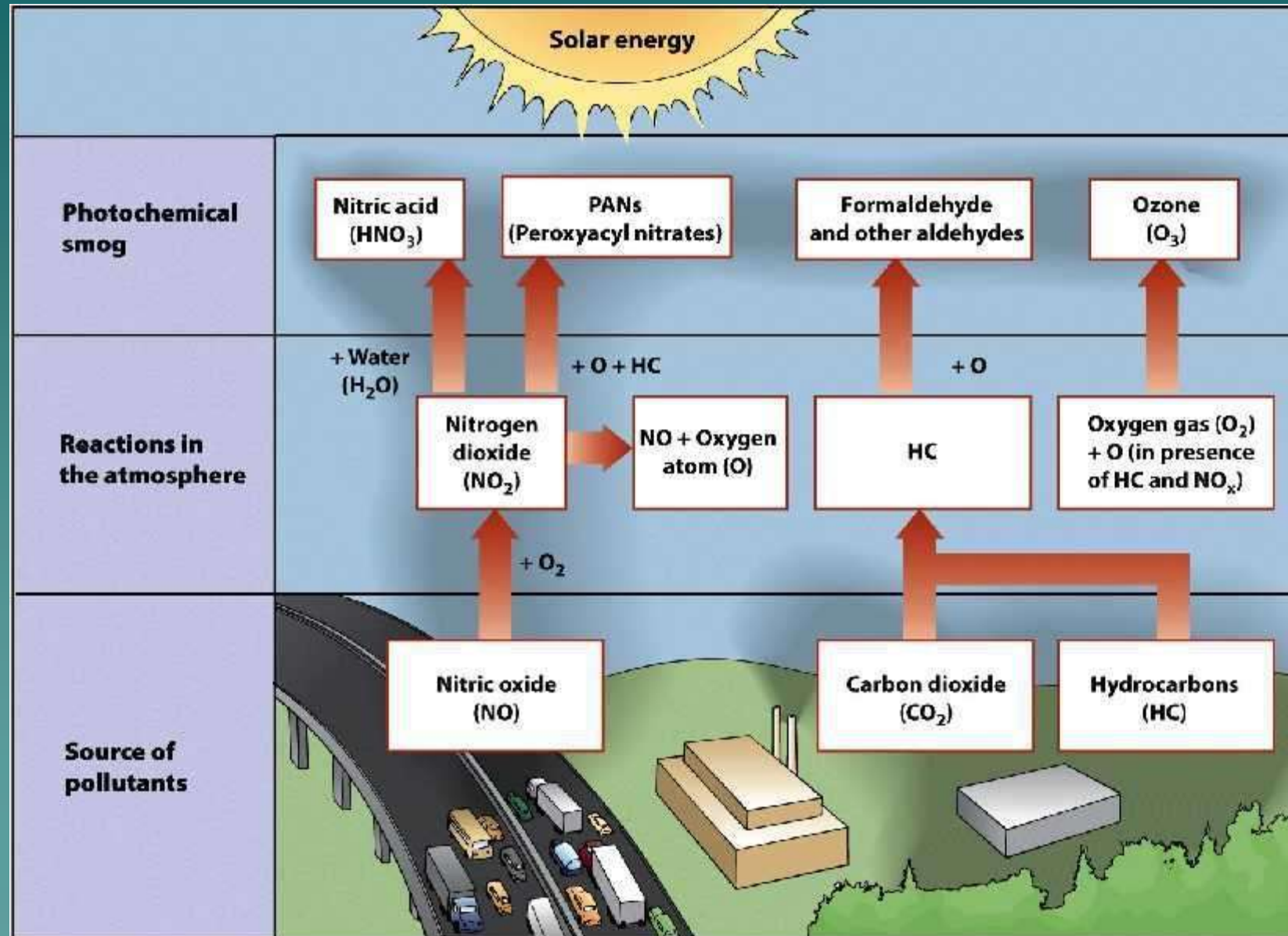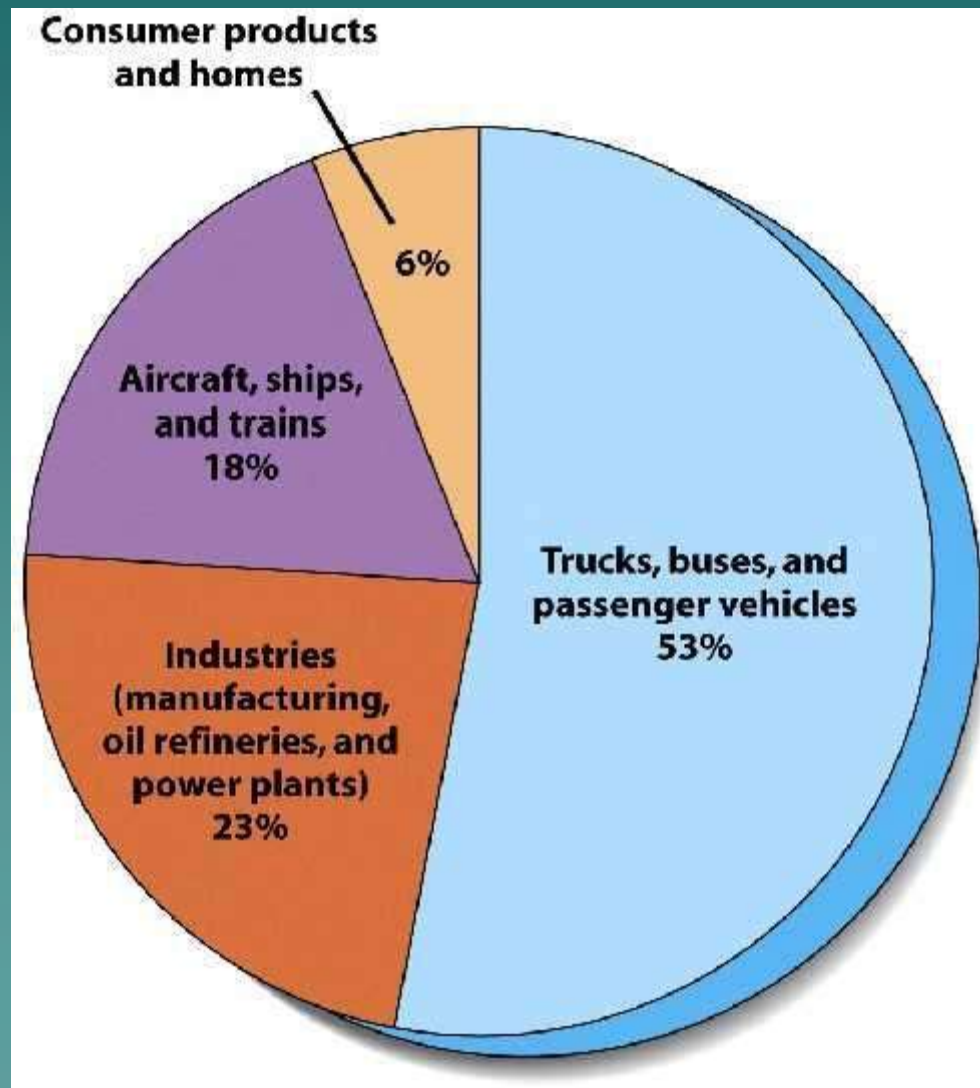o Intentional forest fires is also high
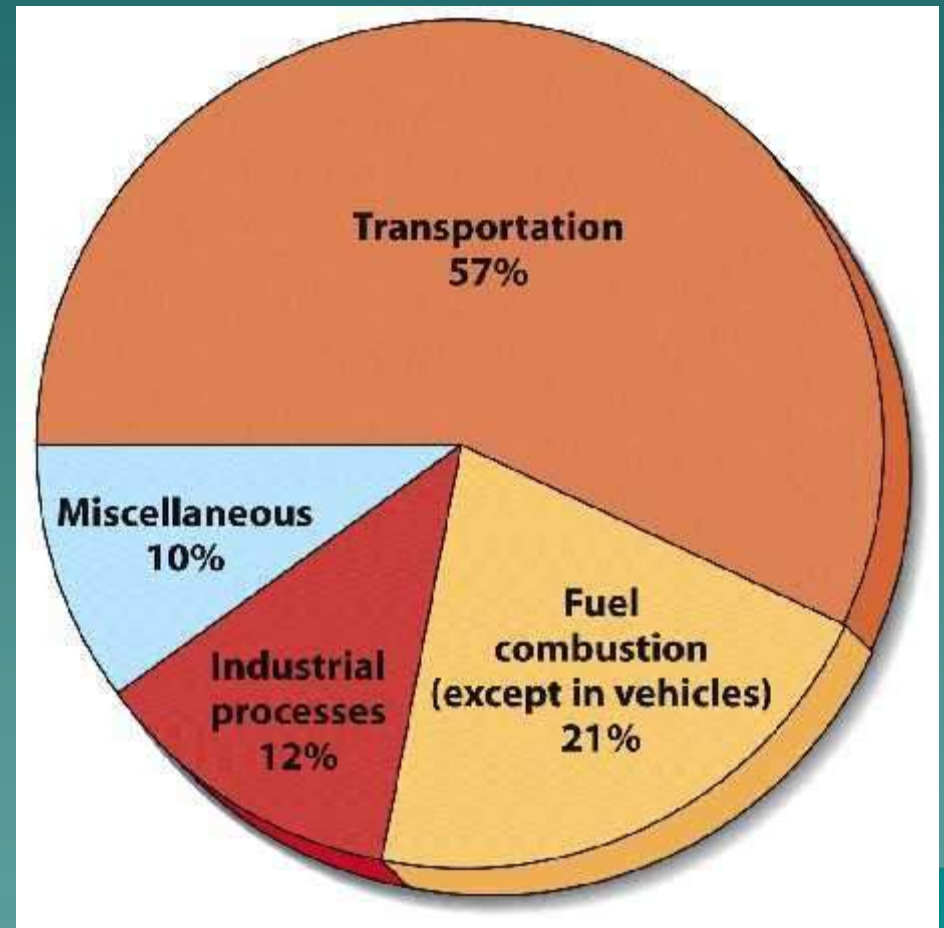
Urban Air Pollution

o Photochemical Smog (ex: Los Angeles below)
- Brownish-orange haze formed by chemical reactions involving sunlight, nitrogen oxide, and hydrocarbons

Formation of Photochemical Smog

Sources of Smog in Los Angeles

Case-In-Point Air Pollution in Beijing and Mexico City

o Beijing (left)

o Mexico City (above)

Effects of Air Pollution

o **Low level exposure**
- Irritates eyes
- Causes inflammation of respiratory tract

o **Can develop into chronic respiratory diseases**

Table 20.2 Health Effects of Several Major Air Pollutants

Pollutant	Source	Effects
Particulate	Industries, electric power plants, motor vehicles, construction, agriculture	Aggravates respiratory illnesses; long-term exposure may cause increased incidence of chronic conditions such as bronchitis; linked to heart disease; suppresses immune system; some particles, such as heavy metals and organic chemicals, may cause cancer or other tissue damage
Nitrogen oxides	Motor vehicles, industries, heavily fertilized farmland	Irritate respiratory tract; aggravate respiratory conditions such as asthma and chronic bronchitis
Sulfur oxides	Electric power plants and other industries	Irritate respiratory tract; same effects as particulates
Carbon monoxide	Motor vehicles, industries, fireplaces	Reduces blood's ability to transport oxygen; headache and fatigue at lower levels; mental impairment or death at high levels
Ozone	Formed in atmosphere (secondary air pollutant)	Irritates eyes; irritates respiratory tract; produces chest discomfort; aggravates respiratory conditions such as asthma and chronic bronchitis

Health Effects of Air Pollution

- Sulfur Dioxide and Particulate material
  - Irritate respiratory tract and impair ability of lungs to exchange gases
- Nitrogen Dioxides
  - Causes airway restriction
- Carbon monoxide
  - Binds with iron in blood hemoglobin
  - Causes headache, fatigue, drowsiness, death
- Ozone
  - Causes burning eyes, coughing, and chest discomfort

Children and Air Pollution

o Greater health threat to children than adults

- Air pollution can restrict lung development
- Children breath more often than adults

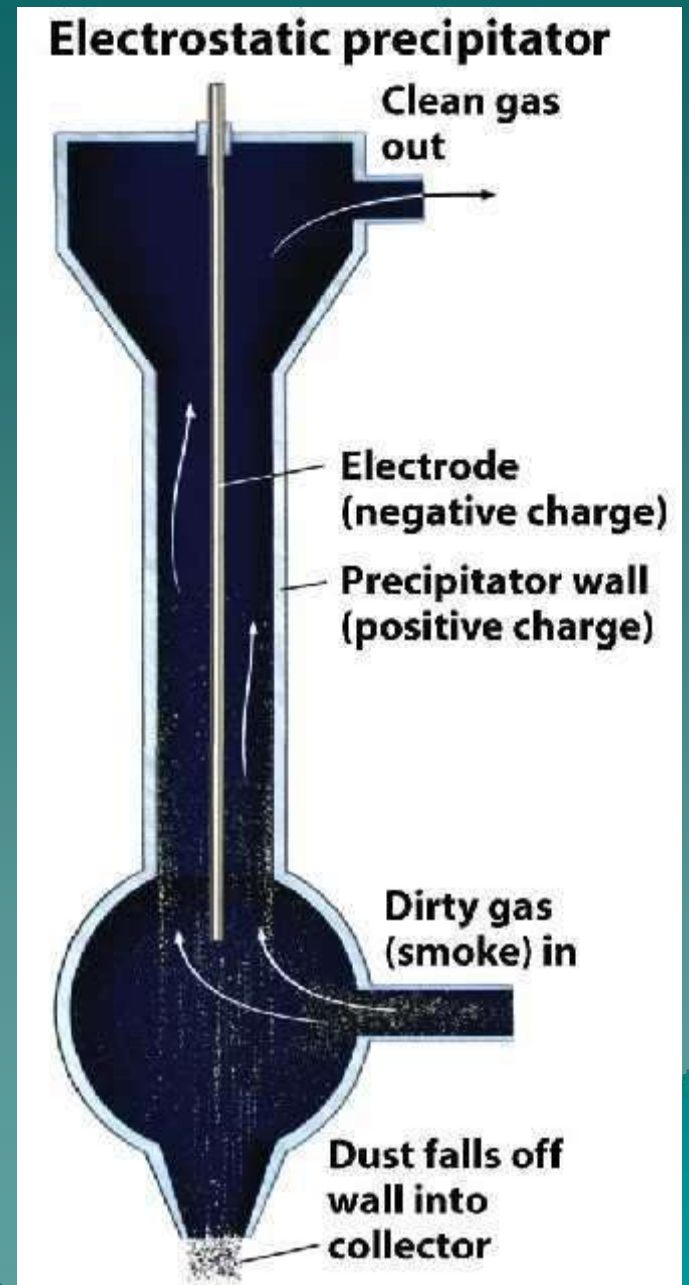o Children who live in high ozone areas are more likely to develop asthma

Controlling Air Pollution in US

o Smokestacks with electrostatic precipitator (right)

Without Electrostatic precipitator

With Electrostatic precipitator

Electrostatic precipitator

Clean gas out

Electrode (negative charge)

Precipitator wall (positive charge)

Dirty gas (smoke) in

Dust falls off wall into collector
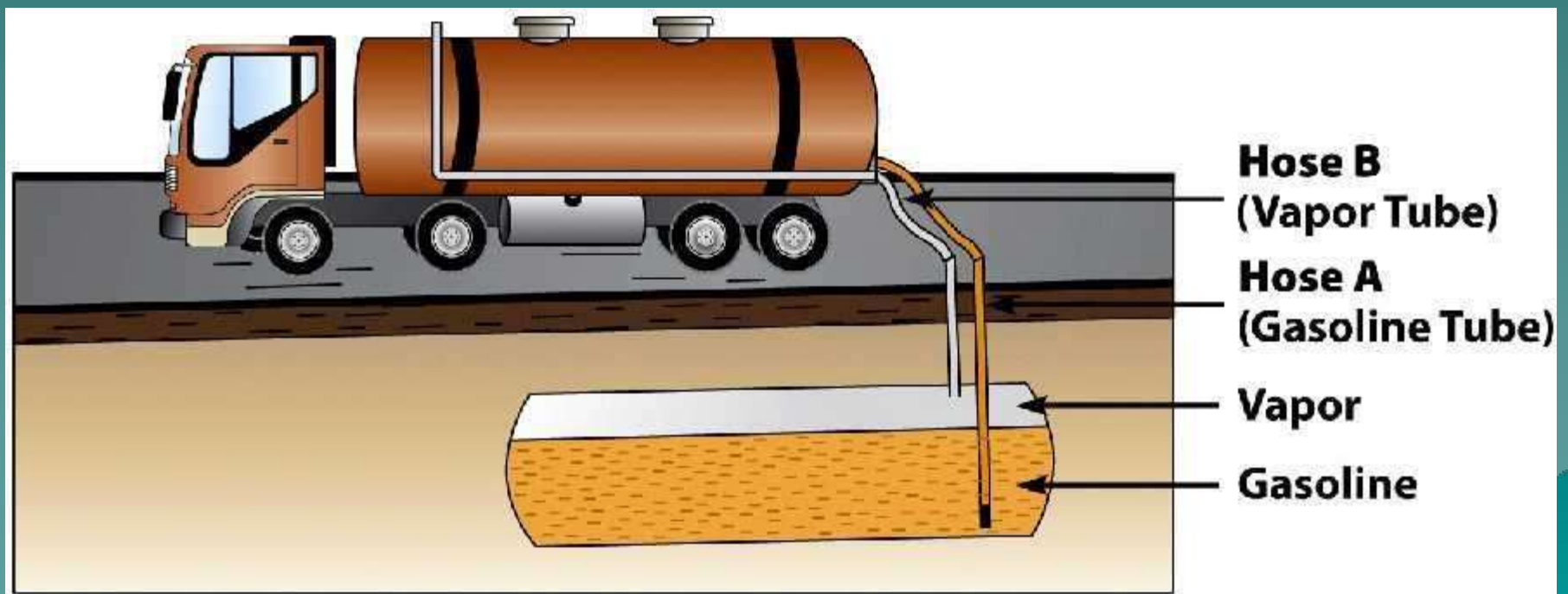
Controlling Air Pollution in the US

o Smokestacks with scrubbers (right)

o Particulate material can also be controlled by proper excavating techniques

Scrubber

Clean gas out

Entrainment separator

Liquid (water) in

Dirty gas in

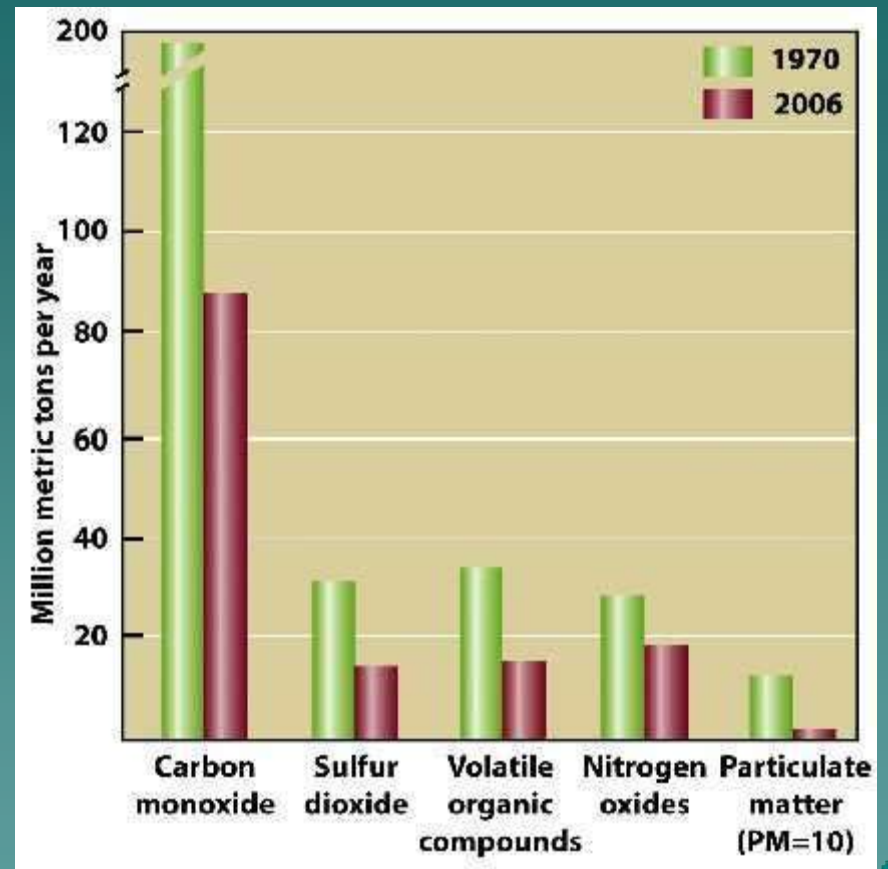Polluted liquid (sludge) out
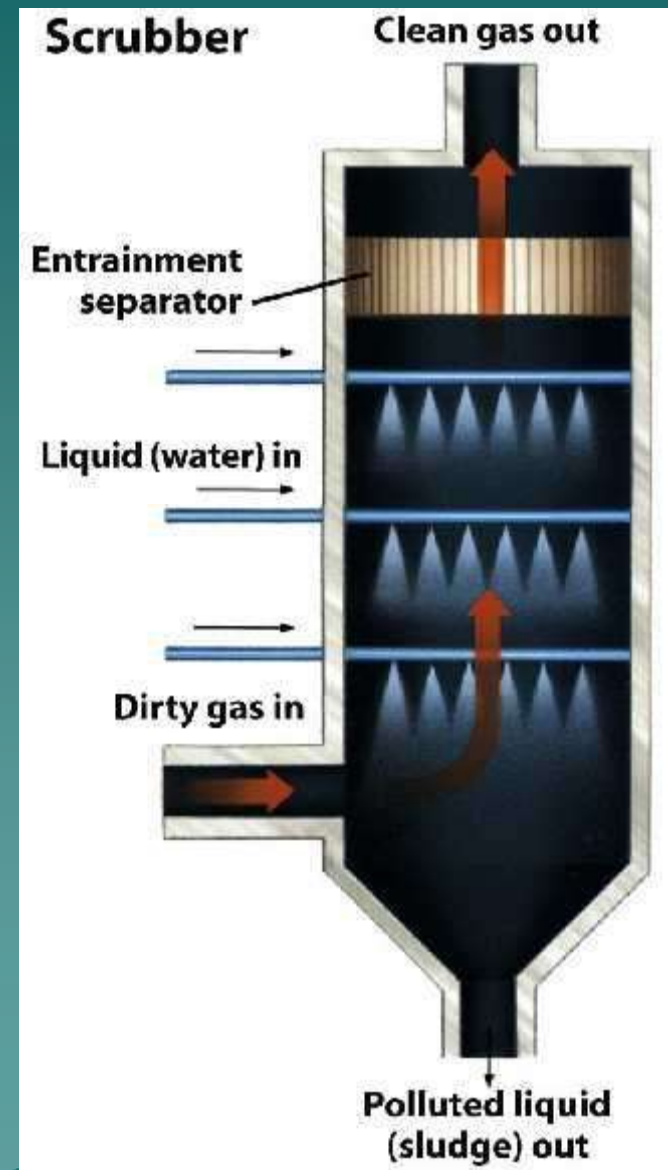
Controlling Air Pollution in the US

o Phase I Vapor Recovery System for gasoline

The Clean Air Act

o **Authorizes EPA to set limits on amount of specific air pollutants permitted**

o **Focuses on 6 pollutants:**
  - lead, particulate matter, sulfur dioxide, carbon monoxide, nitrogen oxides, and ozone

o **Act has led to decreases!**

Table 20.3 U.S. Urban Areas with The Worst Air Quality (Ozone Nonattainment Areas), 2002

Extreme

Los Angeles South Coast Air Basin, California

Very Severe

Chicago, Gary and Lake County, Illinois-Indiana
Houston, Galveston, and Brazoria, Texas
Milwaukee and Racine, Wisconsin
New York City, Northern New Jersey, and Long Island,
   New York-New Jersey-Connecticut
Southeast Desert, California

Severe

Baltimore, Maryland
Philadelphia, Wilmington, Trenton, Pennsylvania-
   New Jersey-Delaware-Maryland
Sacramento, California
San Joaquin Valley, California
Ventura country (between Santa Barbara and Los Angeles),
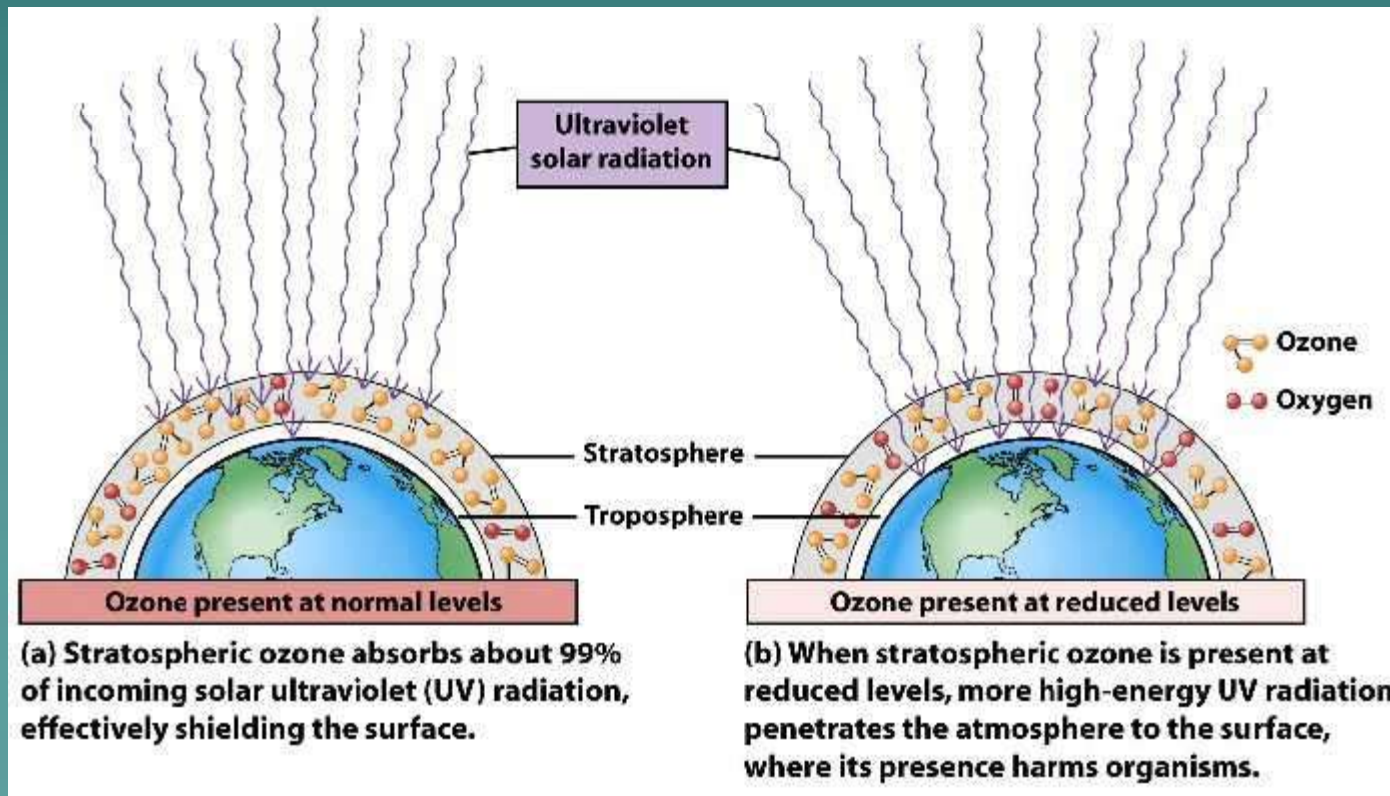   California

Other Ways to Improve Air Quality

o Reduce sulfur content in gasoline from its current average of 330 ppm to 30 ppm

- Sulfur clogs catalytic converters

o Require federal emission standards for all passenger vehicles

- Including SUVs, trucks and minivans

o Require emission testing for all vehicles

- Including diesel
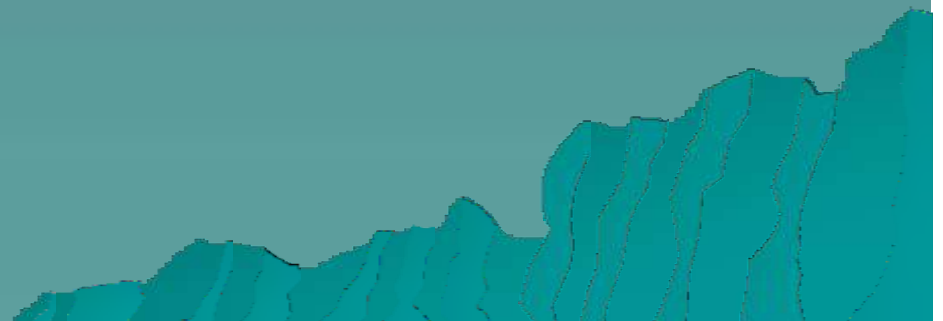
Ozone Depletion in Stratosphere

o Ozone Protects earth from UV radiation
- Part of the electromagnetic spectrum with wavelengths just shorter than visible light

Ultraviolet solar radiation

Ozone
Oxygen

Stratosphere
Troposphere

Ozone present at normal levels

(a) Stratospheric ozone absorbs about 99% of incoming solar ultraviolet (UV) radiation, effectively shielding the surface.

Ozone present at reduced levels

(b) When stratospheric ozone is present at reduced levels, more high-energy UV radiation penetrates the atmosphere to the surface, where its presence harms organisms.

Ozone Depletion in Stratosphere

o Ozone thinning/hole
- First identified in 1985 over Antarctica

o Caused by
- human-produced bromine and chlorine containing chemicals
- Ex: CFCs
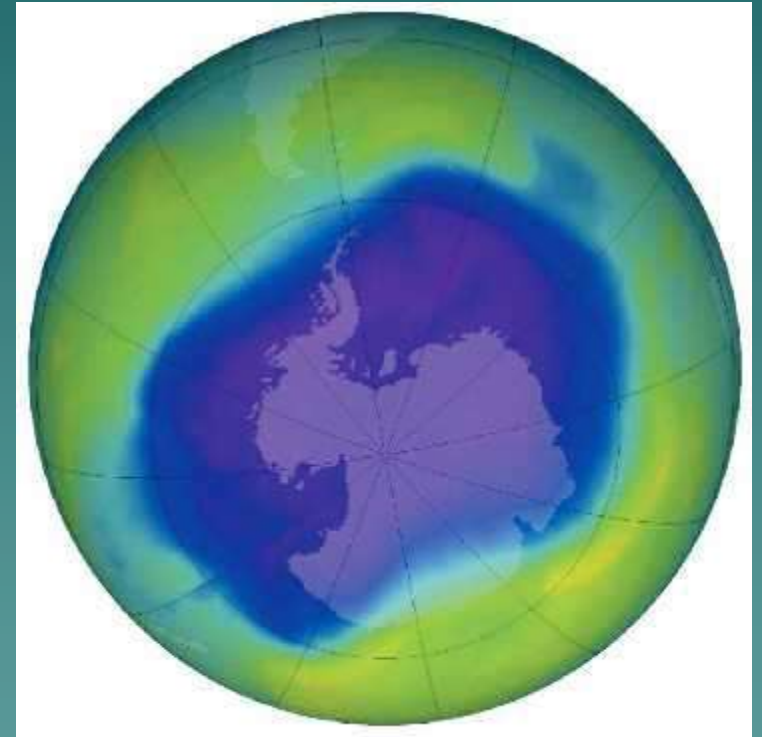
Ozone Depletion in Stratosphere

o Hole over Antarctica requires two conditions:

- Sunlight just returning to polar region
- Circumpolar vortex- a mass of cold air that circulates around the southern polar region
    - Isolates it from the warmer air in the rest of the planet

o Polar stratospheric clouds form

- Enables Cl and Br to destroy ozone

Effects of Ozone Depletion

o Higher levels of UV-radiation hitting the earth
- Eye cataracts
- Skin cancer (right)
- Weakened immunity

o May disrupt ecosystems

o May damage crops and forests

Recovery of Ozone Layer

o Montreal Protocol (1987)

- Reduction of CFCs

- Started using HCFCs (greenhouse gas)

o Phase out of all ozone destroying chemicals is underway globally

o Satellite pictures in 2000 indicated that ozone layer was recovering

o Full recovery will not occur until 2050

Acid Deposition

o Sulfur dioxide and nitrogen dioxide emissions react with water vapor in the atmosphere and form acids that return to the surface as either dry or wet deposition

o pH scale
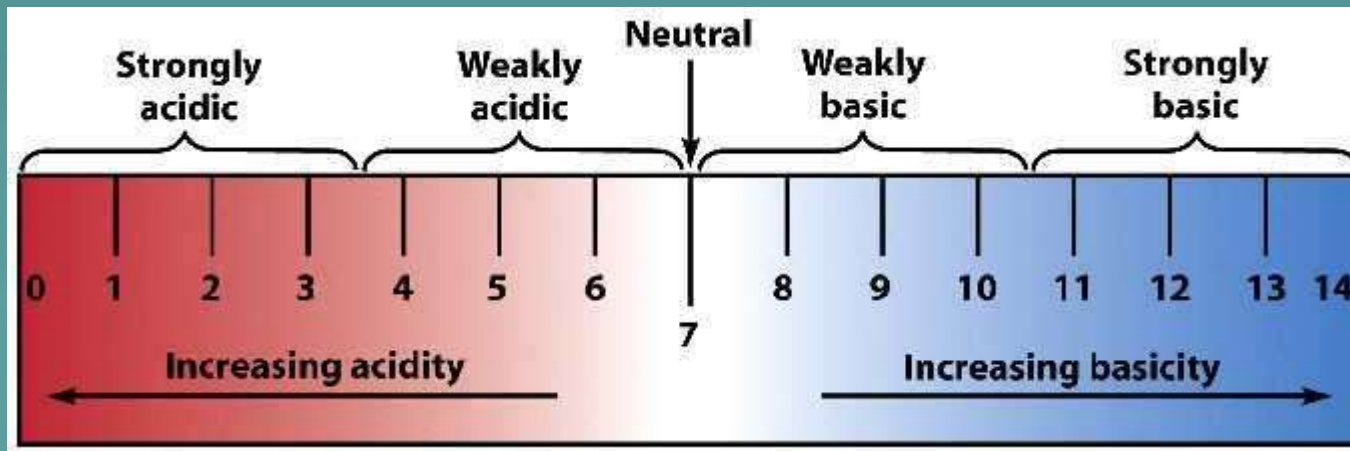
How Acid Deposition Develops
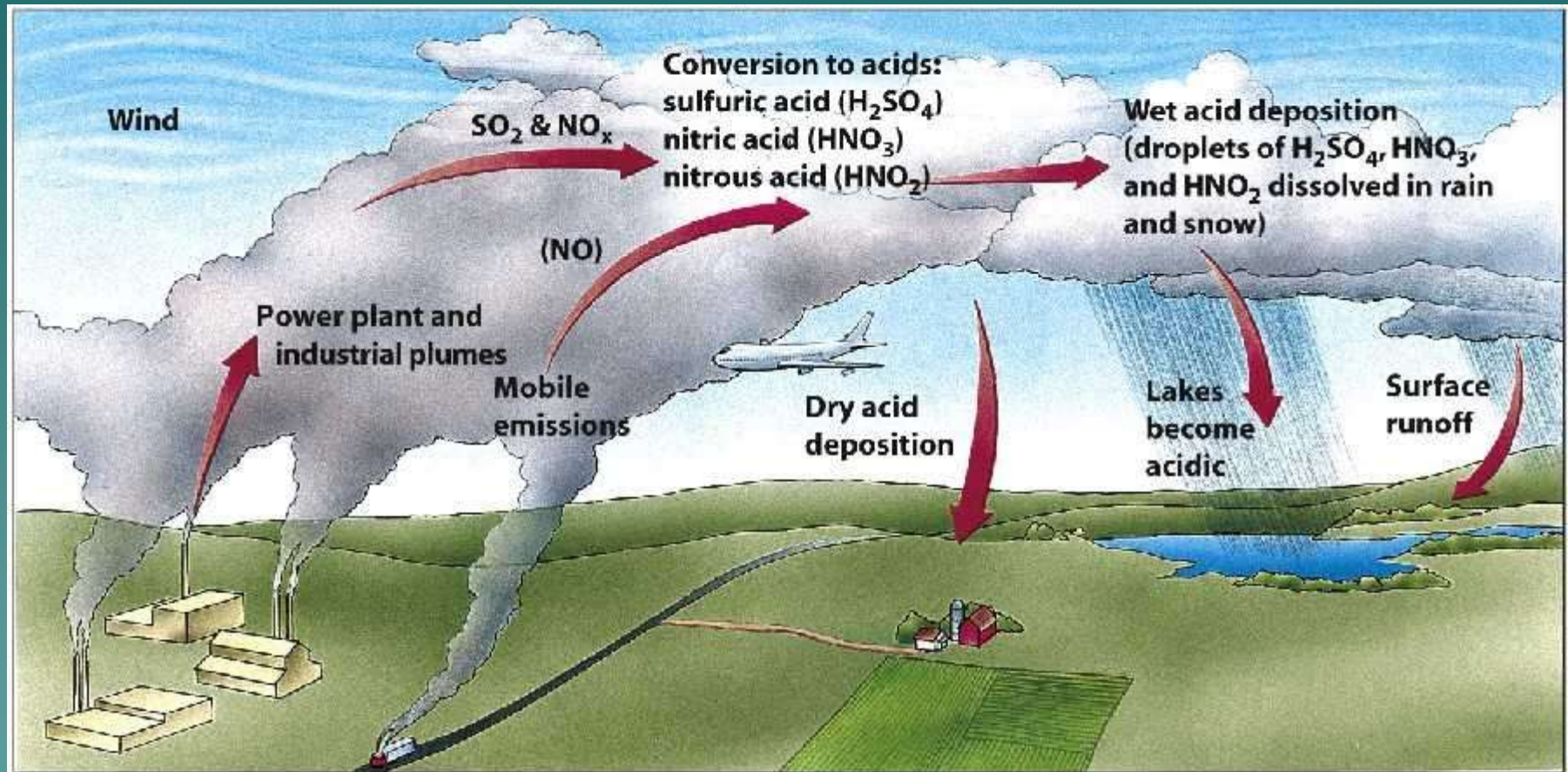
Effects of Acid Deposition

o **Declining Aquatic Animal Populations**

o **Thin-shelled eggs prevent bird reproduction**

- Because calcium is unavailable in acidic soil

o **Forest decline**

- Ex: Black forest in Germany (50% is destroyed)

Acid Deposition and Forest Decline
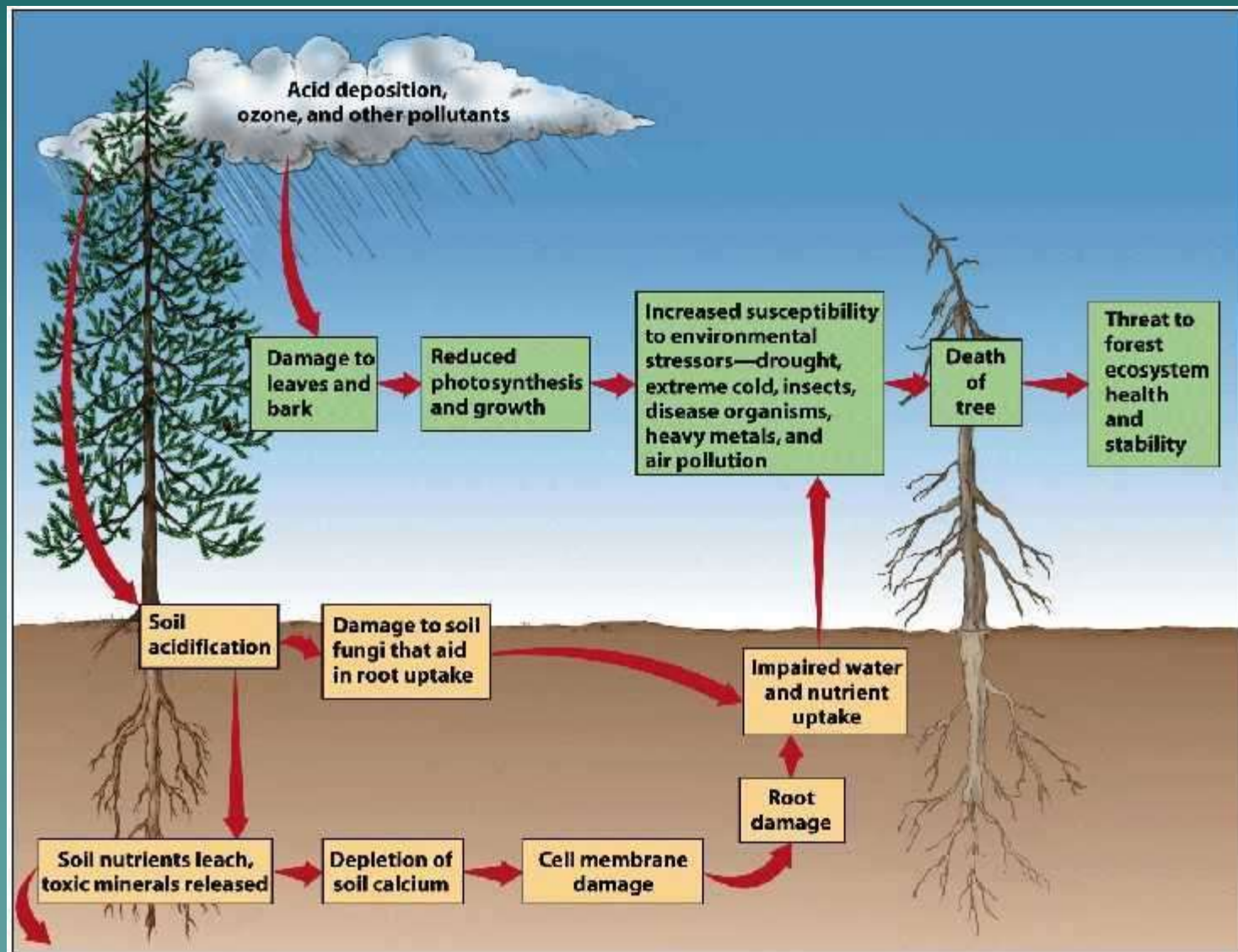
Air Pollution Around the World

- Air quality is deteriorating rapidly in developing countries
- Shenyang, China
  - Residents only see sunlight a few weeks each year
- Developing countries have older cars
  - Still use leaded gasoline
- 5 worst cities in world
  - Beijing, China; Mexico City, Mexico; Shanghai, China; Tehran, Iran; and Calcutta, India

Long Distance Transport of Air Pollutants

Indoor Air Pollution

o Pollutants can be 5-100X greater than outdoors

o Most common:

• Radon, cigarette smoke, carbon monoxide, nitrogen dioxide, formaldehyde pesticides, lead, cleaning solvents, ozone, and asbestos

Carbon monoxide
From: faulty furnace, auto left running

Fungi and bacteria
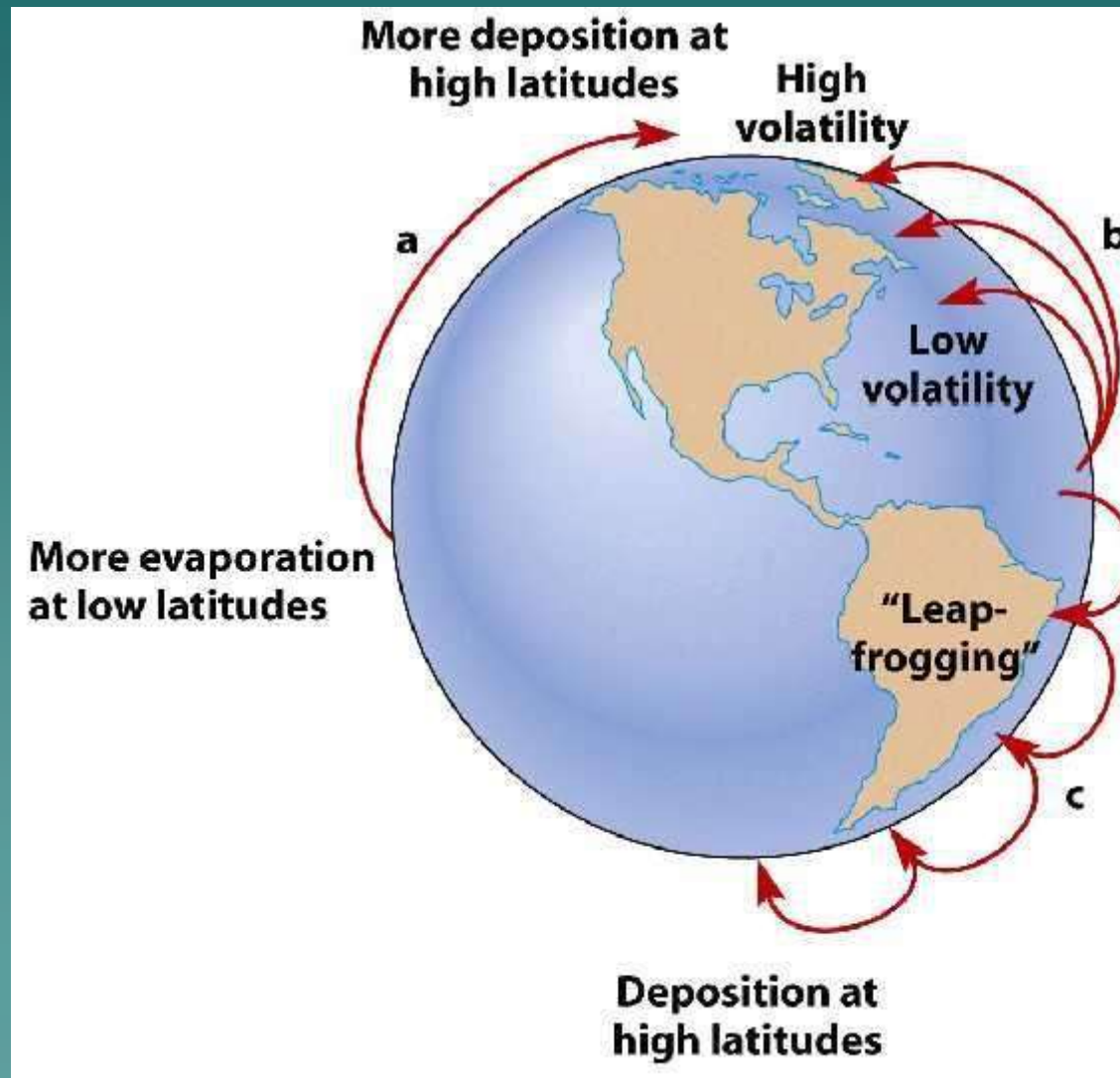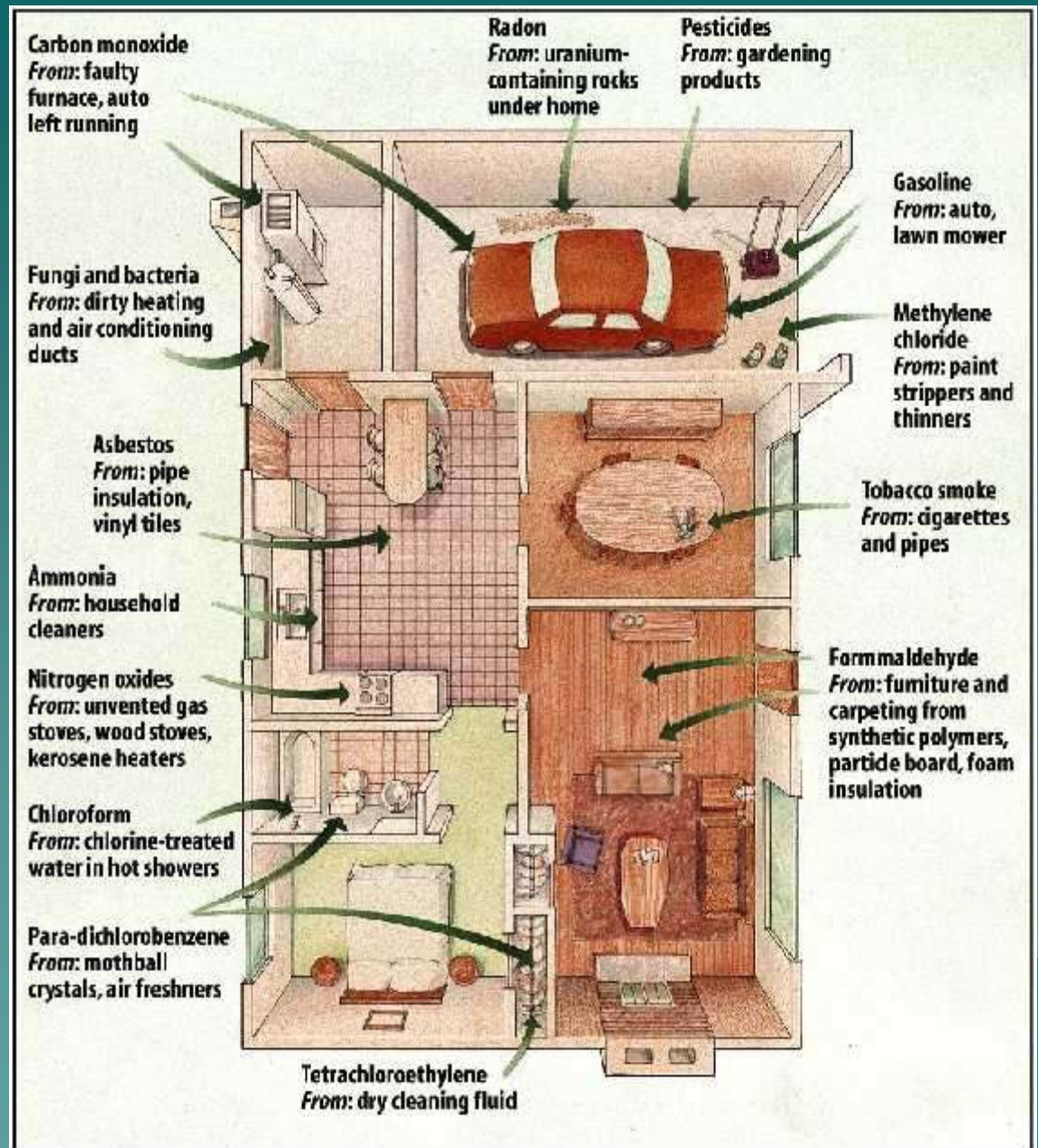*From*: dirty heating and air conditioning ducts

Asbestos
From: pipe insulation, vinyl tiles

Ammonia
From: household cleaners

Nitrogen oxides
From: unvented gas stoves, wood stoves, kerosene heaters

Chloroform
From: chlorine-treated water in hot showers

Para-dichlorobenzene
From: mothball crystals, air freshners

Radon
From: uranium-containing rocks under home

Pesticides
From: gardening products

Gasoline
From: auto, lawn mower

Methylene chloride
From: paint strippers and thinners

Tobacco smoke
From: cigarettes and pipes

Formmaldehyde
From: furniture and carpeting from synthetic polymers, partide board, foam insulation

Tetrachloroethylene
From: dry cleaning fluid

Indoor Air Pollution - Radon

Blow molding

Blow molding (BrE **moulding**) is a specific manufacturing process by which hollow plastic parts are formed and can be joined together: It is also used for forming glass bottles or other hollow shapes. In general, there are three main types of blow molding: extrusion blow molding, injection blow molding, and injection stretch blow molding. The blow molding process begins with melting down the plastic and forming it into a parison or in the case of injection and injection stretch blow moulding (ISB) a preform. The parison is a tube-like piece of plastic with a hole in one end through which compressed air can pass.

The parison is then clamped into a mold and air is blown into it. The air pressure then pushes the plastic out to match the mold. Once the plastic has cooled and hardened the mold opens up and the part is ejected. The cost of blow moulded parts is higher than that of injection – moulded parts but lower than rotational moulded parts.
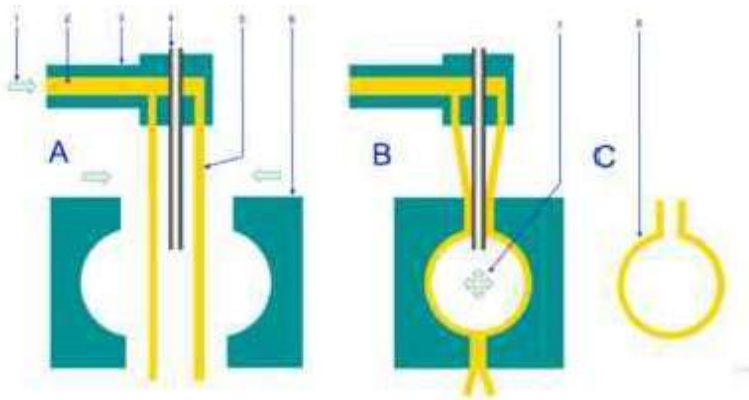
The blow molding process

History

The process principle comes from the idea of glassblowing. Enoch Ferngren and William Kopitke produced a blow molding machine and sold it to Hartford Empire Company in 1938. This was the beginning of the commercial blow molding process. During the 1940s the variety and number of products was still very limited and therefore blow molding did not take off until later. Once the variety and production rates went up the number of products created followed soon afterwards.

The technical mechanisms needed to produce hollow bodied workpieces using the blowing technique were established very early on. Because glass is very breakable, after the introduction of plastic, plastic was being used to replace glass in some cases. The first mass production of plastic bottles was done in America in 1939. Germany started using this technology a little bit later, but is currently one of the leading manufacturers of blow molding machines.

In the United States soft drink industry, the number of plastic containers went from zero in 1977 to ten billion pieces in 1999. Today, even a greater number of products are blown and it is expected to keep increasing.

For amorphous metals, also known as bulk metallic glasses (BMGs), blow molding has been recently demonstrated under pressures and temperatures comparable to plastic blow molding.

Extrusion blow molding

In **extrusion blow molding** (**EBM**), plastic is melted and extruded into a hollow tube (a parison). This parison is then captured by closing it into a cooled metal mold. Air is then blown into the parison, inflating it into the shape of the hollow bottle, container, or part. After the plastic has cooled sufficiently, the mold is opened and the part is ejected.[3] Continuous and Intermittent are two variations of Extrusion Blow Molding. In continuous extrusion blow molding the parison is extruded continuously and the individual parts are cut off by a suitable knife. In Intermittent blow molding there are two processes: straight intermittent is similar to injection molding whereby the screw turns, then stops and pushes the melt out. With the accumulator method, an accumulator gathers melted plastic and when the previous mold has cooled and enough plastic has accumulated, a ro pushes the melted plastic and forms the parison. In this case the screw may turn continuously or intermittently.[4] With continuous extrusion the weight of the parison drags the parison and makes calibrating the wall thickness difficult. The accumulator head or reciprocating screw methods use hydraulic systems to push the parison out quickly reducing the effect of the weight and allowing precise control over the wall thickness by adjusting the die gap with a parison programming device.

EBM processes may be either continuous (constant extrusion of the parison) or intermittent. Types of EBM equipment may be categorized as follows:

Continuous extrusion equipment

- rotary wheel blow molding systems
- shuttle machinery

Intermittent extrusion machinery

- reciprocating screw machinery
- accumulator head machinery

Examples of parts made by the EBM process include most polyethylene hollow products, milk bottles, shampoo bottles, automotive ducting, watering cans and hollow industrial parts such as drums.

Advantages of blow molding include: low tool and die cost; fast production rates; ability to mold complex part; Handles can be incorporated in the design.

Disadvantages of blow molding include: limited to hollow parts, low strength, to increase barrier properties multilayer parisons of different materials are used thus not recyclable. To make wide neck jars spin trimming is necessary.
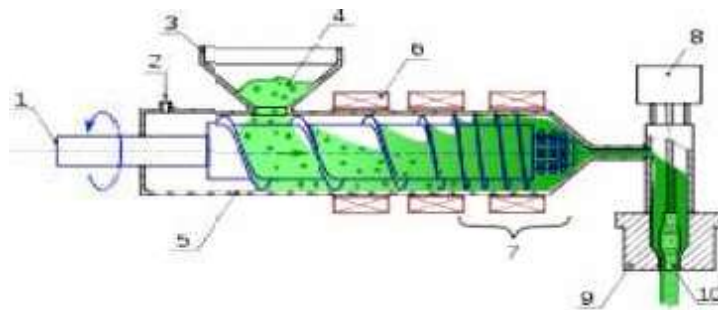
Spin trimming

Containers such as jars often have an excess of material due to the molding process. This is trimmed off by spinning a knife around the container which cuts the material away. This excess plastic is then recycled to create new moldings. Spin Trimmers are used on a number of materials, such as PVC, HDPE and PE+LDPE. Different types of the materials have their own physical characteristics affecting trimming. For example, moldings produced from amorphous materials are much more difficult to trim than crystalline materials. Titanium coated blades are often used rather than standard steel to increase life by a factor of 30 times.

Injection blow molding

The process of **injection blow molding** (**IBM**) is used for the production of hollow glass and plastic objects in large quantities. In the IBM process, the polymer is injection molded onto a core pin; then the core pin is rotated to a blow molding station to be inflated and cooled. This is the least-used of the three blow molding processes, and is typically used to make small medical and single serve bottles. The process is divided into three steps: injection, blowing and ejection.

The injection blow molding machine is based on an extruder barrel and screw assembly which melts the polymer. The molten polymer is fed into a hot runner manifold where it is injected through nozzles into a heated cavity and core pin. The cavity mold forms the external shape and is clamped around a core rod which forms the internal shape of the preform. The preform consists of a fully formed bottle/jar neck with a thick tube of polymer attached, which will form the body. similar in appearance to a test tube with a threaded neck.

The preform mold opens and the core rod is rotated and clamped into the hollow, chilled blow mold. The end of the core rod opens and allows compressed air into the preform, which inflates it to the finished article shape.

After a cooling period the blow mold opens and the core rod is rotated to the ejection position. The finished article is stripped off the core rod and as an option can be leak-tested prior to packing. The preform and blow mold can have many cavities, typically three to sixteen depending on the article size and the required output. There are three sets of core rods, which allow concurrent preform injection, blow molding and ejection.

Advantages: It produces an injection moulded neck for accuracy.

Disadvantages: only suits small capacity bottles as it is difficult to control the base centre during blowing. No increase in barrier strength as the material is not biaxially stretched. Handles can't be incorporated.

Injection stretch blow molding process

This has two main different methods, namely Single-stage and two-stage process. Single-stage process is again broken down into 3-station and 4-station machines. In the two-stage injection stretch blow molding process, the plastic is first molded into a "preform" using the injection molding process. These preforms are produced with the necks of the bottles, including threads (the "finish") on one end. These preforms are packaged, and fed later (after cooling) into a reheat stretch blow molding machine. In the ISB process, the preforms are heated (typically using infrared heaters) above their glass transition temperature, then blown using high-pressure air into bottles using metal blow molds. The preform is always stretched with a core rod as part of the process.

Advantages: Very high volumes are produced. Little restriction on bottle design. Preforms can be sold as a completed item for a third party to blow. Is suitable for cylindrical, rectangular or oval

bottles. Disadvantages: High capital cost. Floor space required is high, although compact systems have become available.

In the single-stage process both preform manufacture and bottle blowing are performed in the same machine. The older 4-station method of injection, reheat, stretch blow and ejection is more costly than the 3-station machine which eliminates the reheat stage and uses latent heat in the preform, thus saving costs of energy to reheat and 25% reduction in tooling. The process explained: Imagine the molecules are small round balls, when together they have large air gaps and small surface contact, by first stretching the molecules vertically then blowing to stretch horizontally the biaxial stretching makes the molecules a cross shape. These "crosses" fit together leaving little space as more surface area is contacted thus making the material less porous and increasing barrier strength against permeation. This process also increases the strength to be ideal for filling with carbonated drinks.

Advantages: Highly suitable for low volumes and short runs. As the preform is not released during the entire process the preform wall thickness can be shaped to allow even wall thickness when blowing rectangular and non-round shapes.

Disadvantages: Restrictions on bottle design. Only a champagne base can be made for carbonated bottles.

Stabilizers are a class of chemical additives commonly added to polymeric materials, such as plastics, to inhibit or retard their degradation.[1]Polymers can be subject to various degradation processes, including oxidation, UV-damage, thermal degradation, ozonolysis, or combinations thereof like photo-oxidation. These processes all degrade the polymer on a chemical level, leading to chain scission that can adversely affect its mechanical properties such as strength and malleability, as well as its appearance and colour.

The use of additives to protect polymers from mechanical wear, for instance by the use of fibre reinforcement, is generally considered separately.

A vast number of chemically distinct polymers exist, with their degradation pathways varying according to their chemical structure, as such an equally wide range of stabilizers exists.

Heat stabilizers

Heat (or thermal) stabilizers are mostly used for PVC, as unstabilized material is particularly prone to thermal degradation. These agents minimize loss of HCl, a degradation process that starts above 70 °C. Once dehydrochlorination starts, it is autocatalytic. Many diverse agents have been used including, traditionally, derivatives of heavy metals (lead, cadmium). Increasingly, metallic soaps (metal "salts" of fatty acids) are favored, species such as calcium stearate.[17] Addition levels vary typically from 2% to 4%. The choice of the best heat stabilizer depends on its cost effectiveness in the end use application, performance specification requirements, processing technology and regulatory approvals.

Stabilizers for polymers are used directly or by combinations to prevent the various effects such as oxidation, chain scission and uncontrolled recombinations and cross-linking reactions that are caused by photo-oxidation of polymers. Polymers are considered to get weathered due to the direct or indirect impact of heat and ultraviolet light. The effectiveness of the stabilizers against weathering depends on solubility, ability to stabilize in different polymer matrix, the distribution in matrix, evaporation loss during processing and use. The effect on the viscosity is also an important concern for processing.

Heat stabilizers are mainly used for construction products made of polyvinyl chloride, for instance window profiles, pipes and cable ducts. Light stabilizers, for instance HALS, are especially needed for polypropylene and polyethylene. The environmental impact of stabilizers for polymers can be problematic because of heavy metal content. In Europe lead stabilizers are increasingly replaced by other types, for example calcium-zinc stabilizers.

Light stabilizers

light stabilizer are used to inhibit polymer photo-oxidation, which is the combined result of the action of light and oxygen. Like autoxidation this is a free radical process, hence the antioxidants described above are effective inhibiting agents, however additional classes of additives are also beneficial, such as UV absorbers, quenchers of excited states and HALS.

UV absorbers

The UV absorbers dissipate the absorbed light energy from UV rays as heat by reversible intramolecular proton transfer. This reduces the absorption of UV rays by the polymer matrix and hence reduces the rate of weathering. Typical UV-absorbers are oxanilides for polyamides, benzophenones for PVC, benzotriazolesand hydroxyphenyltriazines for polycarbonate.

Strongly light-absorbing PPS is difficult to stabilize. Even antioxidants fail in this electron-rich polymer. The acids or bases in the PPS matrix can disrupt the performance of the conventional UV absorbers such as HPBT. PTHPBT, which is a modification of HPBT are shown to be effective, even in these conditions

Quenchers

Photo-oxidation can begin with the absorption of light by a chromophore within the polymer (which may be a dye or impurity) causing it to enter an excited state. This can then react with ambient oxygen, converting it into highly reactive singlet oxygen. Quenchers are able to absorb energy from excited molecules   via

a Förster mechanism and then dissipate it harmlessly as either heat or lower frequency fluorescent light. Singlet oxygen can be quenched by metal chelates, with nickel phenolates being a common example.

Hindered amine light stabilizers(HALS)

The ability of hindered amine light stabilizers (HALS or HAS) to scavenge radicals produced by weathering, may be explained by the formation of aminoxyl radicals through a process known as the Denisov Cycle. The aminoxyl radical (N-O•) combines with free radicals in polymers:

N-O• + R• → N-O-R
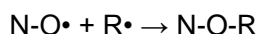
Although they are traditionally considered as light stabilizers, they can also stabilize thermal degradation.

Even though HALS are extremely effective in polyolefins, polyethylene and polyurethane, they are ineffective in polyvinyl chloride (PVC). It is thought that their ability to form nitroxyl radicals is disrupted. HALS act as a base and become neutralized by hydrochloric acid (HCl) that is released by photooxidation of PVC. The exception is the recently developed NOR HALS, which is not a strong base and is not deactivated by HCl.

Acid Scavengers

Acid scavengers, also referred to as antacids, neutralize acidic impurities, especially those that can act as a source of HCl. They are important stabilizers in many types of polymer, particularly PVC, as well as those produced using Ziegler–Natta catalysts, or that use brominated or chlorinated flame retardants. Common examples include metallic soaps, such as calcium stearate, mineral agents like hydrotalcite and hydrocalumite, and basic metal oxides such as zinc oxide.

Antioxidants

Antioxidants inhibit autoxidation that occurs when polymers reacts with atmospheric oxygen. For some compounds this can happen gradually at room temperature but almost all polymers are at risk of thermal-oxidation when they are processed at high temperatures. The molding or casting of plastics (e.g. injection molding) require them to be above their melting point or glass transition temperature (~200-300°C) and under these conditions reactions with oxygen occur much more rapidly. Sensitivity to oxidation varies significantly depending on the polymer in question; without stabilizers polypropylene and unsaturated polymers such as rubber will slowly degrade at room temperature where as polystyrene can be stable even at high temperatures.[3] Antioxidants are of greater importance during this process stage, with long-term stability at ambient temperature increasingly being supplied by hindered amine light stabiizers (HALs). Antioxidants are often referred to as being primary or secondary depending on their mechanism of action.

Primary antioxidants (radical scavengers)

Primary antioxidants act as radical scavengers and remove peroxy radicals (ROO•), as well as to a lesser extent alkoxy radicals (RO•), hydroxyl radicals (HO•) and alkyl radials (R•). Oxidation begins with the formation of alkyl radials, which react very rapidly with molecular oxygen (rate constants ≈ 10^7–10^9 mol^{-1} s^{-1}) to give peroxy radicals,[4] these in turn abstract hydrogen from a fresh section of polymer in a chain propagation step to give new alkyl radials.[5] The overall process is exceedingly complex and will vary between polymers but the first few steps are shown below in general:

R → R•
R• + O_2 → ROO•
ROO• + RH → ROOH + R•
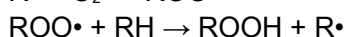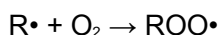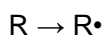
Due to its rapid reaction with oxygen the scavenging of the initial alkyl radical (R•) is difficult unless very strict air-free conditions are maintained. This is often not practical and while some antioxidants baring reactive groups such as acryloyl groups are able to act as efficient C-radical scavengers under normal conditions,[6] the majority of primary antioxidants react instead with the longer lasting peroxy radicals (ROO•). Hydrogen abstraction is usually the rate determining step in the polymer degradation and the peroxy radicals can be scavenged by hydrogen donation from an alternative source, which converts them into organic hydroperoxides. The most important commercial stabilzers for this are hindered phenols such

as BHT or Irganox 1098 and secondary aromatic amines such as alkylated-diphenylamine. Amines are typically more effective, but tend to cause discoloration, which is often undesirable (i.e., in food packaging, clothing). The overall reaction with phenols is shown below:

$$ROO• + ArOH \rightarrow ROOH + ArO•$$
$$ArO• \rightarrow \text{nonradical products}$$
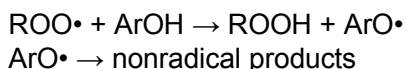
The end products of these reactions are typically quinones, which may also impart unwanted colour. Modern phenolic antioxidants often have a propionate-group at the para position (e.g. ortho-alkylated derivatives of phloretic acid) as the quinones of these can rearrange once to give a hydroxycinnamate, regenerating the phenolic antioxidant group and allowing further radicals to be scavenged.[7] Ultimately however, primary antioxidants are sacrificial and once they are fully consumed the polymer will being to degrade.

Secondary antioxidants (hydroperoxides scavengers)

Secondary antioxidants act to remove organic hydroperoxides (ROOH) formed by the action of primary antioxidants. Hydroperoxides are less reactive than radical species but can undergo hemolytic bond breaking to form new radicals. As they are less chemically active they require a more reactive antioxidant. The most commonly employed class are phosphite esters, often of hindered phenols e.g. Tris(2,4-di-tert-butylphenyl)phosphite. These will convert polymer hydroperoxides to alcohols, becoming oxidized to organophosphates in the process:[8][9]

$$ROOH + P(OR')_3 \rightarrow OP(OR')_3 + ROH$$
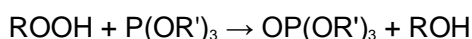
Transesterification can then take place, in which the hydroxylated polymer is exchanged for a phenol:[10]

$$ROH + OP(OR')_3 \rightarrow R'OH + OP(OR')_2OR$$
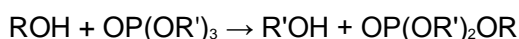
This exchange further stabilizes the polymer by releasing a primary antioxidant, because of this phosphites are sometimes considered multi-functional antioxidants as they can combine both types of activity. Organosulfur compounds are also efficient hydroperoxide decomposers, which thermally stabilize the polymers. Sulfuric acids are produced as the product of decomposition, which catalyse further hydroperoxide decomposition.

Antiozonant

Antiozonants prevent or slow down the degradation of material caused by ozone. This is naturally present in the air at very low concentrations but is exceedingly reactive, particularly towards unsaturated polymers such as rubber, where it causes ozone cracking. The mechanism of ozonolysis is different from other forms of oxidation and hence requires its own class of antioxidant stabilizers. These are primarily based on p-phenylenediamine and work by reacting with ozone faster than it can react with vulnerable functional groups in the polymer (typically alkene groups). They achieve this by having a low ionization energy which allows them to react with ozone via electron transfer, this converts them into radical cations that are stabilized by aromaticity. Such species remain reactive and will react further, giving products such as 1,4-benzoquinone, phenylenediamine-dimers and nitroxyl radicals. Some of these products can then be scavenged by antioxidants.

ANTIMICROBIAL AGENT See Biocides/Fungicides The term 'antimicrobials' is generally defined as substances, or mixtures of substances, used to destroy or suppress the growth of harmful microorganisms, whether they be bacteria, fungi or virus, in, or on, a substrate or article where it is not desired. Historically, the term 'antibiotics' is used in reference to controlling bacterial infections specifically in humans. For substances that control or inhibit yeast and fungi, the term used is 'anti-fungal,' whether on animate or inanimate substrates. Similarly, for inhibiting viruses, we refer to anti-viral substances. Besides these various terms for antimicrobial concepts, in many industries terms like bactericides, fungicides, algaecides, virucides, preservatives and biocides are commonly used. For example, in the coatings industry, the term 'biocide' is historically employed to indicate preserving a wet formulation from microbial spoilage which, in most other industries like personal care or household markets, would be defined as 'preservatives'. In addition to these various terms to indicate chemicals that inhibit or destroy microorganisms, we are also exposed to layman's terminology of 'mildewcide' or 'moldicide' to refer to chemicals controlling unsightly biological defacement on surfaces that are 'black'. Even

though it is implied primarily for fungal growth, it can also be caused by a consortium of other microorganisms including lower forms of algae, moss, amoeba, protozoa, etc. For non-microbiologists, these terms may be confusing, with each term meaning different things depending on the implied uses and claims by different suppliers. All of these chemicals can be referred to as antimicrobials irrespective of their applications, target organisms and mode of activity under a given condition. Government regulations on treated articles, including coatings with antimicrobials, and guidelines on claims come under the Federal Insecticide Fungicide and Rodenticide Act [FIFRA], EPA and FDA. Under FIFRA, an antimicrobial product that claims to control microorganisms such as bacteria and fungi requires registration. According to the EPA, an article or a substance that is treated with, or containing, a registered pesticide is defined as a treated article and is limited to protecting the article itself from microbial spoilage or contamination [for example paints supplemented with fungicides or bactericides to protect the paint in storage or after application, or preservative treatments used in wood to protect wood against insects or fungal infestation]. The EPA in 2000 issued a Pesticide Regulation Notice 2000-1 to clarify the Agency's policy with respect to the scope of the treated article exemption. It is a guidance document that focuses on the various types of antimicrobial claims that the EPA considers acceptable or unacceptable. Antimicrobials used in public or non-public health claim products have to go through a battery of tests using acceptable microbiological methods to show efficacy in the product in use. There are many test methods in microbiology described to demonstrate the antimicrobial nature of a substance and when it is incorporated in an article. There are various screening stages adopted that may include primary, secondary and in-use final testing. A typical primary-screening protocol involves testing for the minimum inhibitory concentration [MIC] of the chemical to be incorporated in an article. Normally the MIC is determined in an invitro system like growth media against a set of bacteria, fungi, virus and/ or algae depending on the target microorganism. After getting selected in the primary screen, the substance enters the secondary screening process in an in-vivo system, meaning the application matrix in which it is expected to be incorporated. Because not all selected antimicrobial substances are expected to be universally acceptable in varied systems, they next go through the rigor of compatibility, stability and efficacy testing evaluations. Some examples of this rigor in coatings applications include the chemical stability in the formulation, pH compatibility, heat stability, color acceptance, shelf storage longevity, exterior weather sustainability, etc., in addition to testing for its bio-availability to function as an antimicrobial throughout the process. With so many scenarios for defining an antimicrobial, the challenge becomes how to test and what test methods to use for demonstrating and claiming broadly the 'antimicrobial' property of a treated article such as a coating. There are several ASTM methods available such as: ASTM D 5589, ASTM D 5590, ASTM D 3273 and ASTM D 2574. Also used is the Japanese Industrial Standard JIS Z 2801-2000: Antimicrobial Products—Test for Antimicrobial Activity and Efficacy. This method was originally developed to test the antibacterial activity of silver ions impregnated in rigid hydrophobic polymers. The method was developed by a consortium of workers comprised of manufacturers of silver-based antimicrobial agents, government-based research organizations and universities, and under organizations such as the Society of Industrial Technology for Antimicrobial Articles (SIAA). This method is a quantitative measurement method that tests survival of low-dose bacterial inoculum deposited between the tested antimicrobial surface and a thin plastic film that keeps the inocula wet and nourished in a nutrient-rich environment throughout the 24 h incubation at 35 ºC. This differs from other traditional methods of testing antimicrobial resistance in coatings surfaces where the surface is not kept deliberately wet or moist with a nutrient medium. Inoculum survival and growth in the other methods depends only on the moisture from either media or humidity created in the incubated unit, so only microorganisms that can survive some level of desiccation on the surfaces in 24 h can be recovered and can be compared to the non-treated surface. In this respect, the JIS Z 2801 method is so severe it is not necessarily a realistic surface contamination model for dry walls and other coated vertical surfaces. In spite of this limitation, JIS Z 2801 has emerged as one of the industry standards for perhaps the 'worst case scenario' of a surface that retains wetness and permits microbial survival. Following the method as written for hydrophobic coatings surfaces, yields results that may provide useful information, but for hydrophilic and porous substrates and surfaces, a deviation in the inoculum delivery and validation for each different substrate would be required to get useful data. There is no one universal test protocol or one pesticide product that can demonstrate all the antimicrobial properties on all surfaces.

BIOCIDES/FUNGICIDES/ANTIMICROBIALS See Enzyme Because coatings are largely organic in nature, they provide a source of food for microorganisms. Microorganisms are found everywhere and they work around the clock trying to cause viscosity loss, putrefaction, gas formation, emulsion breakdown, and other undesirable physical

and chemical changes. These attacking species can cause discoloration, marring, loss of adhesion and finally coating failure. Microorganisms can contaminate paint in different ways during the manufacturing process. Unsanitary conditions may exist, such as for the raw materials (including thickeners, extenders, pigments, emulsions, surfactants and defoamers), water (process water and recycled water), containers and equipment (tanks, pipes, hoses, etc.). The ability of some microorganisms to attach to surfaces and form adherent biofilms is also important. Biofilms are functional consortia of microbial cells entrapped within an extensive matrix of extracellular polymer (glycocalyx) produced by them. Biofilms can be formed in water systems, processing tanks and other areas. Biofilms may be sources of contamination of the product, and may cause corrosion, scaling, the reduction of heat transfer efficiency and other problems in addition to the spoilage. Microbial biofilms are usually resistant to biocide treatments or disinfectants. Depending on the growth conditions (nutrients, minerals, gas composition, temperature, pH, water activity, etc.), microorganisms can reproduce very rapidly in the paint. Coatings need to be protected from microbe attack, and there are a number of microorganisms that the formulator needs to be conscious of when formulating paints. Sometimes the terminology of available agents is confusing: biocide, mildewcide, fungicide, algaecide (also spelled algicide) and so forth. Product literature and the suppliers will certainly assist in this regard. Many of these additives are multi-purpose and can curtail the growth of a number of organisms. Biocides (or microbiocides) are substances that will kill organisms and thus are used to protect coatings from biological attack caused by algae, fungi and other organisms that propagate in moist environments – particularly in warm climates. The "-cide" nomenclature refers to compounds that kill, in this case, microorganisms.

A biostat prevents or interferes with the growth of the organism but does not kill it. The additives are often further defined as follows to describe the particular types or organisms that are killed or affected.

Algaecide/Algicide — Chemical agent used to destroy algae. Bactericide — Compound used at low levels to kill bacteria.

Bacteriostat — Substance that prevents or slows the growth of bacteria.

Biocide — A chemical agent capable of killing organisms responsible for microbiological degradation.

Efficacy — The effect of the microbiocide on the target organism or group of organisms; can be measured as percent killed versus a control containing no biocide. Efficacy can be expressed as MIC, or minimum inhibitory concentration, against a specific organism.

Fungicide — Chemical agent that destroys, retards or prevents the growth of fungi and spores.

Fungistat — Compound that inhibits the growth of a fungus, or prevents the germination of its spores.

Mildewcide — Chemical agent that destroys, retards or prevents the growth of mildew.

Spectrum — Refers to the effect a microbiocide may have on more than one organism such that a broad-spectrum biocide will be affective against more than one group of target organisms.

For coatings we are concerned with bacteria (aerobic and anaerobic), fungi (multicellular [molds], unicellular [yeasts]) and algae (green and blue-green). The addition of an in-can preservative will protect coatings in the wet state during storage and transport. But after a coating has been applied and dried, it becomes susceptible to colonization by fungi and/or algae. Biocidal agents are available to work both "in-the-can or batch" and also in the dried film. For this reason, many manufacturers include a biocide (anti-microbial) agent in the formulation of the paint so that it can kill both bacteria and yeasts that can be present. If not corrected before they start, microorganisms can lead to the production of gases – this can occur in the container and result in can lids popping and cans distending, offensive odors emanating and loss of film and application properties. Bacterial enzymes and certain fungi attack organic thickeners, and this can lead to viscosity changes in the liquid coating. The pH of the paint can be affected and the paint can undergo discoloration. Microbial contaminants can be introduced with water (process water, wash water), with raw materials (latex, fillers, pigments, etc.) and by poor plant hygiene. Bacteria are the most common spoilage organisms, but fungi and yeasts are sometimes responsible for product deterioration. Spoilage of waterborne products, which may go unnoticed until the product reaches the consumer, can result in significant economic loss. Good plant hygiene and manufacturing practices, when combined with the use of an optimized biocide, will minimize the risk of microbial spoilage. Enzymes are organic catalysts, which

means that they are not consumed in any reactions. They are produced by living cells and are protein in chemical nature. Bacteria and their enzymes can degrade the organic components of paint – the polymer and its organic additives. One enzyme molecule can change hundreds of organic molecular structures and degrade them. The most obvious immediate result is a loss of viscosity. This renders the product unstable and unusable. This is more of a problem for architectural coatings, which tend to be warehoused, shipped and then stored on shelves for longer periods than typical industrial coatings, which are usually consumed rapidly. Manufacturers and formulators need to be conscious of the fact that the dried paint film is subject to microbe attack from mold, mildew and algae – particularly in certain climates where temperature and humidity encourage microbe growth. For dried coating films, algae and fungi can cause discoloration, dirt entrapment, cracking, blistering and loss of adhesion. A loss of adhesion is commonly associated with fungi growth as well as corrosion on certain substrates due to the moisture produced by fungi. Dependent on the climate, many exterior surfaces and roofs may be subject to algae growth, and not all fungicides are necessarily effective against algae. Certain areas of the world have already recognized this as a serious problem and one of concern for the preservation of exterior buildings. The type of microorganism that can attack the coating depends on many factors including the presence of nutrients, the moisture content and the composition of both the substrate and the coating itself. Moisture is affected by the amount of rainfall, dew, humidity, temperature and time of year. Local environment conditions such as surfaces that are sheltered from wind and shaded areas also have an impact on microbial growth. Nutrient sources include constituents of the coating, partially biodegradable material from other microorganisms or simply dirt. The substrate may affect the pH of the surface and make it suitable for microbe growth. Fungi favor acidic conditions such as those provide by wood and some species of wood are more susceptible to fungi attack than others. Algae favor alkaline conditions such as those provided by masonry. For use in architectural coatings, it is important that the fungicidal material have a low solubility in water so that it is not readily leached out of the paint film. It should also not cause any weathering effect such as fading, chalking or discoloration. Some antimicrobial agents can cause fading in architectural coatings; therefore, it is always wise to expose the formulation to Weather-Ometer testing. There are thousands of kinds of fungi and algae throughout the world. However, only a relatively few disfigure and deteriorate exterior paint films. In general, research on painted panels and structures from around the world indicates that two types of fungi are the dominant causative agents of disfigurement and degradation of modern exterior paint films. These fungi were identified as Alternaria sp. and Aureobasidium (Pullularia) pullulans. Aureobasidium pullulans is the fungus predominantly responsible for the development of mildew in exterior paints. The Pseudomonas species attacks paints, joint compounds, roof coatings, exterior insulation and finishing systems and clear finishes in the can. There are many effective biocides available for use. It is important to understand the operation of these agents and the differences in their activity. Some may be effective against certain bacteria in one concentration and effective against fungi in another concentration. Some biocides may be biocidal in certain concentrations and in other concentrations exhibit biostatic behavior. It is very important for the formulator to work with the supplier of these agents to understand their use and mode of action. Blends of biocides may often be used to enhance coating performance, as one biocide alone cannot always provide the desired results under demanding and varying climate conditions. Some of the typical chemistries of these agents include: formaldehyde donors; ortho-phenylphenol (OPPs); isothiazolinone derivatives (such as 2-n-octyl-4-isothiazolin-3-one [OIT]); guanides and biguanides (such as PHMB or polyhexamethylene biguanide); carbamates (such as 3-iodo-2-propynylbutyl carbamate [IPBC]) and dithiocarbamates; copper or sodium or zinc pyrithione; benzimidazoles; n-haloalkylthio compounds; 1-(3-chloroallyl)-3,5,7-tri-aza-1-azonia-adamantane chloride; tetrachloroisophthalonitriles; cis[1-(3-chloroallyl)-3,5,7-tri-aza-1-azoniaadamantane] chloride and 2,2-dibromo-3-nitrilopropionamide (DBNPA); and quaternary ammonium compounds. These are but a few examples of the many agents available to the formulator. Some biocides on the market today are two-for-one and eliminate the need for separate in-can preservatives and mildewcides. DCOIT – 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one is an example of one such biocide, which controls bacteria that cause coatings to degrade in the can and prevent mildew growth after the films dry. This particular biocide controls a wide range of microorganisms including fungi, algae and bacteria. The microbiological activity of 2,2-dibromo-3-nitrilopropionamide (DBNPA) was documented as a seed fungicide in 1947 and later as an antimicrobial agent. DBNPA, when formulated as a 20% solution in water and polyethylene glycol, is completely miscible with water and readily disperses upon introduction into a water-based system. The DBNPA molecule begins functioning as an antimicrobial agent immediately upon introduction into a system; the

rate of this activity is not affected by pH, and antimicrobial control is usually achieved before complete degradation occurs. The combination of instantaneous antimicrobial activity and rapid chemical breakdown makes this a costeffective and environmentally friendly biocide. It is used as a quick-kill biocide and short-term preservative in watercontaining systems that require microbe control; it is ideal for the treatment of wastewater generated during the manufacture of paint. The collection and reuse of all wash water used to rinse paint mixing vats has been emphasized as crucial to achieving environmentally responsible production. This wash water contains a high concentration of paint solids and is usually heavily contaminated with microorganisms; it must be decontaminated prior to its re-introduction into the paint production process. DBNPA is ideal for this type of application. Mildewcide (fungicide) and algaecide testing has been very confusing for paint companies. A paint formulation's resistance to attack by fungi and algae is the most difficult performance characteristic to determine; testing requires a specialized laboratory with trained personnel to work accurately with fungi and algae. The use of a single active ingredient may be sufficient to protect a coating against in-can spoilage or dry film defacement, but in many cases it may be advantageous to use a blend of the actives. For example, the combination of certain active ingredients can result in synergy whereby lesser amounts of each active are needed to bring about the same inhibitory effect as the use of either active alone.

SURFACE-ACTIVE AGENTS See Surfactants Surface-active agents are compounds that when added to a liquid alter its properties when it comes in contact with another liquid, solid or gas. These additives alter the interfacial characteristics of the liquid. Surfacecontrol additives are multifunctional, improve leveling, slip and scratch resistance, and prevent craters, orange peel, fish eyes, pin holes and pigment flotation.

SURFACE ADDITIVES/DEFECTS Additives are often used to prevent surface defects that can mar the appearance of the coating and/or the protective properties of the coating. Some of the more common surface defects that appear at the coating-air interface are: orange peel, craters, fisheyes, picture framing and popping. Surface defects that occur at the substrate-coating interface are: crawling or cissing (poor wetting), and telegraphing. There are additives, which have been discussed in other sections of this handbook, that are typically used to prevent and/or eliminate the above mentioned defects. These additives typically fall into the following types of categories: solvents, silicones (polysiloxanes), polyacrylates, fluorosurfactants and a variety of other chemical types.

SURFACE MODIFIER See Surfactants, Surface-Active Agents, Slip-Aid, Waxes A surface modifier is an additive intended to modify a particular surface property. Typical functions of surface modifiers are to: • reduce the effect of friction/surface tension of the film; • improve abrasion resistance; • alter a coating's "feel"; • modify surface appearance; and • enhance other performance properties. For example, an easily cleaned surface is an important target of new developments in architectural coatings and general industrial coatings (such as household appliances), wood coatings (kitchen and bathroom cabinets), plastic coatings (coatings for consumer electronics), marine coatings and so forth. Fluorinated resins are well known for superior durability and for excellent dirt-releasing properties. A specialty application coating in the architectural market utilizes a very hydrophilic surface that is easily cleaned by rain. This easy surface cleaning property, or cleanability, is typically a function of the specific binders selected to form the film. However, good cleanability can also be obtained with conventional binders when they are modified with certain additives. Among those additives, crosslinkable silicone containing polymers provide a unique set of properties. Silicone additives are well known for their beneficial effects in coatings. Polyether- or polyester-modified silicones not only provide good surface flow and substrate wetting, but also improvement of surface slip and mar resistance. However, the improvement of surface slip and mar resistance is limited because the silicone on the coating surface can be washed or wiped off. Hydroxyl functional polyester or polyethermodified silicones can provide longer-lasting surface slip properties, but improvement of surface cleanability is not completely satisfactory. A new, special silicone-modified hydroxyl-functional acrylate additive has been developed to enhance the surface cleaning properties (cleanability) of coatings. Crosslinkable via the –OH groups, the additive provides long-lasting significant improvements in cleanability so that adhering dust and dirt particles as well as graffiti can be removed much easier compared to 'normal' surfaces. This new development not only provides easily cleaned surfaces in hydroxyl-crosslinking binders, but also improves surface flow, substrate wetting, slip and mar resistance. Due to the described properties of this new additive, many

interesting coatings with unique surface properties can be developed for new applications. Potential areas for this new technology are in the following applications. • Polyurethane coatings for buildings, facades and ceramic tiles for tunnels that are graffiti resistant. • Polyurethane wood coatings for kitchen cabinets. • Baking alkyd-melamine and polyester-melamine coatings for household appliances. • Polyurethane coatings with improved foulant-releasing properties due to the low surface energy. • Polyurethane coatings for consumer electronics with easily cleaned and scratch-resistant surfaces. • Interior coatings for metal drums/pails/other technical metal packaging containers to provide more complete drainage. The excellent resistance to graffiti does however severely limit recoat adhesion. This additive (silicone-modified hydroxyl-functional acrylate) is only recommended for those applications not needing recoatability. Recoating is only possible with surface sanding. Wax-based surface modifiers are used to optimize abrasion resistance, raise or lower coefficient of friction, or improve chemical resistance. For a wax to perform, the material must migrate to the surface and sometimes protrude out of the coating. Surface modifiers rely on two mechanisms to migrate: (1) Stacking/ball bearing: this mechanism relies on the wax particle either being similar in size to the coating thickness, or several particles stacking and bridging. (2) Bloom/floating: in coating systems where heat is applied, the wax particles become molten or solubilize and migrate to the surface due to incompatibility or lower specific gravity. The wax may form a thin layer on the surface. If the density of the wax is significantly lower than that of the coating, the particles may float to the surface during the curing. Other variables that effect migration are raw material interaction, coating viscosity/specific gravity, curing conditions, additive chemistry and additive form. Waxes can be divided into synthetic (produced by polymerization), refined (from fossil fuels) and natural. Polyethylene (PE) waxes are produced by the polymerization of ethylene. PE waxes have a broad range of physical characteristics, providing a wide variety of performance possibilities in coatings. Melting points of PE waxes are between 100 ˚C and 130 ˚C. The features and benefits of PE waxes include good slip and matting properties; improved scratch, and mar and abrasion resistance. Polypropylene (PP) waxes are produced by polymerization of propylene. They have a higher melting point than most waxes. They are often blended with PE waxes to use their properties of high elasticity and toughness. The benefits include improved scratch resistance, very good antiblocking properties, excellent abrasion resistance and good migration characteristics. Their disadvantages are cost and poor slip qualities. Mono and bis-amide waxes are semi-synthetic waxes have higher melting points and low penetration hardness and are relatively brittle. The benefits include good matting, excellent sanding, enhancement of silky and soft feel, thickening of liquids, antisettling properties and good migration characteristics. Their disadvantages are reduced gloss, thickening of solventborne paints and they may cause yellowing in light-colored thermoset coatings. Carnauba wax, an ester of long-chain alcohols and acids, is extracted from the leaves of the carnauba palm tree. It melts below 100 ˚C and the benefits include excellent slip and good mar resistance, hardness, excellent clarity and it is FDA-compliant. Disadvantages include cost/ availability due to crop variation and the color may prohibit use in some applications. PTFE is not a wax because it does not dissolve or melt at the temperatures used in coatings, however it functions like one. PTFE produces a very low coefficient of friction in coatings and inks, and is usually used in blends with PE. The benefits include excellent slip; promotes antiblocking; improves stability against polishing; and improves abrasion, scratch, mar and scuff resistance. Its disadvantage is its high cost and it may cause intercoat adhesion problems at high levels. Waxes are available as powders, cold dispersions, and emulsions or precipitations. Particle size of waxes is very important.

SURFACTANTS Surfactants encompass a variety of compounds that are used in various ways. The term 'surfactant' is derived from 'surface-active agents,' and as the name implies, the compounds are used to alter surface phenomena. These chemicals will reduce surface tension and improve wetting and spreading (wetting agents); aid in dispersion of pigments in formulated products (dispersants); inhibit foam formation (defoamers) although others will stabilize foams; and cause or improve emulsion formation (emulsifiers). These topics will be treated individually, but in each case keep in mind that we are really talking about compounds that affect surface activity – surfactants. There is widespread use of surfactants in waterborne coatings where surfactants play a crucial role, and yet the same compounds can cause problems in the final film that is laid down. In the chemical industry, surfactants have been used for many decades to: emulsify oil and water systems; as wetting agents; for dispersion of solids in liquids; as defoamers; and as foam stabilizers in the polyurethane industry. At times it is difficult to categorize, define or associate particular surfactants in an end-use sense, because the same surfactant can be used as a dispersant in one application and as an emulsifier in another application. Thus, the roles of some of these materials can overlap and complement each other. The quantity of surfactant used can also play an

important part in how the compound functions. Sometimes too much of a 'good thing' can turn it into an 'undesirable thing.' For this reason, it is important to discuss surfactant usage with suppliers. Surfactants are chemical compounds that have a hydrophilic or 'water-loving' portion and another portion that is hydrophobic or 'water-hating' in nature. Often the molecules are oligomeric in nature. This is particularly true in the case of nonionic surfactants. Usually the hydrophobic portion of the molecule is comprised of long-chain hydrocarbons such as fatty acids; straight, branched or cyclic hydrocarbons; or aromatic hydrocarbons with or without alkyl side groups. The hydrophilic portion of the molecule will contain groups that attract or are attracted to water molecules. Groups such as hydroxyl, carboxyl, sulfonate, sulfate and the like will be found in the hydrophilic portion of the molecule. In other cases, the hydrophilic portion will be an ethylene oxide chain that is relatively short – it is well known that each oxyethylene group will strongly associate and complex with two or three molecules of water, which markedly changes their nature. In addition, other water molecules will less strongly associate with the water/oxyethylene complex that is formed. Oxyethylene/oxypropylene copolymers are surface active and used in specialty areas. Surfactants preferentially concentrate at interfaces. These interface surfaces or interfacial regions are where one continuous phase ends and another begins. By their chemical nature, surfactants lower the total energy associated with the boundary and stabilize it. For example, consider a container with oil and water. The boundary layer between the two substances will be well defined, and there is a large energy involved in keeping the boundary layer stationary. If the system is shaken, the oil will disperse into the water because energy is being supplied by shaking, and this overcomes the energy holding the boundary in place. However, if allowed to stand under room conditions, the system soon returns to its original condition with a single boundary dividing the substances. If we add surfactant to the system, the oil is broken into droplets and dispersed. However, the process has created a large number of tiny drops of oil that are now dispersed in the water. The system is more or less stable. All of the droplets formed have surfaces that are now in contact with water. There has been a very large increase in the interfacial contact area between the two substances. The only reason this dispersion of oil into droplets can take place and be maintained is because the energy associated with the large surface has been significantly reduced. It should be apparent from this discussion that surfactants can have a marked affect on the interfacial forces between materials. They modify the properties of liquid-liquid, liquid-gas and liquid-solid interfaces by changing the interfacial tension. The usual effect of a surfactant is to decrease the surface tension of an aqueous system such as a waterborne coating. In such systems, the surfactant concentrates at the air/ liquid interface. Surfactants vary in their ability to cause defoaming. As mentioned above, excessive use of surfactants in aqueous coatings can cause the undesirable situation of foam formation and stabilization. Although essential in latex preparation, it should be kept in mind that the hydrophilic portion of the surfactants is immiscible with the polymer matrix, which is hydrophobic in nature. During film formation, this immiscibility results in hydrophilic surfactant domains in the film, and these can have an effect on adhesion, moisture sensitivity and appearance. New surfactants that are copolymerizable or otherwise non-migratory in nature are being developed. In an overall sense, surfactants are classified according to the electronic charge associated with the molecules. They fall into four categories: nonionic, anionic, cationic and amphoteric. 1. Nonionic Surfactants. Nonionic surfactants usually refer to polyoxyethylene derivatives although other surfactants are included in this category. They are usually prepared by the addition reaction of ethylene oxide to hydrophobic compounds that contain one or more active hydrogen atoms. Examples of such hydrophobic compounds are fatty alcohols, alkyl phenols, fatty acids, fatty amine, alkanolamines, fatty mercaptans, fatty amines and certain polyols. The polyols can include oxypropylene polyols, polyesters, and the like. These surfactants do not carry a charge nor do they dissociate. Their surface-active character comes from the oxyethylene portion of the molecule. Both the nature of the hydrophobe and the length of the oxyethylene chain have an effect on the surface-active character. Nonionic surfactants are the most common ones used in latex coatings. In such systems, these surfactants do not ionize. Instead, they hydrate in water through association complex formation and hydrogen bonding at the ether-oxygen sites as well as interaction with the hydroxyl groups that usually, but not necessarily, are found at the end of the molecule. Overall, these groups are weakly hydrophilic in compari son to the hydrophobic portion of the molecule. Also present in many nonionic surfactants are weak ester and amide linkages. Because of this difference, or needed balance between hydrophilic and hydrophobic nature, the oxyethylene portion of the molecule is much larger than the hydrophobic portion in a molecular weight sense. A particular advantage of the nonionic surfactants is that they are compatible with ionic surfactants. For example, many nonionic surfactants function well with anionic surfactants. In such combinations, they impart good freeze-thaw stability to aqueous

systems and are less deleterious to mechanical properties than the ionic compounds. Nonylphenol ethoxylate (NPE) is a typical example of such surfactants. Other examples are: octylphenol ethoxylates (OPE), secondary alcohol ethoxylates, trimethyl nonanol ethoxylates (TMN), specialty alkoxylates, and amine ethoxylates. In emulsion polymerization, alkyl ether sulfates are one of the major surfactants necessary to provide for the stabilization of micelles. Traditionally, these sulfates have been based on alkylphenol ethoxylates (APEOs). Their good cost/performance coupled with their distinctive structural and physical properties led to their widespread use in emulsion polymerization. Typically, emulsion polymerization uses two types of surfactants – one nonionic and the other anionic. Each provides separate stabilization mechanisms for the micelles, but the combination provides better stabilization, especially as temperature increases. The nonionic surfactants bestow a steric separation between micelle groups, while anionic surfactants yield a charged repulsion between the micelles. Alternate surfactants are desired to expand formulators' surfactant options and product materials free of APEOs. Narrow-range alcohol ethoxylates, based on different hydrophobic feedstocks, are effective APEO alternatives as nonionics in emulsion polymerization. New APEO-free ether sulfates have been developed that yield emulsion polymerization characteristics similar to that of the APEO-based ether sulfates. Globally, many areas have banned use of APEOs for applications where surfactants could contact sewer water, and as a result the use of NPEs and NPE sulfates is being phased out. Nonionic surfactants generally perform well over a range of pH values, and they will usually foam less than anionic and cationic surfactants. However, nonionic surfactants may not lower the surface tension as well as anionic or cationic surfactants in complex coating formulations. There are non-ionic polymeric fluorochemical surfactants that provide low surface tensions in organic coating systems. The lower the surface tension, the more effectively a coating wets, levels and spreads. Consequently, these are excellent wetting, leveling and flow-control agents for a variety of waterborne, solventborne and high-solids coatings systems. This is particularly important on surfaces that are not clean, as contamination, surface defects and hard-to-wet surfaces can cause orange peel, cratering, fish eyes and picture framing. When a surfactant is added to a coating, it concentrates at the interface between the liquid and the substrate. That is because surfactant molecules are made up of two groups: a soluble group and an insoluble group. The insoluble end tends to push out of the liquid and the soluble end tends to be pulled in. These combined actions lower the surface energy of a liquid and allow it to better wet, level and flow over a surface. Most of the fluorosurfactants are soluble and compatible with most polymers and continue to be active throughout the drying or curing process. When used in waterborne systems, they tend to reduce the aqueous/organic interfacial tension and remain surface active in the organic portion of the polymer system. Alkyl Phenol-Free Nonionics Because of increasing recommendations to phase out the use of alkyl phenol ethoxylates (APEs), new generations of APE-free nonionic surfactants are available. They are based on C12-16 natural fatty or synthetic alcohols and primary and secondary isomeric alcohols. They are APEfree and biodegradable; have low viscosity, excellent water miscibility, high solids content, low freezing point range and are easier handling at low temperatures.

2. Anionic Surfactants. These surfactants carry a negative charge on the hydrophilic portion of the molecule. They are usually phosphates, sulfates and sulfonates. Anionic surfactants are good emulsifying and wetting agents, but they do not impart good mechanical properties or freeze-thaw stability. These surfactants may or may not contain an oxyethylene chain in their structure. Examples of anionic surfactants are sulfosuccinates, dioctyl sulfosuccinate (DOSS), polyether sulfates, polyether sulfonates, polyether phosphates, sodium lauryl sulfate and phosphate ester-modified alcohol-ethoxylates. Generally speaking, anionic surfactants perform best in alkaline coating systems. Surface-active phosphate esters are a class of anionic surfactants prepared by the reaction of alcohols with an activated phosphoric acid derivative – including phosphoric acid anhydrides and acid chlorides. Typically, phosphate ester commercial products are composed of a mixture of monoester, diester, free-phosphoric acid and free alcohol used in its preparation. The property of the final phosphate ester product is primarily defined by the starting alcohol used as well as on the composition of the four different species. Conversely, the property of the final phosphate product can be tailor-made by altering the alcohol used in the preparation as well as controlling the ratio of the four different components present in the final product. Phosphate ester surfactants are made in the free-acid form, but can also be neutralized to the salt form using any base including sodium hydroxide, potassium hydroxide, ammonium hydroxide or any organic amine. As a result of the surface activity provided by combining the alcohol used (hydrophobic component) and the anionic phosphate moiety (hydrophilic component), these products are widely used in a number of industries because of their wetting, dispersing and emulsifying properties – as wetting and dispersing agent, emulsifier, hydrotrope or

stabilizer. In addition, the presence of the phosphate moiety imparts some complex interactions with metallic surfaces, thereby exhibiting anti-corrosive and metal adhesion properties. Phosphate ester surfactants have also been found to successfully stabilize reactive pigments such as iron oxide and zinc oxide. The phosphate ester moiety does not easily hydrolyze upon exposure to extreme pH conditions – phosphate ester surfactant will be present in the application when needed. General applications of phosphate ester surfactants rely on its surface activity. Initially, phosphate esters were designed for application as cleaners, detergents and scouring agents in textile processing. Over the last 50 years, they have also found wide utility in other industries including emulsion polymerization, agriculture and metal working as wetting and dispersing agents, hydrotropes, emulsifiers, and stabilizers. For coating applications – including water- and solventborne coatings and ink applications – it has been determined that the introduction of the phosphate moiety into the formulation as a wetting and dispersing agent also significantly enhances the gloss and color acceptance properties, reduces the viscosity buildup of the paint with aging, inhibits rust corrosion (flash rusting as well as long-term corrosion resistance), promotes adhesion to metal surfaces, and provides films that exhibit lower water sensitivity (as compared to coatings with conventional surfactant additives). These phosphate esters are typically used as auxiliary dispersants to result in more stable, more homogeneous dispersions. In addition, supplementing certain phosphate esters to low-VOC formulations to replace glycols and other volatile reagents in waterborne formulations result, in most instances, in improved block resistance, open time and freeze-thaw stability. Typically, the phosphate ester surfactants are added into the formulation during paint manufacture – added either in the grind or letdown depending upon the formulation. These additives have also been tested as post-paint formulation additives and have exhibited comparable properties. It has been speculated, and is the focus of a number of investigations, that use of the phosphate ester surfactant before the paint formulation stage – use of phosphate esters in emulsion polymerization as well as post polymerization stabilizer or additive in pigment dispersion – should only benefit the final property of the paint as well as reduce the detrimental effects of additional surfactants into the paint system.

3. Cationic Surfactants. These surfactants carry a positive charge. As a rule, cationic surfactants do not play a significant role in emulsion polymerization. Compounds such as alkyl trimethyl ammonium chloride typify these surfactants. Generally speaking, cationic surfactants perform best in acidic coating systems.

4. Amphoteric Surfactants. Amphoteric surfactants exhibit both positive and negative character. An example of these compounds is lauryl betaine. Amphoteric compounds have been developed for the prevention of flocculation of carbon black and other pigments in high solids systems. They have also been used to prevent viscosity increases where polymer solubility is causing rheology problems.

ANTI-SLIP AGENT : Any material added to a coating that will reduce or eliminate the hazard of slipping on the surface of the dried film. Surface roughness or an increase in coefficient of friction accomplishes this. A coating surface on floors, curbs, streets, porches, decks and so forth may be slippery particularly if damp and, therefore, there is often a need to add an anti-slip agent to the coating to enhance the surface roughness. Polyolefins with high COFs (coefficient of friction) are widely used in both commercial and consumer formulas for floor finishes. This is not to be confused with the slip or lubricity that many coatings are designed to have particularly in manufacturing, packaging and transporting coated goods.

ANTISTATIC AGENTS Anti-stats are materials that, when added to the coating or applied to the film, make it less conductive, or less attractive to dust, lint or other airborne particulates. Conventional antistatic agents used to increase the conductivity of polymeric materials so as to permit dissipation of electrostatic charges can be separated into four general categories. 1. Hydroscopic surfactants such as tertiary fatty amines and their quaternary ammonium salts, monoacyl glycerides, monoalkyl and dialkyl phosphates, alkane sulfonates and sulfonamides work by blooming to the surface and attracting a conductive film of atmospheric moisture. These antistatic surfactants are humidity-dependent and work on the chemical principal of limited polymer solubility, blooming to the polymeric surface to provide sites for water absorption from the atmosphere. Examples are: glycerol monostearate, stearyl phosphate, dodecylbenzene and sulfonamide. 2. Conductive pigments, metal powders and other additives, which dissipate the electronic charge proportionate to their loading in the polymer. Carbon black, graphite fiber, metal powders, barium titanate powders, potassium titanate whiskers, metal-doped

silicas, TiO2 and fibers provide a low-resistance pathway to dissipate the electrostatic charge and provide permanent antistatic protection. 3. Metallocenes that provide a low-energy transfer of electrons between adjacent aromatic layers. The primary example is bis(methyl) cyclopentadienyl cobalt. 4. A new class of antistatic agents based on combined neoalkoxy titanates and/or zirconates and subsequent tri-neoalkoxy zirconates that can be added in minor amounts during compounding. Antistatic agents are in hydrophobic coatings such as the silicones to improve the coating's resistance to dirt pick-up. These additives are usually cationic in nature, but in certain instances they are nonionic hydrophilic compounds. Anti-static additives enhance the electrical conductivity of electrostatic spray paints, improve gloss, reduce the Faraday effect in powder coatings, and retard dust attraction on the finished product. (The Faraday cage effect is observed in the powder coating of parts that have recesses, inside corners, channels or protrusions on the surface of the substrate. The Faraday cage is the area of the part where the external electric field created by the gun does not penetrate.) These static dissipative materials can be blended internally with powder coatings to enhance the electrostatic spray characteristics of the coating and minimize dust attraction. This increases the transfer efficiency, which improves penetration into corners and recesses. The anti-stats seem to have no adverse affect on the physical characteristics of the final powder coating such as: impact resistance, pencil hardness, gloss, gel time, color, adhesion, cure time, salt spray and condensing humidity. These agents are able to control gassing and minimize pinholing in the coating. For powder coatings both charge control and antistatic agents are used. Charge-control agents improve the transfer efficiency and the ability of the powder to penetrate the Faraday cage areas. The function of the antistat agents is to improve the ability of the coating to conduct extraneous electrical charges to ground. These additives are used to decrease the surface resistivity of the powder and the applied powder coating. Antistatic additives reduce the powder resistivity so that the powder particles charge more efficiently. This in turn improves the overall efficiency of the coating process. Several types of materials are used to reduce resistivity. Quaternary ammonium salts (cationic) or alkyl sulfonates (anionic) based on fatty acid derivatives are often used. Some of the cationic antistatic agents are catalysts for epoxy-containing powders and have a tendency to cause yellowing when baking. Barium titanate is also used to promote powder-charging characteristics.

ANTI-BLOCKING AGENT Additive used to prevent the undesirable sticking together or adhesion of painted surfaces under moderate pressure, or specified conditions of pressure, temperature and humidity; or during storage, manufacture, or use. Blocking is a measure of the coating's ability to resist adhesion to itself (on another freshly coated surface) or adhesion to other substrates, for example, weather-stripping, doors, hardware etc. A well-known example of blocking is when a freshly painted window frame is too rapidly closed. Sometimes it can be very difficult to open the window again. Blocking is a key performance parameter for architectural application and, for industrial and OEM applications, block resistance is important in the manufacture of roll stock that will be unrolled at a later date. It is also important for reducing the need for storage space for freshly painted parts. ASTM D 4949 may be used to measure blocking performance. Factors affecting blocking include the coating surface free energy, topography of the coating, the hardness and the Tg of the polymer. One approach to improve the block resistance of a coating is to introduce a surface-active agent that will bloom to the top – the air interface – of a film as it dries/cures. Carbinol-functional silicone polyether copolymers impart mar resistance and anti-blocking properties in addition to leveling and wetting. Methacrylate functional silicone polyether copolymers provide consistent and longlasting slip, mar resistance and anti-blocking to UV-cured coatings. Fluorochemical additives can be mixed into coating formulations, often as post-adds, and migrate to the air interface where they can provide effective protection where it is most needed, without affecting recoat adhesion. Common applications include latex semi- and highgloss architectural paints used on doors and window trim, and applications where painted parts are stacked for shipping. Waxes decrease blocking so that unwanted transfer or adhesion to a contacted surface is prevented. This can be very important for materials that are coated, dried and stacked for storage and shipping. Waxes can be used in any type of coating that could benefit from mar resistance and/or a slip aid. Both water- and solvent borne metal coatings benefit from added lubricity and abrasion resistance. HDPE, paraffin and Carnauba waxes are typically used to counteract blocking. Anti-blocking agents are also very useful for any type of items that are coated, dried and immediately stacked or rolled up for storage or shipment. It should be noted that anti-blocking additives, since they tend to gather near the top surface of a film can change the appearance of a film – the gloss level. The type of paint is also a variable.

BACTERICIDES See Biocides/Fungicides Bactericides are additives that will kill bacteria (single-celled aerobic or anaerobic organisms) that can cause a variety of problems in liquid coatings and coating films. Examples of suitable compounds include: hexahydro-1,3,5-tris (2-hydroxyethyl-s-triazine), sodium pyrithione, isothiazolinone-based chemicals, 1-(3-chloroallyl)-3,5,7-tri-aza-1-azoniaadamantane chloride, formaldehyde-releasing compounds, and biguanides (polyhexamethylene biguanide [PHMB]).

COUPLING AGENT Coupling agents are compounds that promote adhesion between dissimilar compounds. These compounds are often used for the surface modification of fillers, wherein they attach themselves to the filler by means of a hydrolysis reaction and then leave a functional group available for reaction with the coating, ink or adhesive. The main general classes of coupling agents are comprised of the silanes and titanates. Most of the organosilanes have one organic substituent and three hydrolyzable substituents. For surface treatment applications, the alkoxy groups of the trialkoxysilanes are hydrolyzed to form silanolcontaining species. The final result of reacting an organosilane with a substrate ranges from altering the wetting or adhesion characteristics of the substrate, utilizing the substrate to catalyze chemical transformations at the heterogeneous interface, ordering the interfacial region, and modifying its partition characteristics. It includes the ability to effect a covalent bond between organic and inorganic materials. Titanates, zirconates and aluminates are used as coupling agents. Titanates act as organometallic chemical bridges between two dissimi- lar phases such as an inorganic pigment and a polymer binder – or as an adhesion promoter for a coating on a metal substrate. They provide an alternate to silane coupling agents and couple to non-silane reactive substrates such as CaCO3, carbon black and phthalo blue. Titanates have six functions. 1. Coupling to form atomic monolayers on inorganics rendering them hydrophobic and organophilic, thus allowing complete dispersion and deagglomeration of pigments and extenders with minimum shear and work energy. They promote adhesion, significantly lower system viscosity and shift the critical pigment volume concentration (CPVC). 2. Catalysis to lower bake times and temperatures; to induce increased strain strength to the polymer binder to increase mandrel flexibility and reverse impact strength; to compatibilize dissimilar organics; and to synthesize polyesters. 3. Heteroatom to phosphatize and prevent corrosion or intumesce and add flame retardance. 4. Alkyl/aryl functionality to create polarity for adhesion and compatibilization. 5. Thermoset functionality to densify the degree of crosslink and hardness. 6. Molecular structuring to create stable organometallics. Designer waxes are also excellent coupling agents and since they are produced by metallocene catalysis it is possible to tailor their properties to individual applications. They are important additives in wood-plastic composites (WPCs). WPCs are a new type of natural fiber composite with up to 90% wood fiber or wood flour content. The plastic matrix is usually polypropylene or polyethylene, although polyvinylchloride is also used. Since wood and plastic differ, especially in their polarity, suitable coupling agents such as polyolefin grafted with maleic anhydride must be added. They significantly improve the mechanical parameters of tensile stress and bending load in WPCs. The polar functional groups of the coupling agent react with the OH groups of the wood and form a genuine chemical bond. The non-polar areas of the coupling agent have strong affinity to the non-polar polyolefin chains. Solvents that cause two immiscible liquids to homogeneously mix are also referred to as coupling agents.

DEFOAMER See Deaerators for discussion on microfoam. Additive used to reduce or eliminate foam in a coating or coating constituent. The terms 'defoamer' and 'antifoaming' agent are often used interchangeably. In fact, they are not quite the same. A defoamer is a surface-active agent that stops the foam and breaks the bubble once it has been formed. It is a bubble breaker. An antifoaming agent prevents the formation of foam so it never forms. The term "foam-control agent" is a more appropriate term to use. In an aqueous formulation, it is almost impossible (at acceptable use levels) to totally eliminate all foam. The correct foam control agent will help to prevent foam formation, but more importantly, it will allow the dried film to be free of foam and any resultant film defects that might result from an air void in a film. There is a difference between macrofoam and microfoam. Macrofoam is located mostly on the coating surface and is surrounded by a duplex film with two liquid/air interfaces (double layer), whereas microfoam occurs inside of a coating film (air entrapment) and is characterized by a single liquid/air interface. These two types of foam also differentiate defoamers from deaerators. Defoamers are mostly effective against macrofoam, whereas deaerators suppress microfoam. In practice, the terms are

frequently confused and used interchangeably. Many of the commercial products are optimized to prevent macro- as well as microfoam. Both kinds of foam impair the surface optics of the coating and cause surface irregularities, as well as reduce gloss and transparency. Microfoam also adversely affects the coating's protective properties because the effective film thickness is reduced and pinholes can form from the micro bubbles. The function of defoamers is based on disturbance of the double layer of the macrofoam lamella. Substances with very low surface tension are used as they are not wetted by the foam bubble. Foamstabilizing substances move away from the defoamer droplet, which finally causes collapse of the bubble. Surfactants are often used with defoamers to improve the spreading of the defoamer droplet on the bubble surface. Foam may be introduced at various stages of manufacture and use of the coating. The raw materials used to make a coating, such as surfactants, dispersants, etc., enable foam to form. Entrapped air, or foam, is introduced into the manufacture of most paints as part of the process. Manufacturing care must be taken to avoid entrapping air during production by choosing the correct stirring equipment and stirring conditions. Letting the product stand for as long as possible is also helpful in preventing air entrapment. High levels of foam may occur during the milling stage, and defoamers are often used as a component in a grinding paste. Due to the activity of some surfactants at the air/water interface, foam is often created and stabilized in both the pre-mixing and milling chambers of dispersing equipment. Foam slows down the process of dispersion and adversely affects the moisture resistance of the coating. Using silicone anti-foam agents may present an additional potential for surface defects. Foaming occurs during application to some degree, depending on the method of application. For example, curtain coating carries entrapped air continuously around in the system. Entrapped air also occurs with airless spray systems. Airless spray does not use compressed air. Paint is pumped at increased fluid pressures through a small opening at the tip of the spray gun to achieve atomization. When the pressurized paint enters the low-pressure region in front of the gun, the sudden drop in pressure causes the paint to become an aerosol. Airless spraying has several distinct advantages over conventional air-spray methods. It is more efficient than the air spray because airless spray is less turbulent and, therefore, less paint is lost in bounce back. The droplets that are formed are usually larger than conventional spray guns and produce a heavier paint coat in a single pass. The system is also more portable, production rates are nearly double and transfer efficiency is usually greater. Other advantages include the ability to use high-viscosity coatings and to have good penetration in recessed areas of work pieces. One major disadvantage of airless spray is that pinhole formation from air entrapment is possible. Air-assisted airless spray is similar to airless application except that a small amount of atomizing air is used to further improve coating atomization. Spray application in relatively low humidity conditions or in high-temperature conditions can increase the tendency for foam entrapment. Latex paints are stabilized with surfactants that easily generate foam under agitation. Elimination of this foam is essential for the manufacturing process, for storage and for good application properties. Foam reduction can also be somewhat controlled by optimizing the settings on a spray gun and by adjusting the viscosity/solids level in the formulation. Foam is a dispersion of a relatively large volume of gas in a small volume of liquid. Gases are soluble in liquid media to different extents and are influenced by temperature. As the paint film starts to dry, the dissolved gases try to escape in the form of bubbles. A bubble, as a sphere, requires the least amount of surface energy. Large bubbles rise faster than small ones and collect on the surface. They are often covered by a surface film of surfactant or other additive in the coatings system. On the surface, the bubbles pack side by side as densely as possible. In some systems, densely packed microfoam can form on the surface and remain there even after the film has cured. This is possible for high-build systems like some plastisols. In the process of bubble escape, tiny pores may be formed in the film. In lower solids films that dry quickly, the viscosity of the coating is increasing quickly with drying. As this is happening, the smaller micro bubbles are still rising to the surface but quite slowly; in the process these bubbles can form small channels. If the rising bubble penetrates the surface, lack of flow allows for the formation of pinholes – a surface defect. Sometimes these microbubbles cannot penetrate the surface, but they will push a very thin, viscous layer of coating to the front surface. This layer will remain on the surface after drying or curing and becomes a spherical blister. Good defoamers not only need to be good bubble breakers, but they need to be able to keep the action sustained and maintain good defoaming over time in both oven and room temperature aging studies. Good defoamers need to be insoluble in the foaming system. If the product is too soluble it will only increase foaming. Defoamers need to have excellent dispersibility throughout the systems. Spreadability is the ability of the product to spread evenly and uniformly on the surface, coating the bubble particles and eliminating them. They work by lowering the surface tension around the bubble and cause them to coalesce to larger bubbles and eventually to

break. Most foam-control agents for aqueous systems consist of carrier, actives (hydrophobic materials) and other additives that enhance spreading, compatibility, product stability, etc. Some examples of carriers include mineral oils, vegetable oils, glycols, glycol ethers, alcohols, silicone oils and water. Three types of actives are most common: hydrophobic silica, hydrophobic silicone and organic materials that are hydrophobic/lipophilic. Many foam-control agents are blends of the above actives. The other additives vary from surfactants, co-solvents, thickeners, etc.

ANTI-FOAMING AGENT See Defoamer, Foam Control An anti-foam additive is used in coatings manufacture to prevent the formation of foam, or it is added to a mixture to destabilize foam and act as a bubble breaker, breaking the foam that has already formed. The terms 'defoamer' and 'antifoaming' agents are often used interchangeably. In fact, they are not quite the same. A defoamer is a surfaceactive agent that stops the foam and breaks the bubble once it has been formed. It is a bubble breaker. An antifoaming agent prevents the formation of foam so it never forms. The term 'foam-control agent' is a more appropriate term to use and they function by a variety of mechanisms to prevent or rupture foam. Quite often defoamers are proprietary blends of various ingredients such as mineral oils, organic solids and surface-active compounds; fatty oils, surfactants and silica derivatives; alcohols, silica derivatives and surface-active compounds; esters, mineral oils and silica derivatives; and the like. Such blends are compounded for special problems such as:

• quick foam "knock-down" coupled with long-lasting foam prevention in latex manufacture and latex coatings;

 • controlling foam in stripping operations;

• foam control in food applications where FDA product acceptability is needed;

• foam control in paper coating and dyestuff applications;

 • foam elimination in effluent systems;

• prevent air entrainment and/or facilitate air release from coatings during the filtration and filling processes;

• prevention of foam formation during roller application of architectural coatings;

• aid in the breaking of bubbles formed during roller application of latex coatings; and

• prevention of air entrainment in flash tanks and stripping columns. With such product and specific end-use complexity, it is desirable to contact a supplier for product suggestions, point of application and amounts needed to efficiently eliminate difficulties.

DEGASSING AGENTS Specific chemicals that allow for the release of volatiles in a molten powder film. Volatiles can be interstitial air, blocking agents, and lowmolecular-weight polymeric fractions. Benzoin is typically the choice for degassing powder coatings. In the absence of benzoin, the air bubbles start to shrink very slowly as a result of a diffusion-controlled process. Quite remarkably, in the presence of benzoin, the bubble shrinkage process is accelerated to such an extent that most air bubbles disappear before any significant increase in the viscosity occurs due to the curing of the coating. This suggests that benzoin functions by accelerating the rate of bubble shrinkage. Yellowing side effects of benzoin on powder coatings may be associated with the formation of benzyl, the common oxidation product of benzoin.

DYES (FOR USE IN STAINS) Dyes are soluble colorants, which do not scatter light, but which absorb certain wavelengths and transmit others. Dyes are generally soluble in a solvent, or they may exist in such a finely dispersed state that they do not scatter light and behave as if they were in solution. Pigments are basically insoluble in the medium they are in. Dyes are frequently used in the printing and coatings industry where a high level of transparency is required. Dyes have also found their way into automotive finishes because of advanced polymer technology again because of their transparency and color properties. In general, dyes fall into one of three categories: metal-complex dyes, basic dyes and fat-soluble dyes. For wood applications, dyes may offer deeper penetration of the wood surfaces and less grain hiding. However, they also fade more quickly than pigmented stains and require more effort to prepare the wood. Water-based dyes tend to raise the grain on many

woods because the water penetrates the wood and raises the tiny fibers. Wood should be wetted first, then sanded down, before applying water-based dyes. Nongrain-raising (NGR) dyes need to be used in a nongrain-raising solvent. They dry faster than water-based counterparts, so application must be faster to avoid lap marks. Liquid, high-concentration anionic dyes with good light fastness properties can be diluted in water or water/alcohol/glycol mixtures and optimized for interior use in water-based and water-containing wood stains. Neozapon® dyes are metal-complex dyes, available in powder and, in some cases, high-concentration liquid form (Neozapon® L). They are highly soluble in polar solvents, but almost completely insoluble in water. Due to their limited weather fastness, these dyes are recommended for interior use.

FLAME RETARDANTS See Lubricants (Solid) Chemicals or chemical preparations that will reduce flammability or retard the spread of flame. Combustion occurs when a substance is heated to its flammable temperature in the presence of oxygen. As it is being heated it starts to decompose, and, as it does so, it produces flames. Over the years we have become increasingly conscious of safety, and as such, are concerned about the materials that are used in the construction and finishing of buildings. This includes coatings. The application of a flame-retardant coating can help to reduce the combustibility of that coated surface. Flame retardants are compounds that are decomposed by heat into nonflammable fragments. These fragments have the ability of slowing flame spreading and may even retard or suppress the combustion reaction. This is accomplished by suppressing oxygen availability, the building up of protective layers of char at the surface, inhibiting the combustion reaction within the flame area, or by other mechanism. Inorganic compounds that are used as flame retardants include aluminum trihydroxide $Al(OH)_3$, magnesium hydroxide $Mg(OH)_2$ and boric acid. Organic flame retardants tend to fall into two categories: (1) phosphorus compounds such as phosphoric and phosphonic acid esters, such as long-chain ammonium polyphosphate products; and (2) halogenated compounds such as chlorinated paraffins, dibromoneopentyl glycol, tetrabromophthalic acid anhydride, brominated diphenyl, chlorine and bromine containing polyols or diphenyl oxide compounds together with antimony trioxide. Also chlorinated paraffins have been added to latices to impart flame retardancy. Liquid chlorinated paraffins improve the flame resistance of coatings, are cost-effective extenders of most resins and can be nonvolatile plasticizers. They also improve adhesion, water and chemical resistance, and oil and gas resistance. Dispersions and emulsions of resinous, and liquid chlorinated paraffins are available and are useful in both cationic and anionic emulsion systems because of their non-ionic bases. In addition to contributing to flame retardancy, they improve adhesion, impart chemical and water resistance, and allow the user to formulate aqueous rather than solvent systems. Applications include rubber coatings, paper and fabric coatings. Compounds that will cause char formation, particularly those with a large number of carbon-carbon double bonds or those that swell (intumescent systems), such as cellulose and sugar derivatives and melamines, are also used to enhance flame retardation. Zinc borate is used in many fire-retardant and intumescent coatings, usually in combination with chlorowax or some other halogenated source. Other fire-retardant additives, such as antimony oxide and/or alumina trihydrate, are also used to provide synergism leading to a high degree of fire retardancy. Zinc borate behaves as a fire retardant and smoke suppressant. Certain monomers – copolymers of vinyl chloride and vinylidene chloride – tend to be less flammable than non-chlorinated polymers, but because chlorine is less effective than bromine or phosphorus, additive flame retardants are still needed. Work has also been done in this area using dibromostyrene-based latices. These are copolymers of dibromostyrene with various monomers, depending on the desired Tg of the final coating. Dibromostyrene-based butadiene and acrylic latices have the desired physical properties for use in

coatings, adhesives and sealants. Fire-retardant coatings that are non-intumescent provide retardancy through the presence of special additives. The most commonly used is antimony trioxide used with halogenated materials such as chlorinated paraffins. Antimony trioxide alone is not effective; mixed with a halogenated species it is very effective. Zinc borates and barium metaborates are also used to improve the performance of antimony trioxide. When they melt, they form a glasslike material that seals off the substrate from the flames. Phosphates are also good retardant additives, and during a fire they will release phosphoric acid that will break down cellulose into a char and lessen the amount of material evolved and released. These have been used quite effectively. A new, low-load-level flame retardant, FlexB™, is a boron-based, non-halogenated additive for nylon, epoxies and water-based coatings. Material testing has achieved UL-94 V-0 ratings with loading levels as low as 3%. FlexB is targeted at high-performance materials where traditional high load levels negatively affect weight, strength and other physical parameters. FlexB shows increased flame retardancy over the more traditional additives due to its ability to bind into the backbone of the polymer, providing four levels of protection: off-gassing, water production, charring and thermal shielding. Intumescent coatings are particularly interesting because when subjected to the extreme heat of a flame these agents expand to nearly a hundred fold of their initial volume. In the process they prevent the flow of oxygen. Intumescent coatings are fire-retardant coatings that protect the substrate by puffing up when exposed to high temperatures and forming an insulating protective layer over the substrate. Initially this type of coating, when exposed to high temperatures, will char and expand greatly to retard the spread of the flame by essentially forming a foamed barrier. The expanded coating is often over 100 times the thickness of the original coating.

FOAMING AGENTS Foaming agents are materials that increase the stability of a suspension of gas bubbles in a liquid medium, or they can also be blowing agents, which generate inert gases causing a cellular or foam structure.

PLASTICIZERS A material used to increase the flexibility or elongation of an inherently brittle film or to improve flow and processability or reduce brittleness in plastic compositions. Great care must be taken in the choice and level of plasticizer due to possible unwanted side effects such as after-tack, blocking, dirt pick-up and finger printing. Plasticizers are used in the coatings industry to increase the flexibility or distensibility (elongation) of a polymer or coating. This can often be recognized in films as offering greater impact resistance, toughness and adhesion. The organic plasticizers are usually moderately high-molecular-weight materials (liquids) or low-melting solids. By imparting some degree of flexibility to the resin, film cracking can usually be minimized. The mechanism(s) by which plasticizers actually work has been theorized by many. There is general belief that smaller molecules have surrounding them a higher proportion of "free volume" than larger polymeric structures, which tend to be rather resistant to movement. By adding smaller, plasticizer molecules into the resin blend the free volume within the blend is increased and, thereby, permits easier internal motion of macromolecules – resulting in a more flexible film. The action of the plasticizer is such that it appears to actually solvate various points along the polymer chain. It is also felt that this is a very dynamic condition – in other words that the plasticizer molecules are attached to a given group and then are displaced and replaced by other groups and so forth. The addition of plasticizer lowers the softening point – Tg – of the resin. This can give elongation properties to the resin and subsequent coating, such that the film can withstand shock or impact resistance. Some emulsions are very hard and a plasticizer is required to ensure proper film formation. Primary plasticizers are those which are

highly compatible with a given resin system. Secondary plasticizers are those, which upon aging, tend to form droplets or give internal cloudiness or bloom as a crystalline surface. In general, the phthalic anhydride esters – or phthalates – have been used widely throughout the coatings industry as general-purpose plasticizers. The most commonly known are the dibutyl phthalates and dioctyl phthalate. Obviously, whole arrays of plasticizers exist and are chosen for use based on specific performance and/or price considerations. Examples of plasticizers are: abietates, adipates, benzoates, castor oil, epoxidized soybean oil (which can also act as an acid scavenger), phosphates, phthalates, polymeric phthalates, sebacates, and so forth. Acrylic esters of aliphatic dicarboxylic acids, in particular adipic and sebacic acids, provide excellent elasticity in coatings even at low temperatures. They are often mixed with the phthalate plasticizers. In selecting the proper plasticizer for a given resin system, the following factors will influence the effectiveness of the plasticizer: • presence or absence of specific functional groups in the resin; • polarity and hydrogen bonding ability of functional groups; • stearic hindrance; • molecular weight. Plasticizers are not permanently bonded to the resin in a coatings system; therefore they can often be extracted in part from a coating for purposes of analysis. Many types of plasticizers will extract with water as a polar solvent. Nonpolar solvents such as hexane are also often used. Plasticizers have been known to migrate from one polymeric material to another if there is compatibility between them. Plasticizers are very mobile compounds and can easily diffuse. Adipates and phthalates have been known to migrate from vinyl upholstery, handbags and so forth to lacquers and soften or destroy the surface coating. They can migrate into food and beverages, and sometimes affect odor and taste. Some plasticizers tend to migrate to the surface under conditions of high temperature and humidity. A type of water-plasticizer blend occurs that makes the surface feel sticky. In recent years, ortho-phthalate plasticizers such as BBP and DBP have become targets of consumer groups that have demanded the removal of these additives in products that range from toys to coatings. In December 2005, the California Office of Environmental Health Hazard Assessment (OEHHA) added BBP and DBP, along with di-n-hexyl phthalate (DnHP) to the Proposition 65 list of chemicals as being "known to the state to cause reproductive toxicity," prompting manufacturers to seek alternative products. As a result, formulators are looking for non ortho-phthalate alternatives for their coatings. While there are several plasticizers on the market that are compatible with solventborne systems, there are very few that are compatible with both solvent- and waterborne systems. Fewer still have a boiling point over 300 °C to ensure that the plasticizer will remain in the film over an extended period to maintain film flexibility. Over the last few years, several new plasticizers have been introduced, positioned as alternatives to the ortho-phthalate plasticizers (DEHP, DINP, DIDP, DNOP, DBP, and BBP) that have been restricted in the EU and more recently in North America. Alternative chemistries include conventional esters (such as adipates and citrates), naturally derived plasticizers that are vegetable based, diisononylcyclohexane1,2-dicarboxylate, terephthalates (such as DOTP and DEHT), and alkyl sulfonic ester derivatives. There are newer, non-phthalate alternatives, such as some newer coalescents, on the market today with similar boiling points that are compatible with both solvent- and waterborne systems. In addition, they can help formulators meet a number of environmental regulations. Another benefit of this type of additive is that it not only keeps the films flexible but it also aids in film formation of latex systems. This is an important benefit to formulators who are under constant pressure to reduce VOC in coatings. Additives such as co-solvents, thickeners, preservatives and lower-boiling plasticizers can add to the VOC level of the coating. Solvents are also used as fugitive plasticizers. For powder coatings, the purpose is to reduce the viscosity of a binder to enhance flow and leveling. The types used are mainly derivatives of benzoic acid; others used include toluene sulfonamide, dicyclohexyl phthalate and epoxidized soy oil. The levels are usually 1.0-5.0% of the binder. Aqueous fumed silica dispersions are a new form of a well-known, long-standing additive that can improve a variety of performance attributes in waterborne coatings. Its liquid, water-like form overcomes the challenges of using traditional powder versions of fumed silica. Due to their unique ability to prevent cracking and lower MFFT, aqueous fumed silica dispersions serve as a unique tool for the waterborne coatings formulator. Pre-dispersed fumed silica provides

the potential to lower VOCs by improving film formation and the possibility to reduce co solvent with a number of acrylic resins. They also serve as a potential way to gain enhanced durability of waterborne coatings by helping to replace plasticizers commonly used to improve film formation.

UV ABSORBERS AND LIGHT STABILIZERS See Hindered Amine Light Stabilizers, Nanotechnology Materials that preferentially absorb UV radiation in a coating and transform the UV energy into longer wavelength energy. Chemical compositions that protect the coating film, transparent or semi-transparent films, and the substrate from photo-degradation.

The ultraviolet region of the electromagnetic spectrum extends from about 100 to 400 nanometers. It contains the following regions:

• Ultraviolet A: 320 to 400 nanometers (used for photocuring);

• Ultraviolet B: 280 to 320 nanometers (used for photocuring and causes 'sunburn');

• Ultraviolet C: ~15 to 280 nanometers (usually used for sterilization purposes).

Many radiation sources emit ultraviolet wavelengths to some degree. The sun emits very strongly throughout the ultraviolet region, and even though it is only a portion of the total energy reaching the earth, it is the radiation that is particularly harmful to exterior coatings. Ultraviolet radiation is sufficiently energetic to break covalent bonds in polymer structures that hold a coating film together. This energy decreases as wavelength increases and is about 140 kilocalories at 200 nanometers and 70 kilocalories at 400 nanometers. Coatings are not only protective or functional; they also provide decorative effects that are aesthetically pleasing. In either case they must withstand environmental influences and possible subsequent damage. This means that coatings have to be able to withstand deterioration and/or failure of any sort. Ultraviolet radiation is often responsible for polymer degradation in a coating. This radiation, coupled with moisture and various other air pollutants such as acid rain, can quickly cause the degradation of an organic film if it is not adequately protected. The polymeric binder in the coating film is subject to attack by ultraviolet radiation because of its organic nature. When a polymer readily absorbs ultraviolet radiation, and this is the usual case, regions in the polymer are activated to a higher energy state and free radicals can be formed. When these radicals are formed, the degradation process has begun. Certain polymers have chromophores as a part of the chemical structure of the polymer-aromatic-group containing polymers in particular. These readily absorb radiation. However, even the binder polymers that do not contain chromophores as a part of their polymer structure end up being formulated and cured in a system that contains crosslinking agents, pigments, fillers, extenders, catalysts, flow-control agents, biocides and other ingredients that will absorb radiation and thus can lead to degradation. Merely because chromophores exist in the molecular structure and ultraviolet radiation is absorbed, it does not mean that bond breakage and degradation will occur. It only means that the potential for degradation exists. Sunlight, oxygen and water all work together to cause coating degradation of the polymer. In the process free radicals are formed that react with atmospheric oxygen to generate peroxy radicals. These very quickly form hydroperoxides, which in turn generate a radical on the polymer backbone itself. The weak hydroperoxide will cleave easily in the presence of heat and sunlight and produce more radicals. As this process occurs, the polymers mechanical and chemical structure is slowly degraded and broken down. We usually see this in the form of peeling, flaking, chalking and

fading. Absorption and degradation are very complicated processes. For purposes of simplicity here we can look at the process as follows: Polymer-R absorbs ultraviolet radiation to generate a photoexcited state:

Polymer-R*

Excited Polymer-R* —-> Polymer-R

• free radical Free Radical Polymer-R• + O2 —-> Polymer-ROO

• a peroxy radical The peroxy radical then abstracts a hydrogen from a molecule, R-H, in the system that has an available hydrogen to form Polymer-ROOH and R•, a new free radical.

Then the process continues.

All of the commercial UV absorbers (UVAs) and stabilizers that we use as additives act on one of the above processes. The UV absorbers prevent the excitation state by absorbing the UV radiation that would produce it. Absorbers today have good thermal stability and some have the capability of being crosslinked to the coating polymer. UV absorbers are designed such that they preferentially absorb UV radiation, dissipate the absorbed energy and do not cause degradation of the polymeric film. UV absorbers are incorporated into organic films that are subjected to exterior exposures. Their function is to absorb incoming UV radiation and dissipate the energy before it can be absorbed by the polymer in the coating. This action has to continue to occur over the lifetime of the coating. The most important UV absorbers are: 2-(2′-hydroxyphenyl) benzotriazoles, 2-hydroxyphenyltriazines, 2-hydroxybenzophenones, cyanoacrylates, salicylates, and oxanilides. The benzotriazoles and triazines have excellent spectral coverage, high extinction coefficients, and excellent photo-permanence. Recent UVA developments have focused on increasing molecular weight and/or adding functionality, which minimizes migration out of the coating, improvements on increasing extinction coefficients and photo-permanence and designing encapsulation techniques which facilitate waterborne systems without the need for solvents or pre-emulsification. UV absorbers compete for the incoming UV radiation with the polymer itself. The more effective the use of UV absorbers in an exterior coating, the less prone the coating will be to the visual effects of UV degradation such as chalking, loss of gloss etc. UV absorbers depend on the thickness of the coating to be effective. The thinner the coating, the less effective they are. UV absorbers are even more effective when used in combination with Hindered Amine Light Stabilizers. [See HALS for more information on these additives.] For coatings used in exterior environments the combination of UV absorbers and hindered amine light stabilizers (HALS) is effective in reducing the damaging effects of ultraviolet radiation. The development of new reactive HALS and UVAs can meet needs for improved compatibility in polar coatings as well as reduced migration. In addition, work continues on development of high-purity powder forms that are also ideal for use in the powder coatings. These systems are compatible with highly polar, highly crosslinked systems such as polyester (or acrylic) urethanes and melamines. A non-reactive HALS – or NOR-HALS – possesses a reactive hydroxy functionality enabling it to co-condense with melamine and isocyanate crosslinkers. As a result, it exhibits improved compatibility and migration resistance in many coatings systems. These may be combined with other HALS that contain reactive hydroxy functionality to achieve nonmigrating systems. Potential applications include coatings-over-plastic substrates (particularly polyurethanes), acid-catalyzed clearcoats, clearcoats over acid-catalyzed basecoats and powder coatings. The reactable HALS and UVAs react quickly, are noninteracting and exhibit outstanding solubility, thermal permanence and radiation stabilizing effectiveness. Their migration resistance makes them attractive for use in wet-on-wet applications. There are also reactables with low melting ranges for use in powder coating applications and UV/powder hybrid applications. In powder coatings, the purpose of UV absorbers is to reduce the rate of polymer degradation due to the environmental exposure of UV radiation. The chemistry is usually based on benzotriazole but can also be benzophenone based. These materials absorb harmful

UV radiation and convert it into low levels of heat energy. The levels are usually 1.0- 5.0% and they are normally used in combination with a hindered amine light stabilizer. Inorganic UV Absorbers Titanium dioxide white pigments are designed by their particle size for optimum light scattering in the visible region. For high light refraction, a maximum refractive index is a prerequisite. However, this is not sufficient – the particle size has to be fine-tuned as well. Unlike standard-sized titanium dioxide pigments, ultra-fine titanium dioxides, which were initially developed for transparent UV protection, ideally do not scatter visible light. However, standard-size and ultra-fine titanium dioxides have the same refractive index, so it is the finest particle size that is responsible for the transparency of the coating. The finer the dispersed particles the more transparent the coating. Thus, for transparent UV absorption the finest grades in optimum dispersion are applied. It has to be noted as well, that certain ultra-fine titanium dioxides grades with selected 'intermediate' primary particle size do scatter blue light. This is why these nanosized TiO2 particles are used in metallic coatings and other pigmented systems in which sophisticated color effects are desired. Titanium dioxide absorbs UV radiation and serves as a photo-semiconductor. This property is practically independent from the particle size. Energy absorption leads to the transfer of an electron from the valence band to the conduction band. This process creates two mobile charged particles: the negatively charged electron in the conduction band, and the positive charge (hole) in the valence band. UV radiation is absorbed and transformed into thermal energy. However, unlike organic substances, the chemically inert titanium dioxide does not decompose, so that the long-term stability of the entire system is increased. In order to tame the UV radiation and prevent it from causing damage by forming radicals, foreign ions such as trivalent aluminum (Al+3) are incorporated into the inner crystal lattice of TiO2. In addition, the surface of the pigment may be encapsulated with an inorganic coating consisting of aluminum oxide (Al2O3) and/or silica (SiO2). This stabilizing technology is generally used for photo-resistant and weather-resistant white pigments and inorganic UV absorbers. Typical white pigments have a crystallite size of 200 to 350 nm. They are available as anatase or rutile pigments. The inorganic TiO2-based UV absorbers have a primary particle size of 10 to 50 nm and are usually offered as rutiles with a highsurface coating. These surface coatings make it possible to modify not only the photoactivity but also the optical and colloidal properties of the white pigment. It is also a must to achieve good dispersibility of the ultra-fine titanium dioxides. For this reason, the pigments are treated with an additional organic substance. There are two types of ultra-fine titanium dioxides in the rutile modification (both containing > 99% rutile) that differ mainly in their primary crystal size and doping. The type that was specially developed for transparent wood coatings has a primary crystal size of ~10 nm and a specific surface of ~110 m2/g (Mikrorutile 10 nm). The second product has a primary crystal size of 15 nm and accordingly a smaller specific surface area of ~70 m2/g (Mikrorutile 15 nm). Nano zinc oxide is also used as a UV absorber and adds to the improvement of other coating properties. Cerium Oxide Nanoparticles Cerium oxide is largely used in the catalysis field (mainly for diesel engines), and in chemical and mechanical polishing (CMP). However, cerium oxide is also well known for its optical properties and ability to filter UV rays. Stable sols of cerium oxide nanoparticles with diameters of 10 nm are available. These sols appear as a clear liquid, since the particles are small enough to be totally transparent. Despite their small size, cerium oxide nanoparticles are very effective in terms of UV filtration. According to theory, cerium oxide shows a UV cut-off threshold at around 370 nm, similar to that of nano titanium oxide. Cerium oxide and titanium oxide are both semi-conductors (with a band gap around 3.0 - 3.2 eV) and present the same classical UV absorption mechanism: under UV-light illumination, the absorption of a photon with a higher energy than the band gap creates an electron-hole pair. In the case of titanium oxide, these holes and electrons migrate to the surface of the particles (rather than recombining together inside the particles). When holes and electrons are at the surface, they can react with oxygen, water or hydroxyls to form free radicals. These free radicals are oxidant entities, and can cause the degradation of organic molecules, in particular polymers, which is an important issue for protective coatings. In contrast, cerium oxide absorbs UV without being photoactive. Indeed, cerium oxide has a localized electron (4 f orbital), while titanium oxide has less localized
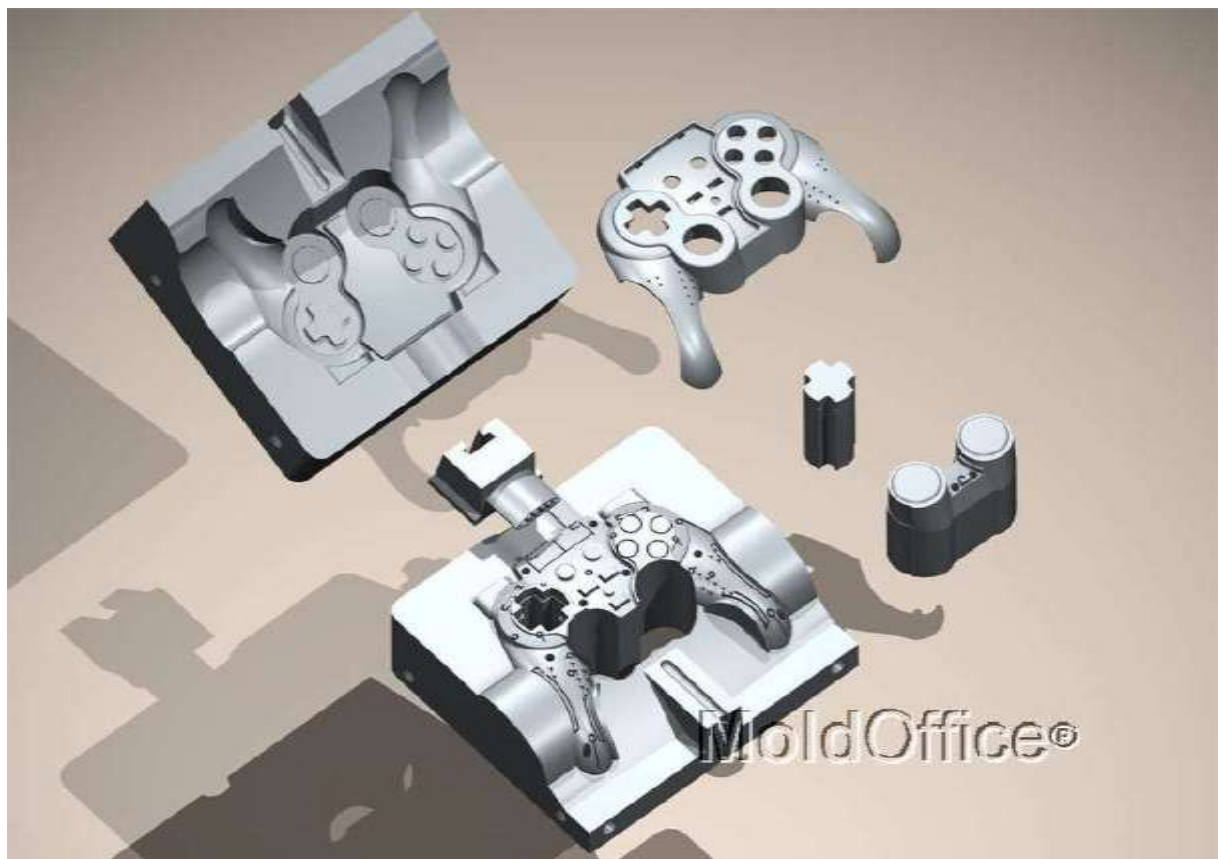
electrons than cerium oxide (3 d orbital). So the cerium-oxygen bonding is more ionic than the titanium-oxygen bonding and, logically, the charge carriers (holes and electrons centers) creation is lower than in the case of titanium oxide. Moreover, cerium oxide shows a very fast recombination of charge carriers before they can migrate to the surface (because of crystal defects, oxido-reduction reaction) so there is no further creation of free radicals. Due to the combination of these two phenomena, cerium oxide does not show any photocatalytic effect. Cerium oxide nanoparticles, properly dispersed in coating formulations, combine the advantages of organic ultraviolet (UV) absorbers with those of mineral additives. The cerium oxide nanoparticles ensure the durability of the UV absorption function while improving the hardness and strengthening the organic binders currently used in wood coating technology. Since the nanoparticles do not scatter light, the coating remains transparent. Transparency (i.e., no coloration, no whitening) is an important requirement for the wood coating industry; since wood is a natural material, the coating must be as neutral as possible. When the durability is targeted, colored pigments are often added to help, but this negatively impacts the aesthetics of the end product. Organic UV absorbers are also efficient but their actions are limited because of progressive destruction of active molecules (migration, leaching, photochemical activity). The surface mechanical properties (hardness and scratch resistance) of a coating are clearly improved by cerium oxide nanoparticles. The bulk characteristics of the organic host matrix are also strongly modified in the presence of cerium oxide nanoparticles: tensile strength, elongation-atbreak or yield stress are significantly improved. The homogeneous distribution of cerium oxide nanoparticles throughout the matrix does not support the hypothesis of the formation of an inorganic surface network to explain the reinforcement of the polymer film surface. Therefore, it is probable that a modification of the structural organization of the polymer chains around the particles occurs during the drying. From a practical point of view, the improvement in mechanical properties combined with the UV filter protection delays the occurrence of cracks, and allows the coating to better follow the dimensional variations of the wood piece due to moisture pick-up and swelling. Improved scratch resistance contributes to better appearance and durability (e.g., the inhibition of weaknesses and micro cracks due to handling). The introduction of cerium oxide nanoparticles into the organic matrix results in a significant modification of hydrophilic properties of the coating, leading to an improvement in water resistance. The contact angle of a water droplet characterizes the water resistance of a surface. This important parameter is significantly increased upon addition of cerium oxide nanoparticles. Organic UV Absorbers The most common UV absorbers for coatings are 2-hydroxyphenyl benzotriazoles, 2-hydroxy-benzophenones, 2-hydroxy-phenyltriazines, and oxalanilides. Salicylates, formamidines and cyanoacrylates may also be used on an individual basis. The photoprotection mechanism resides in the ability to form reversible intramolecular hydrogen bonds between an o-hydroxyl group and a heteroatom such as nitrogen. Upon absorption of UV-light, an electron is promoted to an excited singlet state and, via intersystem crossing, to an excited triplet state. This is followed by an excited state intramolecular proton transfer, or enolization, with proton transfer taking place along the intramolecular hydrogen bond. The quinonoid intermediate tautomerizes through a rapid non-radiative relaxation process (heat) and return proton transfer, thus regenerating the original ketone. This process, called the keto-enol tautomerism mechanism, is nothing but a continuously repetitive proton transfer. Due to the bathochromic shift of the absorption maximum toward the long-wavelength spectrum, halogenated benzotriazoles are particularly suited for the protection of photo-sensitive wood. The halogen substituent modifies the electron density and expands the delocalized electron system. As a result, less energy is required to bring the electrons into the excited state and the absorption of radiation is shifted towards lower frequencies. In this case the absorption maximum reaches the areas of the visible sunlight, thus more efficiently protecting the substrate from the damaging effect of this type of radiation. In the late 1970s, oxanilide UV absorbers were already almost entirely replaced by various hydroxy-phenyl-benzotriazoles (BTZ), which became the dominant UV absorber class during the 1980s and continue to be so for a variety of traditional applications. These materials were already characterized by much broader spectral coverage and much better

photo stability. In spite of the dominant position of the hydroxyphenyl-benzotriazoles, there are still requirements that cannot be satisfactorily met with these products due to certain technical limitations of their chemistry. These include limited absorption at shorter wavelengths, interaction issues with certain metal (e.g. Al-based) catalysts, leading to significant yellowing, as well as inadequate protection of the substrate at reduced film build. Development efforts in the 1990s resulted in the introduction of the first generation of hydroxy-phenyltriazine (HPT) UV absorbers. Generally speaking, hydroxy-phenyl-triazines exhibit much less tendency to interact with certain metal catalysts and even better photo stability than hydroxy-phenyl-benzotriazoles, as well as high absorption at shorter wavelengths. These features make this UV absorber class highly versatile in terms of both traditional and advanced applications such as UV curing. Furthermore, combinations with BTZ allow broader spectral coverage than HPT alone, along with superior protection at short wavelengths versus BTZ alone. Conventional BTZ and HPT UV absorbers exhibit fairly similar extinction, except in the 300 nm range. Adequate UV protection at low film builds can therefore only be achieved through significantly higher dose levels, which in turn may compromise the secondary properties of the paint film. The more recent development of advanced chromophores based on hydroxy-phenyl-triazine chemistry has allowed up to 3.5 times higher extinction than the state of the art. This extremely high extinction allows the application of thin films along with superior UV protection at comparatively low dose levels. The position of the absorption maximum in the 320-330 nm range also makes these chromophores interesting candidates for the protection of substrates sensitive at this wavelength range, e.g. polycarbonate. The efficacy of a UV absorber depends both on its absorption characteristics and on its secondary properties, such as photo stability, which needs to be very high. This is particularly important in thin film applications, where the product's inherent stability rather than the internal filter effect (i.e. UV absorber molecules protecting each other) plays the dominant role. Advanced hydroxy-phenyl-triazine technology allows superior protection at low film builds, whereas delamination is observed in the presence of conventional UV absorbers. The spectral coverage as such as well as the position of the absorption maximum are determining factors in UV stabilization of substrates sensitive at wavelengths that are not or not sufficiently covered either by conventional or advanced chromophores. These wavelengths extend from the ≥ 360 nm range to the visible and slightly above. A shift of the absorption spectrum of the UV absorber can be achieved to a significant extent through specific substitution patterns; however, there are obviously limitations both in terms of chemistry and color. The more the spectrum is shifted towards the visible, the higher the risk of bringing in too much color. This in turn means that a proper balance needs to be achieved between the spectral coverage and the product's inherent color. Both the UV and the visible light lead to decomposition of the lignin structure of the wood, resulting in discoloration/darkening of pale woods in particular. In order to filter out the UV light component as far as possible, broader spectral coverage is needed than can be achieved with conventional UV absorbers. Cutting out the UV light either by cut-off filters (which allow a certain wavelength range to be selectively cut out, e.g. a filter labeled GG 320 excludes all wavelengths below 320 nm, a filter labeled GG 385 excludes all wavelengths below 385 nm, etc.) or by the red-shifted tris-resorcinol- triazine (TRITA) UV absorber in lieu of a filter can greatly reduce the formation of colored chromophores. Since such species, however, are also being formed in the visible range, sufficient protection can scarcely be achieved by the UV absorber alone. In order to fully prevent their formation, spectral coverage as far out as > 450 nm would be needed (Figure 8), which in turn would result in a major color impact by the UV absorber. Therefore, a modified concept involving specific co-stabilization was developed. Such co-stabilizers, which are chemically based on free nitroxyl radical chemistry, are typically used for pretreatment purposes. Such materials can trap the radicals formed on the wood surface by the visible light, thereby preventing photo-oxidation of lignin. The range of UV absorbers available today includes both conventional and advanced UV absorber technology. In traditional applications conventional hydroxy-phenyl-benzotriazoles as well as hydroxylphenyl-triazines will certainly continue to play an important role. These products, however, do not meet the requirements for thin film applications or for applications   requiring

enhanced or specific protection at certain wavelengths. Development work has led to an extension of the available product range beyond conventional technologies, thereby allowing applications previously considered difficult or even impossible. Advanced hydroxy-phenyl-triazines are closing the gap for thin film applications or applications where enhanced protection at shorter wavelengths is necessary. Superior protection of wood substrates can be achieved by a specific concept, i.e. the combined use of red-shifted triazine-based UV absorbers and lignin stabilizers. Protection of systems or composites based on aromatic epoxies can be considered the biggest challenge in terms of the UV absorber properties needed. Today this can be realized through novel red-shifted UV absorber technology, which combines comparatively low color with broad spectral coverage reaching into the near visible. Furthermore, the application of the various products as such or combinations thereof allow paint companies to adjust the protection to the level needed. In water-based coatings – although not further discussed in this paper – this is achieved through specific water compatible product forms. New mini-emulsion polymerization techniques have developed aqueous preparations of hydrophobic UV absorbers, which enables easy incorporation and effective use in waterborne coatings. The products can be added as supplied by simple stir-into the formulations without any cosolvent at any stage of the manufacturing process and are ideal for post addition. These products also allow dispersion of hydrophobic substances into aqueous systems without separation problems upon storage. The dispersed additive does not influence the optical properties of clear coatings such as gloss and transparency. These products also show high water leaching resistance and excellent long-term protection.

Design and manufacturing of plastic injection mould

Content

1 Injection molding

From Wikipedia, the free encyclopedia

Injection molding (British: **moulding**) is a manufacturing technique for making parts from both thermoplastic and thermosetting plastic materials in production. Molten plastic is injected at high pressure into a mold, which is the inverse of the product's shape. After a product is designed, usually by an industrial designer or an engineer, molds are made by a moldmaker (or toolmaker) from metal, usually either steel or aluminium, and precision-machined to form the features of the desired part. Injection molding is widely used for manufacturing a variety of parts, from the smallest component to entire body panels of cars. Injection molding is the most common method of production, with some commonly made items including bottle caps and outdoor furniture. Injection molding typically is capable of tolerances equivalent to an IT Grade of about 9–14.

The most commonly used thermoplastic materials are polystyrene (low cost, lacking the strength and longevity of other materials), ABS or acrylonitrile butadiene styrene (a ter-polymer or mixture of compounds used for everything from Lego parts to electronics housings), polyamide (chemically resistant, heat resistant, tough and flexible – used for combs), polypropylene (tough and flexible – used for containers), polyethylene, and polyvinyl chloride or PVC (more common in extrusions as used for pipes, window frames, or as the insulation on wiring where it is rendered flexible by the inclusion of a high proportion of plasticiser).

Injection molding can also be used to manufacture parts from aluminium or brass (die casting). The melting points of these metals are much higher than those of plastics; this makes for substantially shorter mold lifetimes despite the use of specialized steels. Nonetheless, the costs compare quite favorably to sand casting, particularly for smaller parts.

1.1 History

In 1868 John Wesley Hyatt became the first to inject hot celluloid into a mold, producing billiard balls. He and his brother Isaiah patented an injection molding machine that used a plunger in 1872, and the process remained more or less the same until 1946, when James Hendry built the first screw injection molding machine, revolutionizing the plastics industry. Roughly 95% of all molding machines now use screws to efficiently heat, mix, and inject plastic into molds.

1.2 Equipment

Injection molding machines, also known as presses, hold the molds in which the components are shaped. Presses are rated by tonnage, which expresses the amount of clamping force that the machine can generate. This pressure keeps the mold closed during the injection process. Tonnage can vary from less than 5 tons to 6000 tons, with the higher figures used in comparatively few manufacturing operations.

1.2.1 Mold

Mold (Tool and/or Mold) is the common term used to describe the production tooling used to produce plastic parts in molding.

Traditionally, molds have been expensive to manufacture. They were usually only used in mass production where thousands of parts were being produced. Molds are typically constructed from hardened steel, pre-hardened steel, aluminium, and/or beryllium-copper alloy. The choice of material to build a mold is primarily one of economics. Steel molds generally cost more to construct, but their longer lifespan will offset the higher initial cost over a higher number of parts made before wearing out. Pre-hardened steel molds are less wear resistant and are used for lower volume requirements or larger components. The steel hardness is typically 38-45 on the Rockwell-C scale. Hardened steel molds are heat treated after machining. These are by far the superior in terms of wear resistance and lifespan. Typical hardness ranges between 50 and 60 Rockwell-C (HRC). Aluminium molds can cost substantially less, and when designed and machined with modern computerized equipment, can be economical for molding tens or even hundreds of thousands of parts. Beryllium copper is used in areas of the mold which require fast heat removal or areas that see the most shear heat generated. The molds can be manufactured by either CNC machining or by using Electrical Discharge Machining processes

1.2.2   Design

Molds separate into two sides at a parting line, the *A side*, and the *B side*, to permit the part to be extracted. Plastic resin enters the mold through a *sprue* in the A plate, branches out between the two sides through channels called *runners*, and enters each part *cavity* through one or more specialized *gates*. Inside each cavity, the resin flows around protrusions (called *cores*) and conforms to the cavity geometry to form the desired part. The amount of resin required to fill the sprue, runner and cavities of a mold is a *shot*. When a core *shuts off* against an opposing mold cavity or core, a hole results in the part. Air in the cavities when the mold closes escapes through very slight gaps between the plates and pins, into shallow plenums called *vents*. To permit removal of the part, its features must not overhang one another in the direction that the mold opens, unless parts of the mold are designed to move from between such overhangs when the mold opens. Sides of the part that appear parallel with the direction of *draw* (the direction in which the core and cavity separate from each other) are typically angled slightly with (*draft*) to ease release of the part from the mold, and examination of most plastic household objects will reveal this. Parts with bucket-like features tend to shrink onto the cores that form them while cooling, and cling to those cores when the cavity is pulled away. The mold is usually designed so that the molded part reliably remains on the ejector (B) side of the mold when it opens, and draws the runner and the sprue out of the (A) side along with the parts. The part then falls freely when ejected from the (B) side. *Tunnel gates* tunnel sharply below the parting surface of the B side at the tip of each runner so that the gate is sheared off of the part when both are ejected. Ejector pins are the most popular method for removing the part from the B side core(s), but air ejection, and stripper plates can also be used depending on the application. Most ejector plates are found on the moving half of the tool, but they can be placed on the fixed half if spring loaded. For thermoplastics, coolant, usually water with corrosion inhibitors, circulates through passageways bored through the main plates on both sides of the mold to enable temperature control and rapid part solidification.

To ease maintenance and venting, cavities and cores are divided into pieces, called *inserts*, and subassemblies, also called *inserts*, *blocks*, or *chase blocks*. By substituting interchangeable inserts, one mold may make several variations of the same part.

More complex parts are formed using more complex molds. These may have sections called *slides*, that move into a cavity perpendicular to the draw direction, to form overhanging part features. Slides are then withdrawn to allow the part to be released when the mold opens. Slides are typically guided and retained between rails called *gibs*, and are moved when the mold opens and closes by angled rods called *horn pins* and locked in place by *locking blocks*, both of which move cross the mold from the opposite side.

Some molds allow previously molded parts to be reinserted to allow a new plastic layer to form around the first part. This is often referred to as overmolding. This system can allow for production of one-piece tires and wheels.

2-shot or multi shot molds are designed to "overmold" within a single molding cycle and must be processed on specialized injection molding machines with two or more injection units. This can be achieved by having pairs of identical cores and pairs of different cavities within the mold. After injection of the first material, the component is rotated on the core from the one cavity to another. The second cavity differs from the first in that the detail for the second material is included. The second material is then injected into the additional cavity detail before the completed part is ejected from the mold. Common applications include "soft-grip" toothbrushes and freelander grab handles.

The core and cavity, along with injection and cooling hoses form the mold tool. While large tools are very heavy weighing hundreds and sometimes thousands of pounds, they usually require the use of a forklift or overhead crane, they can be hoisted into molding machines for production and removed when molding is complete or the tool needs repairing.

A mold can produce several copies of the same parts in a single "shot". The number of "impressions" in the mold of that part is often incorrectly referred to as cavitation. A tool with one impression will often be called a single cavity (impression) tool. A mold with 2 or more cavities of the same parts will likely be referred to as multiple cavity tooling. Some extremely high production volume molds (like those for bottle caps) can have over 128 cavities.

In some cases multiple cavity tooling will mold a series of different parts in the same tool. Some toolmakers call these molds family molds as all the parts are not the same but often part of a family of parts (to be used in the same product for example).

1.2.3   Machining

Molds are built through two main methods: standard machining and EDM machining. Standard Machining, in its conventional form, has historically been the method of building injection molds. With technological development, CNC machining became the predominant means of making more complex molds with more accurate mold details in less time than traditional methods.

The electrical discharge machining (EDM) or spark erosion process has become widely used in mold making. As well as allowing the formation of shapes which are difficult to machine, the process allows pre-hardened molds to be shaped so that no heat treatment is required. Changes to a hardened mold by conventional drilling and milling normally require annealing to soften the steel, followed by heat treatment to harden it again. EDM is a simple process in which a shaped electrode, usually made of copper or graphite, is very slowly lowered onto the mold surface (over a period of many hours), which is immersed in paraffin oil. A voltage

applied between tool and mold causes erosion of the mold surface in the inverse shape of the electrode.

1.2.4   Cost

The cost of manufacturing molds depends on a very large set of factors ranging from number of cavities, size of the parts (and therefore the mold), complexity of the pieces, expected tool longevity, surface finishes and many others.

1.3   Injection molding cycle

For the injection molding cycle to begin, four criteria must be met: mold open, ejector pins retracted, shot built, and carriage forward. When these criteria are met, the cycle begins with the mold closing. This is typically done as fast as possible with a slow down near the end of travel. Mold safety is low speed and low pressure mold closing. It usually begins just before the leader pins of the mold and must be set properly to prevent accidental mold damage. When the mold halves touch clamp tonnage is built. Next, molten plastic material is injected into the mold. The material travels into the mold via the sprue bushing, then the runner system delivers the material to the gate. The gate directs the material into the mold cavity to form the desired part. This injection usually occurs under velocity control. When the part is nearly full, injection control is switched from velocity control to pressure control. This is referred to as the pack/hold phase of the cycle. Pressure must be maintained on the material until the gate solidifies to prevent material from flowing back out of the cavity. Cooling time is dependent primarily on the wall thickness of the part. During the cooling portion of the cycle after the gate has solidified, plastication takes place. Plastication is the process of melting material and preparing the next shot. The material begins in the hopper and enters the barrel through the feed throat. The feed throat must be cooled to prevent plastic pellets from fusing together from the barrel heat. The barrel contains a screw that primarily uses shear to melt the pellets and consists of three sections. The first section is the feed section which conveys the pellets forward and allows barrel heat to soften the pellets. The flight depth is uniform and deepest in this section. The next section is the transition section and is responsible for melting the material through shear. The flight depth continuously decreases in this section, compressing the material. The final section is the metering section which features a shallow flight depth, improves the melt quality and color dispersion. At the front of the screw is the non-return valve which allows the screw to act as both an extruder and a plunger. When the screw is moving backwards to build a shot, the non-return assembly allows material to flow in front of the screw creating a melt pool or shot. During injection, the non-return assembly prevents the shot from flowing back into the screw sections. Once the shot has been built and the cooling time has timed out, the mold opens. Mold opening must occur slow-fast-slow. The mold must be opened slowly to release the vacuum that is caused by the injection molding process and prevent the part from staying on the stationary mold half. This is undesirable because the ejection system is on the moving mold half. Then the mold is opened as far as needed, if robots are not being used, the mold only has to open far enough for the part to be removed. A slowdown near the end of travel must be utilized to compensate for the momentum of the mold. Without slowing down the machine cannot maintain accurate positions and may slam to a stop damaging the machine. Once the mold is open, the ejector pins are moved forward, ejecting the part. When the ejector pins retract, all criteria for a molding cycle have been met and the next cycle can begin.

The basic injection cycle is as follows: Mold close – injection carriage forward – inject plastic – metering – carriage retract – mold open – eject part(s) Some machines are run by electric motors instead of hydraulics or a combination of both. The water-cooling channels that assist in cooling the mold and the heated plastic solidifies into the part. Improper cooling can result in distorted molding. The cycle is completed when the mold opens and the part is ejected with the assistance of ejector pins within the mold.

The *resin*, or raw material for injection molding, is most commonly supplied in pellet or granule form. Resin pellets are poured into the feed hopper, a large open bottomed container, which is attached to the back end of a cylindrical, horizontal barrel. A screw within this barrel is rotated by a motor, feeding pellets up the screw's grooves. The depth of the screw flights decreases toward the end of the screw nearest the mold, compressing the heated plastic. As the screw rotates, the pellets are moved forward in the screw and they undergo extreme pressure and friction which generates most of the heat needed to melt the pellets. Electric heater bands attached to the outside of the barrel assist in the heating and temperature control during the melting process.

The channels through which the plastic flows toward the chamber will also solidify, forming an attached frame. This frame is composed of the *sprue*, which is the main channel from the reservoir of molten resin, parallel with the direction of draw, and *runners*, which are perpendicular to the direction of draw, and are used to convey molten resin to the *gate(s)*, or point(s) of injection. The sprue and runner system can be cut or twisted off and recycled, sometimes being granulated next to the mold machine. Some molds are designed so that the part is automatically stripped through action of the mold.

1.4 Molding trial

When filling a new or unfamiliar mold for the first time, where shot size for that mold is unknown, a technician/tool setter usually starts with a small shot weight and fills gradually until the mold is 95 to 99% full. Once this is achieved a small amount of holding pressure will be applied and holding time increased until gate freeze off has occurred, then holding pressure is increased until the parts are free of sinks and part weight has been achieved. Once the parts are good enough and have passed any specific criteria, a setting sheet is produced for people to follow in the future.

Process optimization is done using the following methods. Injection speeds are usually determined by performing viscosity curves. Process windows are performed varying the melt temperatures and holding pressures. Pressure drop studies are done to check if the machine has enough pressure to move the screw at the set rate. Gate seal or gate freeze studies are done to optimize the holding time. A cooling time study is done to optimize the cooling time.

1.5 Molding defects

Injection molding is a complex technology with possible production problems. They can either be caused by defects in the molds or more often by part processing (molding)

| Molding Defects	Alternative name	Descriptions	Causes

Blister	Blistering	Raised or layered zone on surface of the part	Tool or material is too hot, often caused by a lack of cooling around the tool or a faulty heater
Burn marks	Air Burn/ Gas Burn	Black or brown burnt areas on the part located at furthest points from gate	Tool lacks venting, injection speed is too high
Color streaks (US)	Colour streaks (UK)	Localized change of color/colour	Masterbatch isn't mixing properly, or the material has run out and it's starting to come through as natural only
Delamination		Thin mica like layers formed in part wall	Contamination of the material e.g. PP mixed with ABS, very dangerous if the part is being used for a safety critical application as the material has very little strength when delaminated as the materials cannot bond
Flash	Burrs	Excess material in thin layer exceeding normal part geometry	Tool damage, too much injection speed/material injected, clamping force too low. Can also be caused by dirt and contaminants around tooling surfaces.
Embedded contaminates	Embedded particulates	Foreign particle (burnt material or other) embedded in the part	Particles on the tool surface, contaminated material or foreign debris in the barrel, or too much shear heat burning the material prior to injection
Flow marks	Flow lines	Directionally "off tone" wavy lines or patterns	Injection speeds too slow (the plastic has cooled down too much during injection, injection speeds must be set as fast as you can get away with at all times)
Jetting		Deformed part by turbulent flow of material	Poor tool design, gate position or runner. Injection speed set too high.

Polymer degradation		polymer breakdown from hydrolysis, oxidation etc	Excess water in the granules, excessive temperatures in barrel
Sink marks		Localized depression (In thicker zones)	Holding time/pressure too low, cooling time too low, with sprueless hot runners this can also be caused by the gate temperature being set too high
Short shot	Non-fill / Short mold	Partial part	Lack of material, injection speed or pressure too low
Splay marks	Splash mark / Silver streaks	Circular pattern around gate caused by hot gas	Moisture in the material, usually when hygroscopic resins are dried improperly
Stringiness	Stringing	String like remain from previous shot transfer in new shot	Nozzle temperature too high. Gate hasn't frozen off
Voids		Empty space within part (Air pocket)	Lack of holding pressure (holding pressure is used to pack out the part during the holding time). Also mold may be out of registration (when the two halves don't center properly and part walls are not the same thickness).
Weld line	Knit line / Meld line	Discolored line where two flow fronts meet	Mold/material temperatures set too low (the material is cold when they meet, so they don't bond)
Warping	Twisting	Distorted part	Cooling is too short, material is too hot, lack of cooling around the tool, incorrect water temperatures (the parts bow inwards towards the hot side of the tool)

2 Injection molding machine

From Plastics Wiki, free encyclopedia

Injection molding machines consist of two basic parts, an injection unit and a clamping unit. Injection molding machines differ in both injection unit and clamping unit. The name of the injection molding machine is generally based on the type of injection unit used.
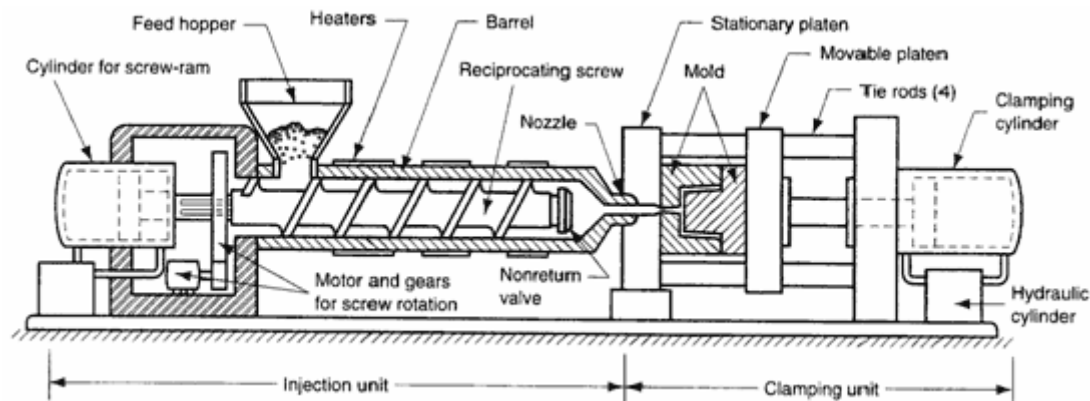
2.1   Types of injection molding machines

Machines are classified primarily by the type of driving systems they use: hydraulic, electric, or hybrid.

2.1.1   Hydraulic

Hydraulic presses have historically been the only option available to molders until Nissei Plastic Industrial Co., LTD introduced the first all-electric injection molding machine in 1983. The electric press, also known as Electric Machine Technology (EMT), reduces operation costs by cutting energy consumption and also addresses some of the environmental concerns surrounding the hydraulic press.

2.1.2   Electric

Electric presses have been shown to be quieter, faster, and have a higher accuracy, however the machines are more expensive.

2.1.3   Hybrid

Hybrid injection molding machines take advantage of the best features of both hydraulic and electric systems. Hydraulic machines are the predominant type in most of the world, with the exception of Japan.

2.2   Injection unit

The injection unit melts the polymer resin and injects the polymer melt into the mold. The unit may be: ram fed or screw fed.

The **ram fed injection molding machine** uses a hydraulically operated plunger to push the plastic through a heated region. The high viscosity melt is then spread into a thin layer by a "torpedo" to allow for better contact with the heated surfaces. The melt converges at a nozzle and is injected into the mold.

Reciprocating screw A combination melting, softening, and injection unit in an injection molding machine. Another term for the **injection screw**. Reciprocating screws are capable of turning as they move back and forth.

The reciprocating screw is used to compress, melt, and convey the material. The reciprocating screw consists of three zones (illustrated below):
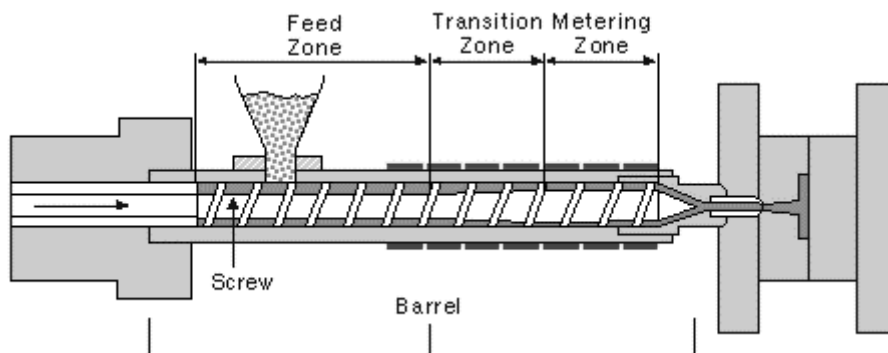
- feeding zone
- compressing zone
- metering zone

While the outside diameter of the screw remains constant, the depth of the flights on the reciprocating screw decreases from the feed zone to the beginning of the metering zone. These flights compress the material against the inside diameter of the barrel, which creates viscous (shear) heat. This shear heat is mainly responsible for melting the material. The heater bands outside the barrel help maintain the material in the molten state. Typically, a molding machine can have three or more heater bands or zones with different temperature settings.

Injection molding reciprocating screw An extruder-type screw rotates within a cylinder, which is typically driven by a hydraulic drive mechanism. Plastic material is moved through the heated cylinder via the screw flights and the material becomes fluid. The injection nozzle is blocked by the previous shot, and this action causes the screw to pump itself backward through the cylinder. (During this step, material is plasticated and accumulated for the next shot.) When the mold clamp has locked, the injection phase takes place. At this time, the screw advances, acting as a ram. Simultaneously, the non-return valve closes off the escape passages in the screw and the screw serves as a solid plunger, moving the plastic ahead into the mold. When the injection stroke and holding cycle is completed, the screw is energized to return and the non-return valve opens, allowing plastic to flow forward from the cylinder again, thus repeating the cycle.

2.2.1 Feed hopper

The container holding a supply molding material to be fed to the screw. The hopper located over the barrel and the feed throat connects them.

2.2.2   Injection ram

The ram or screw that applies pressure on the molten plastic material to force it into the mold cavities.

2.2.3   Injection screw

The reciprocating-screw machine is the most common. This design uses the same barrel for melting and injection of plastic.

The alternative unit involves the use of separate barrels for plasticizing and injecting the polymer. This type is called a screw-preplasticizer machine or two-stage machine. Plastic pellets are fed from a hopper into the first stage, which uses a screw to drive the polymer forward and melt it. This barrel feeds a second barrel, which uses a plunger to inject the melt into the mold. Older machines used one plunger-driven barrel to melt and inject the plastic. These machines are referred to as plunger-type injection molding machines.

2.2.4   Barrel

Barrel is a major part that melts resins transmitted from hopper through screws and structured in a way that can heat up resins to the proper temperature. A band heater, which can control temper atures in five sections, is attached outside the barrel. Melted resins are supplied to the mold passing through barrel head, shot-off nozzle, and one-touch nozzle.

2.2.5   Injection cylinder

Hydraulic motor located inside bearing box, which is connected to injection cylinder load, rotates screw, and the melted resins are measures at the nose of screw. There are many types of injection cylinders that supply necessary power to inject resins according to the characteristics of resins and product types at appropriate speed and pressure. This model employs the double cylinder type. Injection cylinder is composed of cylinder body, piston, and piston load.

2.3   Clamping unit

The clamping unit holds the mold together, opens and closes it automatically, and ejects the finished part. The mechanism may be of several designs, either mechanical, hydraulic or hydromechanical.

Toggle clamps - a type clamping unit include various designs. An actuator moves the crosshead forward, extending the toggle links to push the moving platen toward a closed position. At the beginning of the movement, mechanical advantage is low and speed is high; but near the end of the stroke, the reverse is true. Thus, toggle clamps provide both high speed and high force at different points in the cycle when they are desirable. They are actuated either by hydraulic cylinders or ball screws driven by electric motors. Toggle-clamp units seem most suited to relatively low-tonnage machines.

Two clamping designs: (a) one possible toggle clamp design (1) open and (2) closed; and (b) hydraulic clamping (1) open and (2) closed. Tie rods used to guide movuing platens not shown.
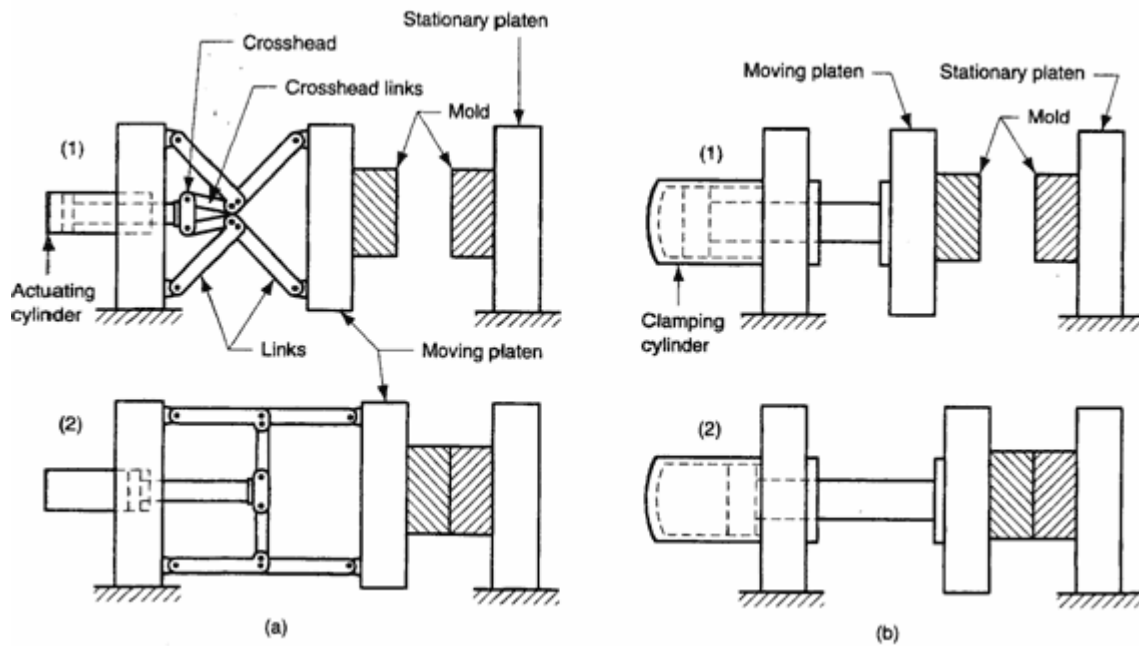
Hydraulic clamps are used on higher-tonnage injection molding machines, typically in the range 1300 to 8900 kN (150 to 1000 tons). These units are also more flexible than toggle clamps in terms of setting the tonnage at given positions during the stroke.

Hydraulic Clamping System is using the direct hydraulic clamp of which the tolerance is still and below 1 %, of course, better than the toggle system. In addition, the Low Pressure Protection Device is higher than the toggle system for 10 times so that the protection for the precision and expensive mold is very good. The clamping force is focus on the central for evenly distribution that can make the adjustment of the mold flatness in automatically.

Hydromechanical clamps - clamping units are designed for large tonnages, usually above 8900 kN (1000 tons); they operate by (1) using hydraulic cylinders to rapidly move the mold toward closing position, (2) locking the position by mechanical means, and (3) using high pressure hydraulic cylinders to finally close the mold and build tonnage.

2.3.1   Injection mold

There are two main types of injection molds: cold runner (two plate and three plate designs) and hot runner – the more common of the runnerless molds.

2.3.2   Injection platens

Steel plates on a molding machine to which the mold is attached. Generally, two platens are used; one being stationary and the other moveable, actuated hydraulically to open and close the mold. It actually provide place to mount the mould. It contains threaded holes on which mould can be mounted using clamps.

2.3.3   Clamping cylinder

A device that actuates the chuck through the aid of pneumatic or hydraulic energy.

2.3.4 Tie Bar

Tie bars support clamping power, and 4 tie bars are located between the fixing platen and the support platen.

3 Injection mould

Mold A hollow form or cavity into which molten plastic is forced to give the shape of the required component. The term generally refers to the whole assembly of parts that make up the section of the molding equipment in which the parts are formed. Also called a tool or die.

Moulds separate into at least two halves (called the core and the cavity) to permit the part to be extracted; in general the shape of a part must be such that it will not be locked into the mould. For example, sides of objects typically cannot be parallel with the direction of draw (the direction in which the core and cavity separate from each other). They are angled slightly; examination of most household objects made from plastic will show this aspect of design, known as draft. Parts that are "bucket-like" tend to shrink onto the core while cooling and, after the cavity is pulled away, are typically ejected using pins. Parts can be easily welded together after moulding to allow for a hollow part (like a water jug or doll's head) that couldn't physically be designed as one mould.

More complex parts are formed using more complex moulds, which may require moveable sections, called slides, which are inserted into the mould to form particular features that cannot be formed using only a core and a cavity, but are then withdrawn to allow the part to be released. Some moulds even allow previously moulded parts to be re-inserted to allow a new plastic layer to form around the first part. This system can allow for production of fully tyred wheels.

Traditionally, moulds have been very expensive to manufacture; therefore, they were usually only used in mass production where thousands of parts are being produced.

Molds require: Engineering and design, special materials, machinery and highly skilled personnel to manufacture, assemble and test them.

Dies and Molds

Locating Ring

Sprue Bushing

Top Clamp Plate

Front Cavity (A Plate)

Guide Pin

Cavities

Guide Bushing

Rear Cavity (B Plate)

Support Plate

Ejector Pin

Sprue Puller Pin

Ejector Return Pin

Ejector Retainer Plate

Ejector Plate

Ejector Housing
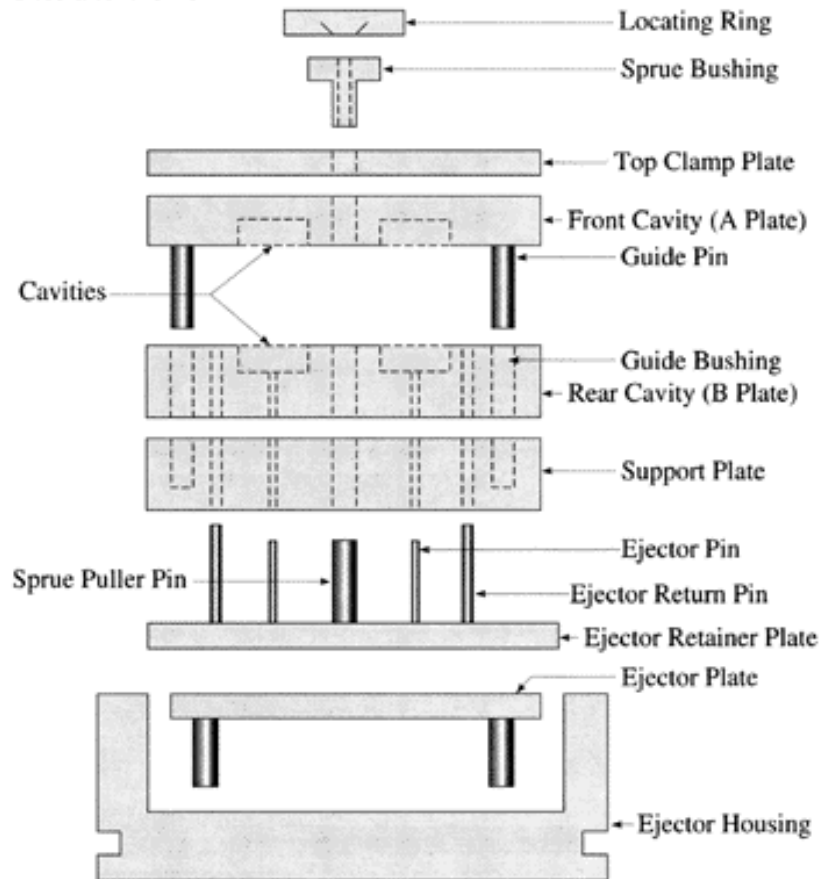
Cold-runner mold

Cold-runner mold Developed to provide for injection of thermoset material either directly into the cavity or through a small sub-runner and gate into the cavity. It may be compared to the hot-runner molds with the exception that the manifold section is cooled rather than heated to maintain softened but uncured material. The cavity and core plates are electrically heated to normal molding temperature and insulated from the cooler manifold section.

3.1.1 Types of Cold Runner Molds

There are two major types of cold runner molds: two plate and three plate.

3.1.2 Two plate mold

A two plate cold runner mold is the simplest type of mold. It is called a two plate mold because there is one parting plane, and the mold splits into two halves. The runner system must be located on this parting plane; thus the part can only be gated on its perimeter.

3.1.3 Three plate mold

A three plate mold differs from a two plate in that it has two parting planes, and the mold splits into three sections every time the part is ejected. Since the mold has two parting planes, the runner system can be located on one, and the part on the other. Three plate molds are used

because of their flexibility in gating location. A part can be gated virtually anywhere along its surface.

3.1.4   Advantages

The mold design is very simple, and much cheaper than a [hot runner system](). The mold requires less maintenance and less skill to set up and operate. Color changes are also very easy, since all of the plastic in the mold is ejected with each cycle.

3.1.5   Disadvantages

The obvious disadvantage of this system is the waste plastic generated. The runners are either disposed of, or reground and reprocessed with the original material. This adds a step in the manufacturing process. Also, regrind will increase variation in the injection molding process, and could decrease the plastic's mechanical properties.

3.1.6   Hot runner mold

Hot-runner mold - [injection mold]() in which the runners are kept hot and insulated from the chilled cavities. Plastic freezeoff occurs at gate of cavity; runners are in a separate plate so they are not, as is the case usually, ejected with the piece.

Hot runner molds are [two plate molds]() with a heated runner system inside one half of the mold.

A hot runner system is divided into two parts: the [manifold]() and the [drops](). The manifold has channels that convey the plastic on a single plane, parallel to the parting line, to a point above the cavity. The drops, situated perpendicular to the manifold, convey the plastic from the manifold to the part.

3.1.7   Types of Hot Runner Molds

There are many variations of hot runner systems. Generally, hot runner systems are designated by how the plastic is heated. There are internally and externally heated drops and manifolds.

3.1.8   Externally heated hot runners

Externally heated hot runner channels have the lowest pressure drop of any runner system (because there is no heater obstructing flow and all the plastic is molten), and they are better for color changes none of the plastic in the runner system freezes. There are no places for material to hang up and degrade, so externally heated systems are good for thermally sensitive materials.

3.1.9   Internally heated hot runners

Internally heated runner systems require higher molding pressures, and color changes are very difficult. There are many places for material to hang up and degrade, so thermally sensitive materials should not be used. Internally heated drops offer better gate tip control. Internally

heated systems also better separate runner heat from the mold because an insulating frozen layer is formed against the steel wall on the inside of the flow channels.

3.1.10 insulated hot runners

A special type of hot runner system is an insulated runner. An insulated runner is not heated; the runner channels are extremely thick and stay molten during constant cycling. This system is very inexpensive, and offers the flexible gating advantages of other hot runners and the elimination of gates without the added cost of the manifold and drops of a heated hot runner system. Color changes are very easy. Unfortunately, these runner systems offer no control, and only commodity plastics like PP and PE can be used. If the mold stops cycling for some reason, the runner system will freeze and the mold has to be split to remove it. Insulated runners are usually used to make low tolerance parts like cups and frisbees.

3.1.11 Disadvantages

Hot-runner mold is much more expensive than a cold runner, it requires costly maintenance, and requires more skill to operate. Color changes with hot runner molds can be difficult, since it is virtually impossible to remove all of the plastic from an internal runner system.

3.1.12 Advantages

They can completely eliminate runner scrap, so there are no runners to sort from the parts, and no runners to throw away or regrind and remix into the original material. Hot runners are popular in high production parts, especially with a lot of cavities.

Advantages Hot Runner System Over a Cold Runner System include:

- no runners to disconnect from the molded parts
- no runners to remove or regrind, thus no need for process/ robotics to remove them
- having no runners reduces the possibility of contamination
- lower injection pressures
- lower clamping pressure
- consistent heat at processing temperature within the cavity
- cooling time is actually shorter (as there is no need for thicker, longer-cycle runners)
- shot size is reduced by runner weight
- cleaner molding process (no regrinding necessary)
- nozzle freeze and sprue sticking issues eliminated

4 Gate type

As important as selecting the optimal gate size and location is the choice of the type of gate. Gate types can be divided between manually and automatically trimmed gates.

Manually trimmed gates

Manually trimmed gates are those that require an operator to separate parts from runners during a secondary operation. The reasons for using manually trimmed gates are:

- The gate is too bulky to be sheared from the part as the tool is opened.
- Some shear-sensitive materials (e.g., PVC) should not be exposed to the high shear rates inherent to the design of automatically trimmed gates.
- Simultaneous flow distribution across a wide front to achieve specific orientation of fibers of molecules often precludes automatic gate trimming.

Gate types trimmed from the cavity manually include:

- Sprue gate
- Edge gate
- Tab gate
- Overlap gate
- Fan gate
- Film gate
- Diaphragm gate
- External ring
- Spoke or multipoint gate

Automatically trimmed gates

Automatically trimmed gates incorporate features in the tool to break or shear the gate as the molding tool is opened to eject the part. Automatically trimmed gates should be used to:

- Avoid gate removal as a secondary operation.
- Maintain consistent cycle times for all shots.
- Minimize gate scars.

Gate types trimmed from the cavity automatically include:

- Pin gate
- Submarine (tunnel) gates
- Hot runner gates
- Valve gates

4.1   Sprue gate

Recommended for single cavity molds or for parts requiring symmetrical filling. This type of gate is suitable for thick sections because holding pressure is more effective. A short sprue is favored, enabling rapid mold filling and low-pressure losses. A cold slug well should be included opposite the gate. The disadvantage of using this type of gate is the gate mark left on the part surface after the runner (or sprue) is trimmed off. Freeze-off is controlled by the part thickness rather than determined the gate thickness. Typically, the part shrinkage near the sprue gate will be low; shrinkage in the sprue gate will be high. This results in high tensile stresses near the gate.

Dimensions

The starting sprue diameter is controlled by the machine nozzle. The sprue diameter here must be about 0.5 mm larger than the nozzle exit diameter. Standard sprue bushings have a taper of 2.4 degrees, opening toward the part. Therefore, the sprue length will control the diameter of the gate where it meets the part; the diameter should be at least 1.5 mm larger than or approximately twice the thickness of the part at that point. The junction of sprue and part should be radiused to prevent stress cracking

- A smaller taper angle (a minimum of one degree) risks not releasing the sprue from the sprue bushing on ejection.
- A larger taper wastes material and extends cooling time.
- Non-standard sprue tapers will be more expensive, with little gain.

4.2   Edge gate

The edge or side gate is suitable for medium and thick sections and can be used on multicavity two plate tools. The gate is located on the parting line and the part fills from the side, top or bottom.

Dimensions

The typical gate size is 80% to 100% of the part thickness up to 3.5 mm and 1.0 to 12 mm wide. The gate land should be no more than 1.0 mm in length, with 0.5 mm being the optimum.

4.3   Tab gate

A tab gate is typically employed for flat and thin parts, to reduce the shear stress in the cavity. The high shear stress generated around the gate is confined to the auxiliary tab, which is trimmed off after molding. A tab gate is often used for molding P.

Dimensions

The minimum tab width is 6 mm. The minimum tab thickness is 75% of the depth of the cavity.

4.4   Overlap gate

An overlap gate is similar to an edge gate, except the gate overlaps the wall or surfaces. This type of gate is typically used to eliminate jetting.

Dimensions

The typical gate size is 10% to 80% of the part thickness and 1.0 to 12 mm wide. The gate land should be no more than 1.0 mm in length, with 0.5 mm being the optimum.

4.5   Fan gate

A fan gate is a wide edge gate with variable thickness. This type is often used for thick-sectioned moldings and enables slow injection without freeze-off, which is favored for low stress moldings or where warpage and dimensional stability are main concerns. The gate should taper in both width and thickness, to maintain a constant cross sectional area. This will ensure that:

- The melt velocity will be constant.
- The entire width is being used for the flow.
- The pressure is the same across the entire width.

Dimensions

As with other manually trimmed gates, the maximum thickness should be no more than 80% of the part thickness. The gate width varies typically from 6 mm up to 25% of the cavity length.

4.6   Film or flash gate

A film or flash gate consists of a straight runner and a gate land across either the entire length or a portion of the cavity. It is used for long flat thin walled parts and provides even filling. Shrinkage will be more uniform which is important especially for fiber reinforced thermoplastics and where warpage must be kept to a minimum.

Dimensions

The gate size is small, typically 0.25mm to 0.5mm thick. The land area (gate length) must also be kept small, approximately 0.5 to 1.0 mm long.

4.7   Diaphragm gate

A diaphragm gate is often used for gating cylindrical or round parts that have an open inside diameter. It is used for single cavity molds that have a small to medium internal diameter. It is used when concentricity is important and the presence of a weld line is not acceptable.

Dimensions

Typical gate thickness is 0.25 to 1.5 mm.

4.8   Internal ring gate.

4.9   External ring gate

This gate is used for cylindrical or round parts in a multicavity mould or when a diaphragm gate is not practical. Material enters the external ring from one side forming a weld line on the opposite side of the runner this weld line is not typically transferred to the part.

Dimensions

Typical gate thickness is 0.25 to 1.5 mm.

4.10 Spoke gate or multipoint gate

This kind of gate is used for cylindrical parts and offers easy de-gating and material savings. Disadvantages are the possibility of weld lines and the fact that perfect roundness is unlikely.

Dimensions

Typical gate size ranges from 0.8 to 5 mm diameter.

4.11 Pin gates

Pin gates are only feasible with a 3-plate tool because it must be ejected separately from the part in the opposite direction The gate must be weak enough to break off without damaging the part. This type of gate is most suitable for use with thin sections. The design is particularly useful when multiple gates per part are needed to assure symmetric filling or where long flow paths must be reduced to assure packing to all areas of the part.

Dimensions

Gate diameters for unreinforced thermoplastics range from 0.8 up to 6 mm. Smaller gates may induce high shear and thus thermal degradation. Reinforced thermoplastics require slightly larger gates > 1 mm The maximal land length should be 1 mm. Advised gate dimensions can be found in the table below.

Dimensions of gates (* wall thickness larger than 5 mm should be avoided).

Wall Thickness mm (in)	Gate Diameter / Length mm (in)
0.7 - 1.2 mm (0.02 - 0.05)	0.7 - 1.0 / 0.8 - 1 (0.02 - 0.04 / 0.03 - 0.04)
1.2 - 3.0 mm (0.05 - 0.12)	0.8 - 2.0 / 0.8 - 1 (0.03 - 0.08 / 0.03 - 0.04)
3.0 - 5.0 mm (0.12 - 0.20)	1.5 - 3.5 / 0.9 - 1 (0.06 - 0.14 / 0.04 - 0.04)
≥ 5.0* (0.20)	3.5 - 6.0 / 0.9 - 1 (0.14 - 0.24 / 0.03 - 0.04)

4.12 Submarine (tunnel) gates

A submarine gate is used in two-plate mold construction. An angled, tapered tunnel is machined from the end of the runner to the cavity, just below the parting line. As the parts and runners are ejected, the gate is sheared at the part. The tunnel can be located either in the moving mould half or in the fixed half. A sub-gate is often located into the side of an ejector pin on the non-visible side of the part when appearance is important. To degate, the tunnel requires a good taper and must be free to bend.

Dimensions

Typical gate sizes 0.8 mm to 1.5 mm, for glass reinforced materials sizes could be larger.

A variation of the tunnel gate design is the curved tunnel gate where the tunnel is machined in the movable mold half. This is not suitable for reinforced materials.

4.13   Curved tunnel gate.

4.14   Hot runner gates

Hot runner gates are also known as sprueless gating. The nozzle of a runnerless mold is extended forward to the part and the material is injected through a pinpoint gate. The face of the nozzle is part of the cavity surface; this can cause appearance problems (matt appearance and rippled surface). The nozzle diameter should therefore be kept as small as possible. Most suitable for thin walled parts with short cycle times, this avoid freezing of the nozzle.

4.15   Valve gates

The valve gate adds a valve rod to the hot runner gate. The valve can be activated to close the gate just before the material near the gate freezes. This allows a larger gate diameter and smoothes over the gate scar. Since the valve rod controls the packing cycle, better control of the packing cycle is maintained with more consistent quality.

5 Why Molds are Expensive

5.1.1.1 Introduction:

The simple answer is that Injection Molds are expensive because they are very complex mechanical systems. Molds require: Engineering and design, special materials, machinery and highly skilled personnel to manufacture, assemble and test them.

The injection molding process is one where molten plastic material is forced into a mold cavity under high pressure. The mold cavity is an exact hollow negative of the part to be produced. In order for the part to be released, the mold must open at the widest place on the part. The molten plastic pressure during injection ranges from 5,000 to over 20,000 psi. This pressure multiplied by the area of the part gives rise to huge forces seeking to open the mold. The mold must be constructed to withstand the very high clamping forces exerted by the injection molding machine to contain this pressure

The injection molding process is capable of rapidly producing large quantities of parts with very high precision. Tolerances of a few thousandths of an inch are routinely achieved. With the right combination of material, part design and mold construction, even sub one thousandth inch tolerances can be achieved for small features.

The cost of injection molds can range from a few thousand dollars to hundreds of thousands of dollars.

5.1.1.2 Materials:

The materials used to construct injection molds range from aluminum to hardened steel:

Aluminum for simple low production prototypes.

The relative low strength of aluminum that makes it quicker to fabricate into molds likewise limits its useful life. Aluminum molds are typically intended to produce from a few thousand to a few hundred thousand parts with relatively simple features.
Prehardened tool steel for moderate production, more complex molds.
Prehardened tool steel molds are much stronger and more durable, yet still soft enough to be worked by conventional machining processes such as milling and turning. Prehardened tool steel molds are typically intended to produce from one hundred thousand to five hundred thousand parts, and can have a wide array of features such as slides and more intricate shapes that might break in an aluminum mold.
Hardened tool steel for high production, long life molds.
Hardened tool steel molds are the most durable and expensive because part way through fabrication their components are heat treated to achieve a hardness greater than can be machined. From that point on, the fabrication must continue using grinding and EDM processes.

Hardened steel molds are intended to produce one million or more parts. Their hardness enables them to resist wear from their own operation and the abrasion of the plastic material, particularly glass fiber reinforced materials. Hybrid construction is very common, where steel

parts are used in an aluminum mold to add strength to a slender feature, or parts of a steel mold are hardened to prevent wear at a rotating or sliding mold feature.

5.1.1.3 Molds:

Single cavity molds offer the lowest tooling costs and highest precision at the penalty of higher unit costs. Multi-cavity molds are utilized to increase capacity and lower unit costs.

Family molds, multi-cavity molds with different items together, offer both the lowest mold cost and low unit cost. However, they present other problems of matching the process conditions for each part and balancing supply when the product mix or yield at a later manufacturing step varies.

5.1.1.4 Engineering and Design:

The design of injection molds begins with a review of part specifications including: Aesthetics: color, clarity, high gloss, matte, special texture, etc. Material: strength, toughness, hardness, chemical and environmental resistance Interaction with mating parts: fits and tolerances Demand and unit cost goals

From this review process the mold design concept is evolved and decisions are made resulting in a mold specification:

Single, multiple cavity or family molds The grade of mold: aluminum, prehardened tool steel or hardened tool steel Material flow considerations Parting lines and gates Finish: high gloss, texturing, embedded text and graphics, etc. Accuracy and tolerances Cooling passages Ejection system Runners or runnerless system design

The next step is the actual design of the mold. Highly skilled designers using very complex and expensive computer software programs perform this. The design tasks include:

Modeling of the products and mold components in 3D. Mold flow analysis CNC tool path design and calculation Mold materials procurement list

Early in the design process, materials and components are ordered so that manufacturing can commence as soon as possible.

5.1.1.5 Manufacturing:

Once the design is completed manufacturing begins. Mold making involves many steps, most of which are very exacting work requiring highly skilled moldmakers. One mistake can ruin or cause major repair expense to a work piece that has undergone a series of manufacturing steps over several weeks. The processes employed in mold making include:
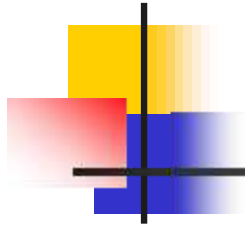
- o Milling and turning
- o Heat-treating
- o Grinding and honing
- o Electrical discharge machining
- o Polishing and texturing

To save cost, common mold components are purchased from suppliers. Frequently, outside services are required from subcontractors, which use specialty equipment such as thread grinding, etc.

When all of the parts are completed the next step is to fit, assemble and test the mold. All of the mold component parts must fit together precisely to achieve an aesthetic result on the product and for the mold to not wear out rapidly or break. The mold must be fluid tight to contain the molten plastic. Yet, at the same time the mold must have venting features added to allow the air to escape. The behavior of the plastic material when molded has been anticipated, however there can be some variance in the actual result. The mold must be tested to insure the products are correct and that the mold is performing properly. Where high accuracy is required, the mold may intentionally be made "metal safe" with the final adjustments coming after the first molding trial.

5.1.1.6 Conclusion:

As can be seen from the above, the engineering and creation of injection molds is a time consuming process. The work is demanding in terms of knowledge, skills and exacting attention to details. This will always be expensive, however this expense must be viewed in terms of what is achieved: Unsurpassed sophistication in part design and aesthetic appearance with low cost mass production.

Logic Gates

- Logic gates are electronic digital circuit perform logic functions. Commonly expected logic functions are already having the corresponding logic circuits in Integrated Circuit (I.C.) form.
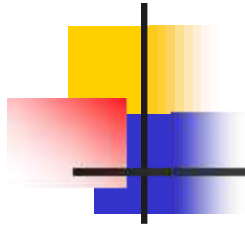
Design of Circuit Procedures

1. Obtain a precise circuit specification
2. Development of a truth table
3. Identifying the minterms corresponding to each row in the table.
4. Drawing Karnaugh maps
5. Forming groups of 1's on the Karnough map
6. Writing the reduced expression
7. Converting the reduced expression into a realizable expression
8. Drawing the circuit diagram
9. Construct and test a prototype circuit.
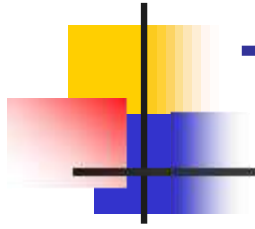
Types of Logic Gates

AND Gate

NAND Gate
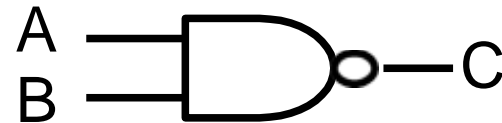
OR Gate

NOR Gate
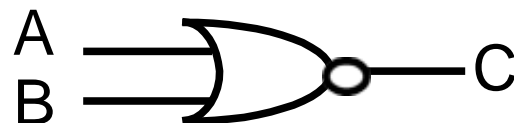
NOT Gate

Exclusive - OR Gate

$A \oplus B = C$
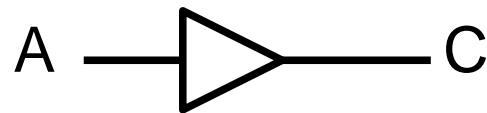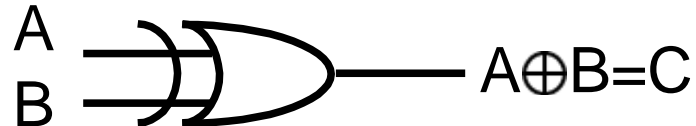
Basic Gates

AND , OR , NOT

AND Gate

- The AND gate implements the Boolean AND function where the output only is logical 1 when all inputs are logical 1.

- The standard symbol and the truth tabel for a two input AND gate is:

0 1=0
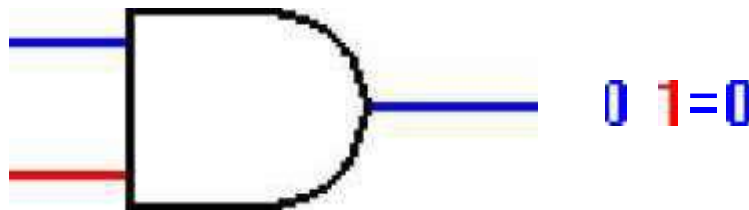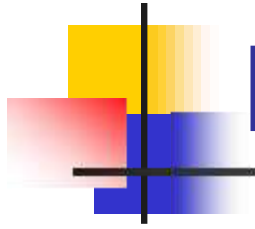
Boolean expression of AND
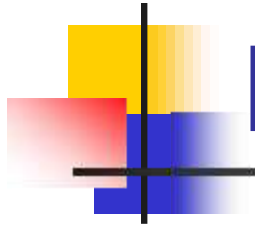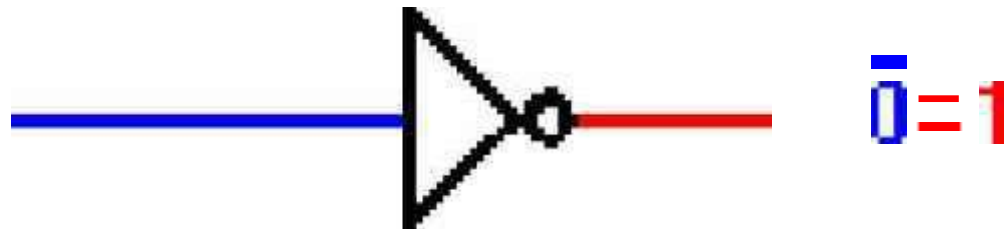
The Boolean expression for the AND gate is R=A.B

A	B	R
0	0	0
0	1	0
1	0	0
1	1	1

OR Gate

- The OR gate implements the Boolean OR function where the output is logical 1 when just input is logical 1.

- The standard symbol and the truth table for a two input OR gate is:

$$0 + 1 = 1$$
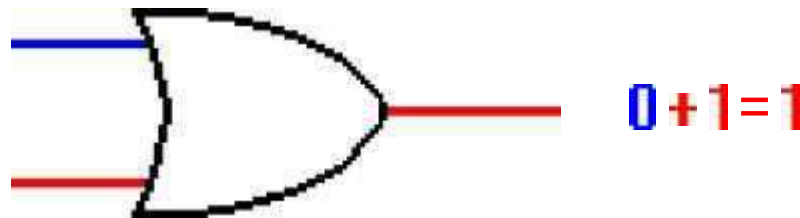
Boolean Expression of OR

The Boolean expression for the OR gate is: R=A+B

A	B	R
0	0	0
0	1	1
1	0	1
1	1	1

NOT Gate

- The NOT gate implements the Boolean NOT function where the output is the inverse of the input.

- The standard symbol and the truth table for the NOT gate is:

$$\bar{0}=1$$

Boolean Expression of NOT

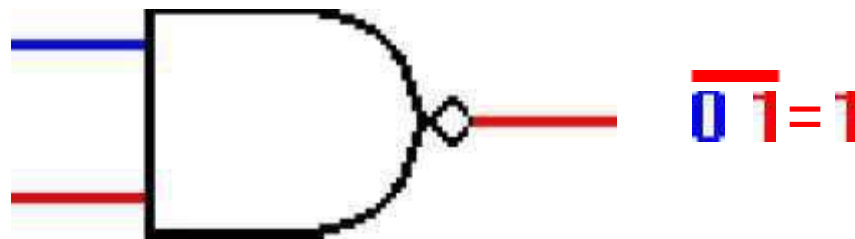- The Boolean expression for the NOT gate is: R=-A
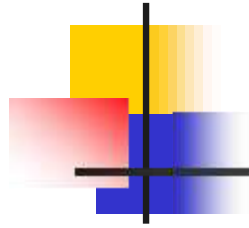
A	R
0	1
0	0

Derived Gates

NAND , NOR , XOR

NAND Gate

- The NAND gate is an AND gate followed by a NOT gate. The output is logical 1 when one of the inputs are logical 0

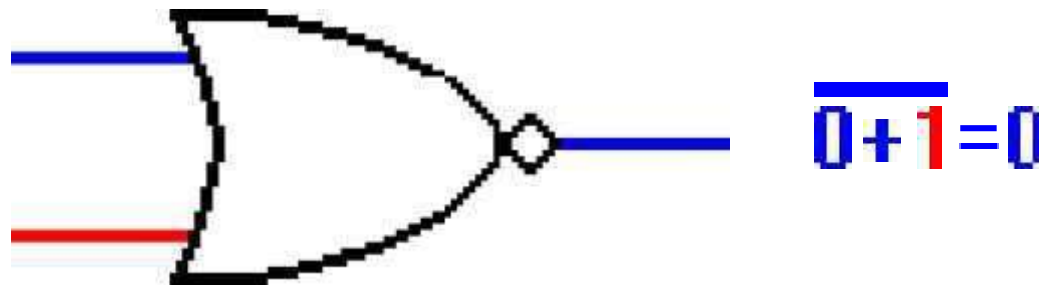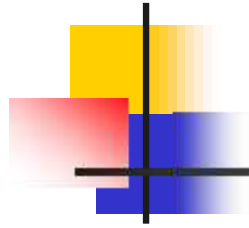- The standard symbol and the truth table for the NAND gate is:

$$\overline{0}\,\overline{1} = 1$$

Boolean expression of NAND

A	B	R
0	0	1
0	1	1
1	0	1
1	1	0

NOR Gate

- The NOR is a combination of an OR followed by a NOT gate. The output is logical 1 when non of the inputs are logical 0

- The standard symbol and the truth table for the NOR gate is:

$$\overline{0+1}=0$$

Boolean Expression of NOR

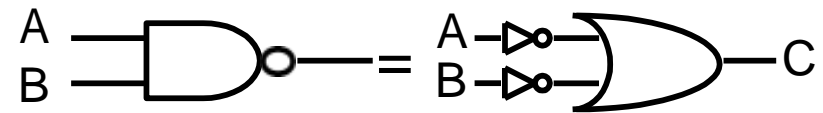| A	B	R
0	0	1
0	1	0
1	0	0
1	1	0

XOR Gate

- The XOR gate produces a logic 1 output only if its two inputs are *different*. If the inputs are the same, the output is a logic 0

- The XOR symbol is a variation on the standard OR symbol. It consists of a plus (+) sign with a circle around it. The logic symbol, as shown here, is a variation on the standard OR symbol.
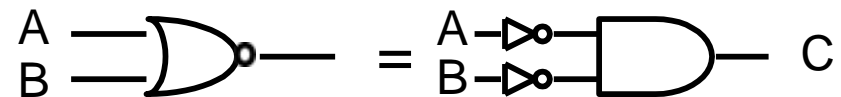
$$0 \oplus 1 = 1$$
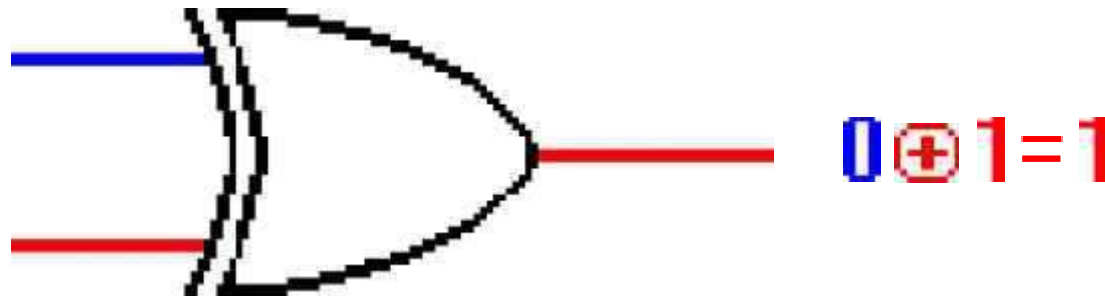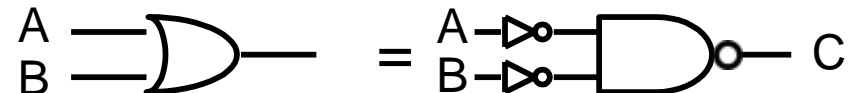
De-Morgan's Theorem and Logic Conversion

1) $\overline{(A \bullet B)} = \overline{A} + \overline{B}$

2) $\overline{(A + B)} = \overline{A} \bullet \overline{B}$

3) $A + B = \overline{\overline{A + B}} = \overline{\overline{A} \bullet \overline{B}}$
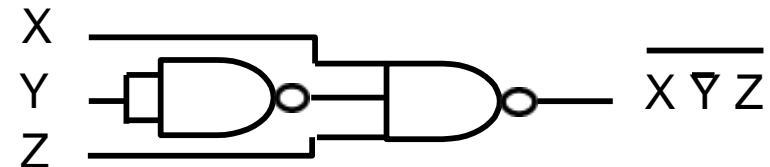

4) $A \bullet B = \overline{\overline{A \bullet B}} = \overline{\overline{A} + \overline{B}}$
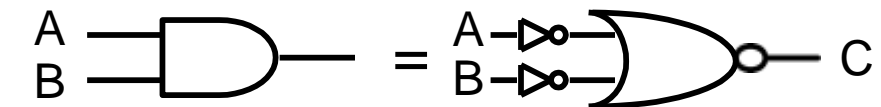
Implement the logic expression using NAND gates only

1)

$$Z = \overline{X} + Y + \overline{Z}$$

$$= \overline{\overline{\overline{X} + Y + \overline{Z}}}$$

$$= \overline{X \bullet \overline{Y} \bullet Z}$$

$\overline{X \, \overline{Y} \, Z}$

2)

$$Z = XY + \overline{X}Z + Y\overline{Z}$$

$$= \overline{\overline{XY + \overline{X}Z + Y\overline{Z}}}$$

$$= \overline{\overline{XY} \bullet \overline{\overline{X}Z} \bullet \overline{Y\overline{Z}}}$$

$XY + \overline{X}Z + Y\overline{Z}$
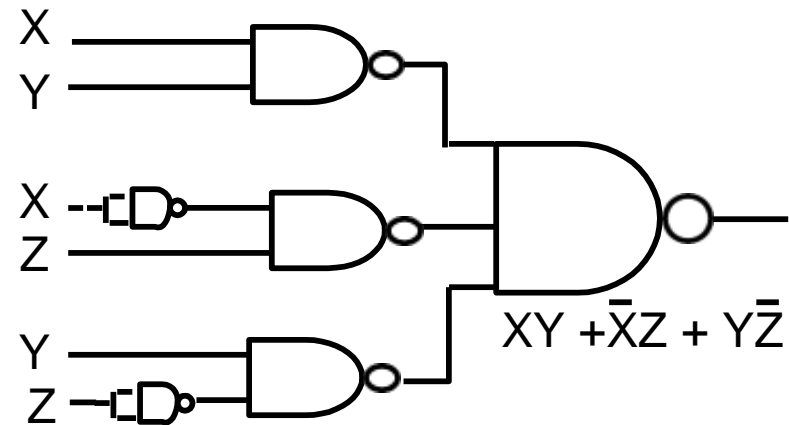
Implement logic expression using NOR gates only

1)

$$Z = (X + Y) \bullet (\overline{X} + Y)$$

$$= \overline{\overline{(X + Y) \bullet (\overline{\overline{X}} + Y)}}$$

$$= \overline{\overline{X + Y} + \overline{\overline{\overline{X}} + Y}}$$
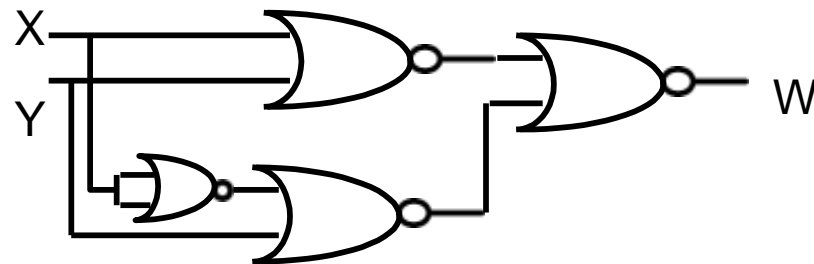
Combinational Logic Designs

- A combinational logic circuit can be described by the block schematic shown

I_1 → | Combinational | → O_1

Combinational

Logic

I_n → | Logic | → O_n
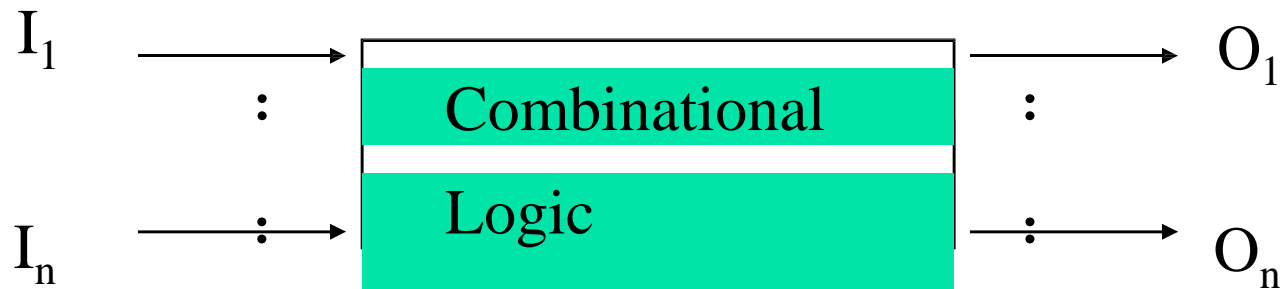
- Each output is a function of some or all of the input variables, Hence

$$O_1=f(I_1,I_2,....,I_n) \qquad O_2=f(I_1,I_2,…,I_n) …$$
and $O_n=f(I_1,I_2,…,I_n)$

Half Adder

What is a Half adder?

- Logic gate that perform addition for 1-bit
- When 1 + 1 occurs, a carry produce 1

Half Adder

Perform arithmetic additions

- two inputs A, B to half-adder. Resultants are Sum(S) and Carry(C_{out})

$$A \quad \boxed{\text{H.A}} \quad S$$
$$B \qquad \qquad C_{out}$$

- Using K-Map to simplify the sum term, we get

$S = \overline{A}B + A\overline{B}$

$\quad = A \oplus B$

$C = AB$
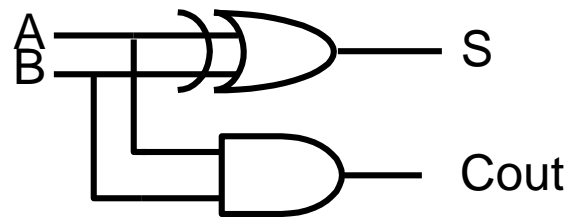
A	B	S	C
0	0	0	0
0	1	1	0
1	0	1	0
1	1	0	1
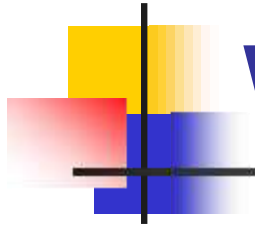
Full Adder

What is Full Adder?

- A full adder is a circuit that computes the sum of three bits and gives a two-bit answer.

- A circuit for adding two 16-bit numbers can be built from 16 full-adder circuits. Each full-adder does one column of the sum.

- The full adder for a given column adds two bits from the input numbers together with a one-bit carry from the previous column to the right. The adder produces a two-bit answer; one of these bits is used as a carry into the next column.

Full Adder

A ⟶ [Full Adder] ⟶ S

B ⟶
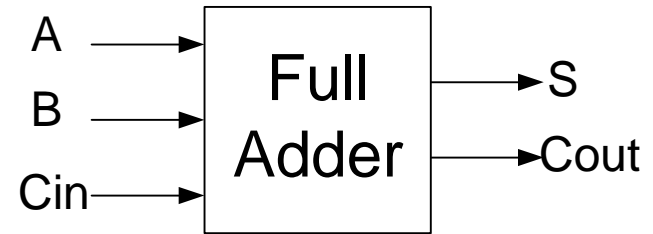
Cin ⟶ ⟶ Cout

- A full adder has 3 inputs and 2 outputs
- The truth table of the full-adder can be drawn with inputs A,B and Cin with outputs S and Cout
- From the truth table we can write the Boolean equation for the S and Cout

$$S = \overline{A}\,\overline{B}C_{in} + \overline{A}B\overline{C}_{in} + A\overline{B}\,\overline{C}_{in} + ABC_{in}$$

$$C_{out} = \overline{A}BC_{in} + A\overline{B}C_{in} + AB\overline{C}_{in} + ABC_{in}$$

- Simplify using Boolean Algebra and K-map, we get

$$S = A \oplus B \oplus C_{in}$$

$$C_{out} = AC_{in} + BC_{in} + AB$$

Sum = Any 2 of the three inputs are 1
Cout = XOR between A, B, Cin

A	B	Cin	Sum	Cout
0	0	0	0	0
0	0	1	0	1
0	1	0	0	1
0	1	1	1	0
1	0	0	0	1
1	0	1	1	0
1	1	0	1	0
1	1	1	1	1

Full Adder diagram
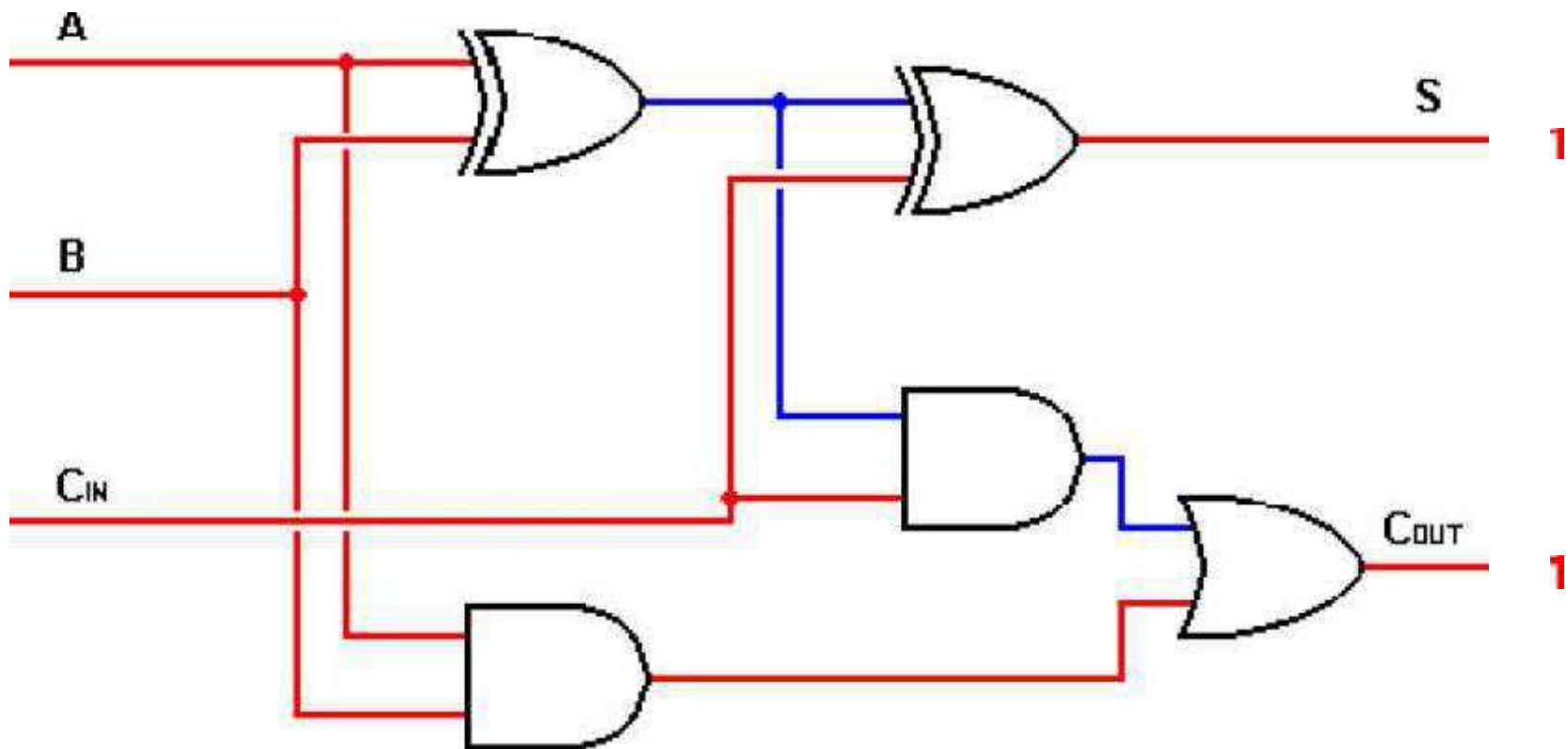
Half Subtractor

What is a Half Subtractor

- A logic gate that perform 1 bit subtraction
- When 0-1 occurs, a carry produces 1

Half Subtractor

A_0	B_0	D_0	C_1
0	0	0	0
0	1	1	1
1	0	1	0
1	1	0	0

A_0

B_0

D_0

C_1

$$1 \quad \overset{2}{\underset{0}{}}$$

$$\begin{array}{r} 1\,2 \\ 0 \\ -1 \\ \hline 1 \end{array}$$
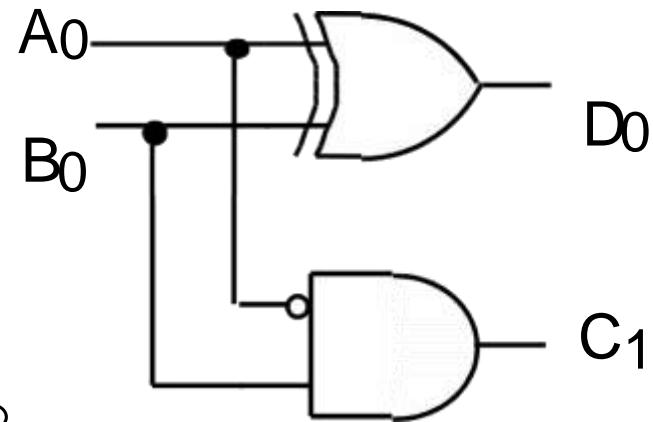
Half Subtractor

- Operation: A - B

$$D = \overline{A}B + A\overline{B}$$

$$B_{out} = \overline{A}B$$

A	B	D	B_{out}
0	0	0	0
0	1	1	1
1	0	1	0
1	1	0	0
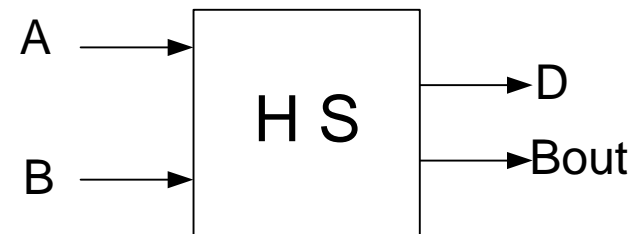
Full Subtractor

What is a Full Subtraction?

- Logic gates that perform two bits subtraction

Full Subtractor

C_i	A_i	B_i	D_i	C_{i+1}
0	0	0	0	0
0	0	1	1	1
0	1	0	1	0
0	1	1	0	0
1	0	0	1	1
1	0	1	0	1
1	1	0	0	0
1	1	1	1	1

C_i \ A_iB_i	00	01	11	10
0		1		1
1	1		1	

D_i

$$D_i = C_i \; \$ \; (A_i \; \$ \; B_i)$$

Same as S_i in full adder

Full Subtractor

C_i	A_i	B_i	D_i	C_{i+1}
0	0	0	0	0
0	0	1	1	1
0	1	0	1	0
0	1	1	0	0
1	0	0	1	1
1	0	1	0	1
1	1	0	0	0
1	1	1	1	1

A_iB_i

C_i	00	01	11	10
0		1		
1	1	1	1	

$$C_{i+1}$$

```
C     =  !A   &  B
 i+1       i      i
         #  C   &  !A   &  !B
             i       i       i
         #  C   &  A   &  B
             i      i      i
```

Full Subtractor

$$C_{i+1} = !A_i \& B_i$$
$$\# \ C_i \& !A_i \& !B_i$$
$$\# \ C_i \& A_i \& B_i$$

$$C_{i+1} = !A_i \& B_i$$
$$\# \ C_i \& (!A_i \& !B_i \# A_i \& B_i)$$

$$C_{i+1} = !A_i \& B_i \# C_i \& !(A_i \$ B_i)$$
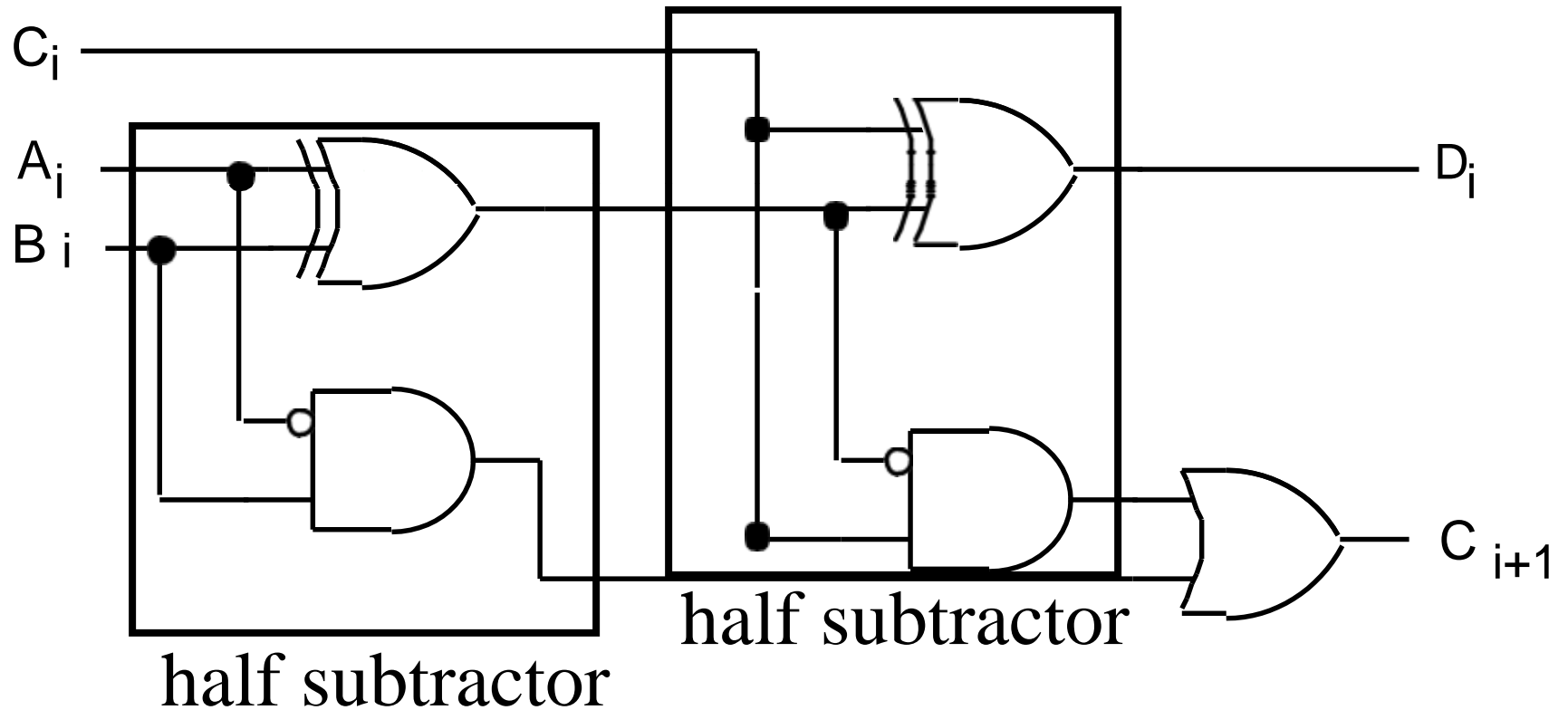
Recall:

$$D_i = C_i \$ (A_i \$ B_i)$$

$$C_{i+1} = !A_i \& B_i \# C_i \& !(A_i \$ B_i)$$

Full Subtractor

$$D_i = C_i \ \$ \ (A_i \ \$ \ B_i)$$

$$C_{i+1} = !A_i \ \& \ B_i \ \# \ C_i \ \& \ !(A_i \ \$ \ B_i)$$

C_i

A_i

B_i

D_i

C_{i+1}

half subtractor

half subtractor

Full Subtractor

- Operation: A - B - B$_{in}$

$$D = \overline{A}\,\overline{B}B_{in} + \overline{A}B\overline{B}_{in} + ABB_{in} + A\overline{B}\,\overline{B}_{in}$$

$$B_{out} = \overline{A}B_{in} + \overline{A}B + BB_{in}$$
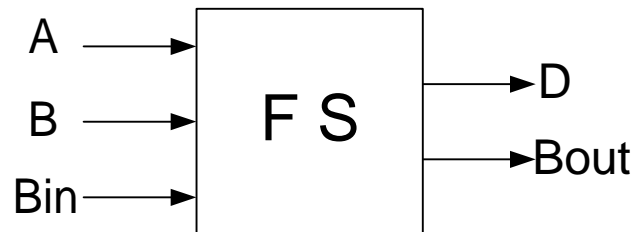
A	B	B$_{in}$	D	B$_{out}$
0	0	0	0	0
0	0	1	1	1
0	1	0	1	1
1	0	0	1	0
1	0	1	0	0
1	1	0	0	0
1	1	1	1	1

Adder/Subtractor - 1

A_0

S_0

B_0

C_1

Half adder

A_0

D_0

B_0

C_1

Half subtractor

A_0

SD

E = 0: Half adder

B_0

0
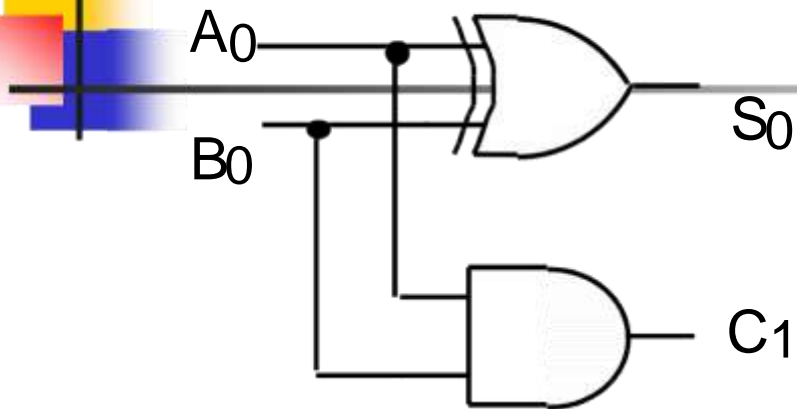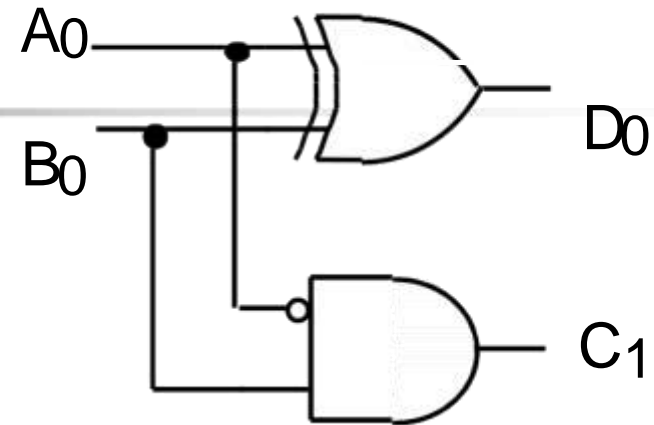
E = 1: Half subtractor

E

CB_1
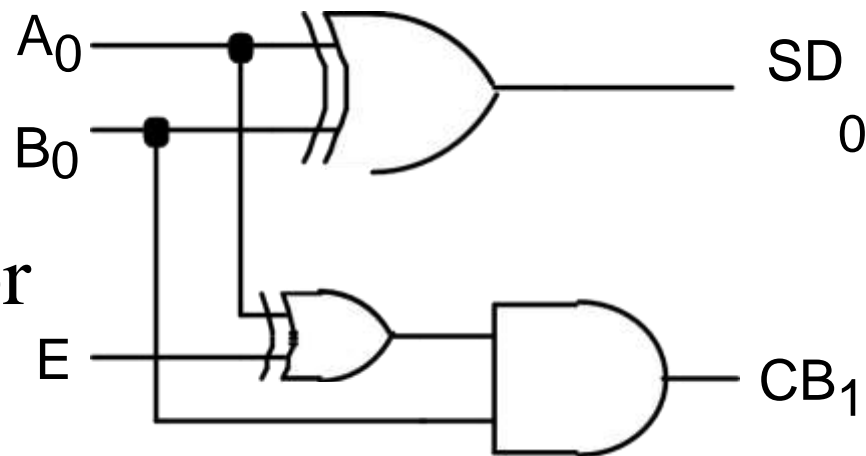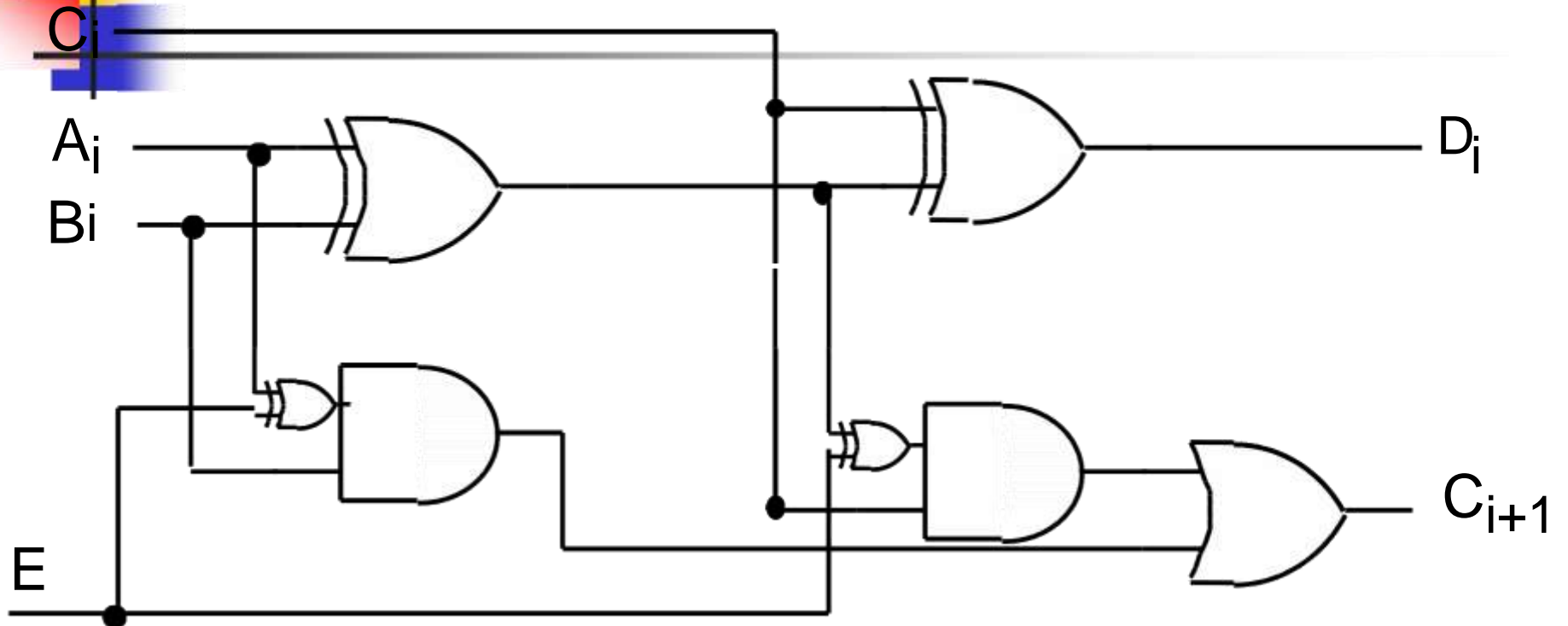
Adder/Subtractor-1

E = 0: Full adder
E = 1: Full subtractor

Full Adder

C_i	A_i	B_i	S_i	C_{i+1}
0	0	0	0	0
0	0	1	1	0
0	1	0	1	0
0	1	1	0	1
1	0	0	1	0
1	0	1	0	1
1	1	0	0	1
1	1	1	1	1

Reordered Full Adder

C_i	A_i	B_i	S_i	C_{i+1}
1	0	1	0	1
1	0	0	1	0
1	1	1	1	1
1	1	0	0	1
0	0	1	1	0
0	0	0	0	0
0	1	1	0	1
0	1	0	1	0

Full Subtractor

C_i	A_i	B_i	D_i	C_{i+1}
0	0	0	0	0
0	0	1	1	1
0	1	0	1	0
0	1	1	0	0
1	0	0	1	1
1	0	1	0	1
1	1	0	0	0
1	1	1	1	1

NOT

Making a full subtractor from a full adder
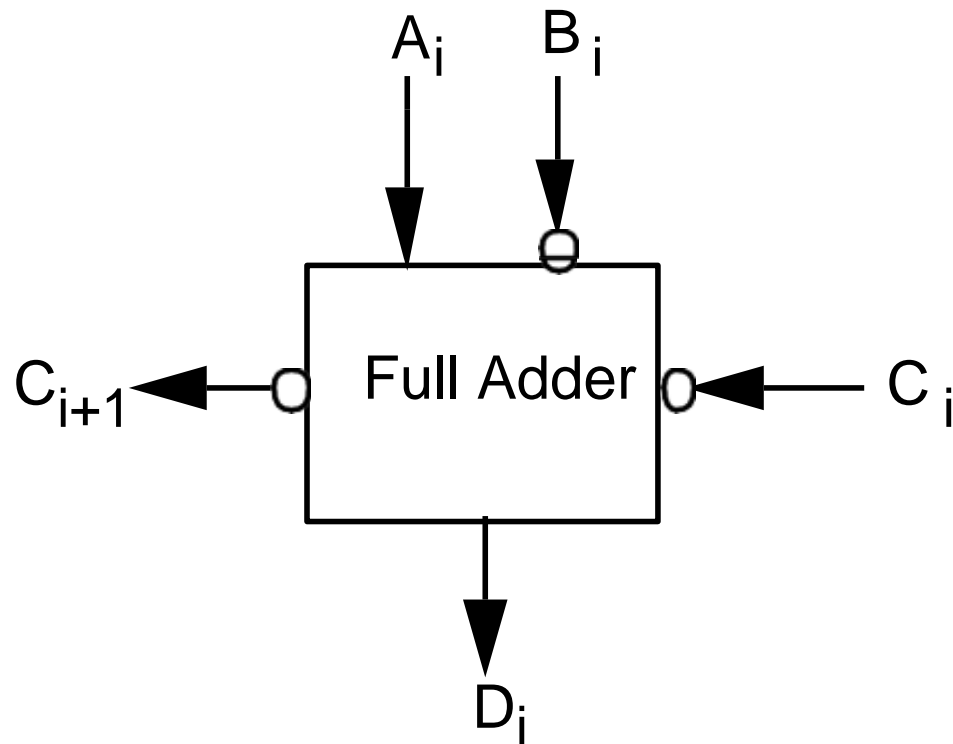
Four-Bit Parallel Adder
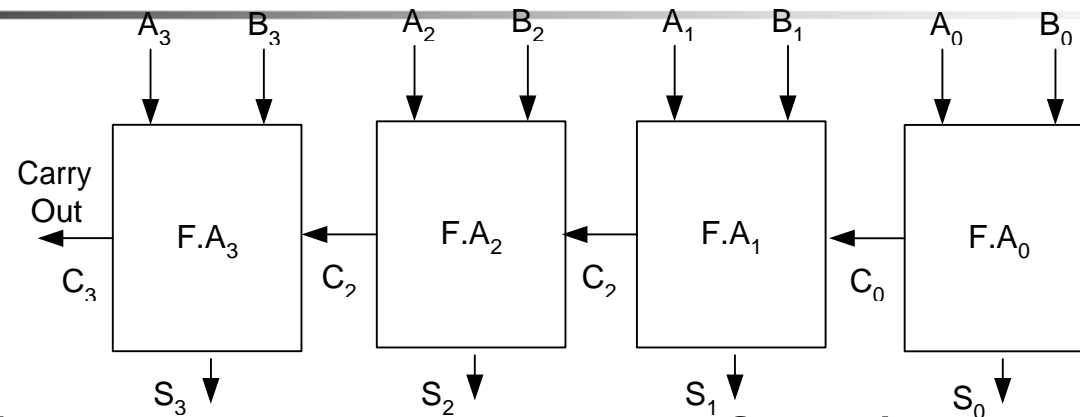
- This circuit is sometimes referred to as a ripple-through adder
- $C0$ ripples through four two-level logic circuits and hence the sum cannot be completed until eight gate delays
- For this kind of adder, the maximum delay is directly proportional to the number of stages n.

Adder/Subtractor-2
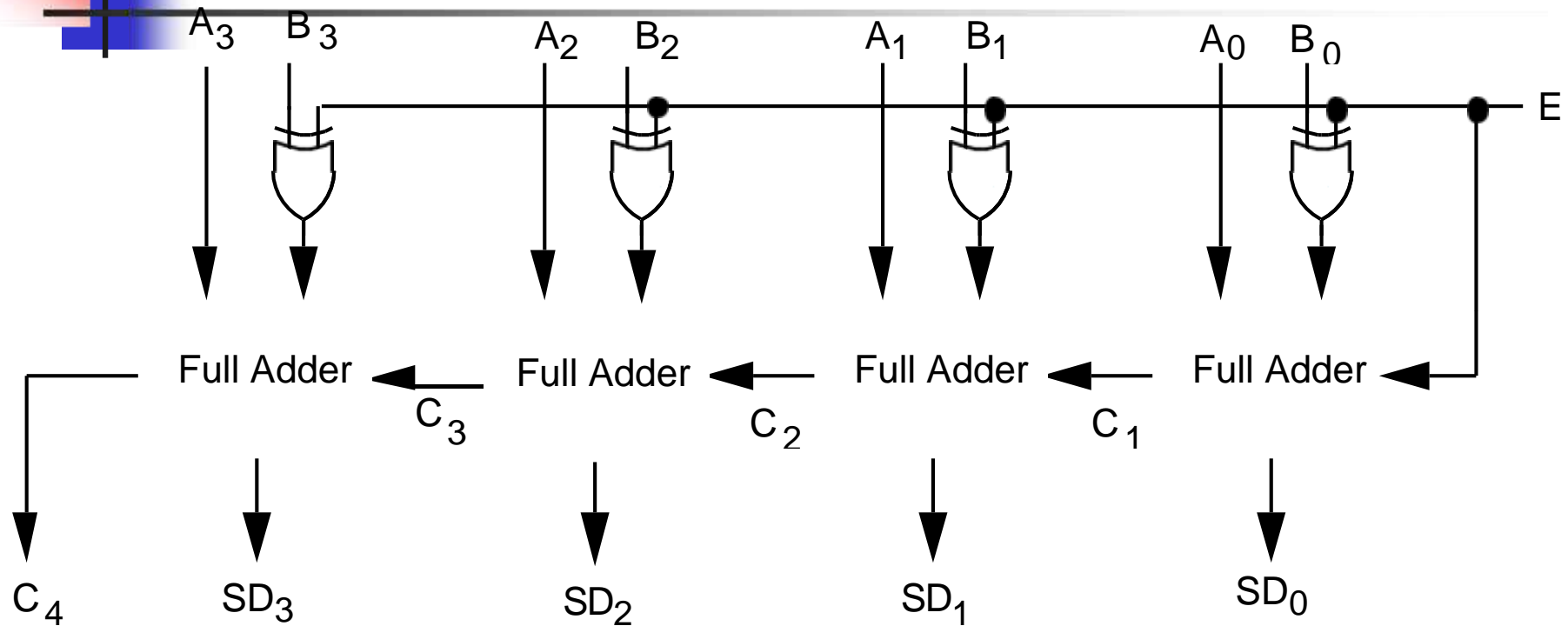
$E = 0$: 4-bit adder

$E = 1$: 4-bit subtractor

Carry Look-Ahead Circuit

- To improve the speed of addition

- Consider the carry output equation for a full adder is

$$C_{out} = \overline{A}BC_{in} + A\overline{B}C_{in} + AB\overline{C}_{in} + ABC_{in}$$

- Which can be expressed as follows

$$C_{out} = (A \oplus B)C_{in} + AB$$

- or as $C_{out} = PC_{in} + G$

- where $P = A \oplus B$

$$G = AB$$

Carry Look-Ahead Circuit

- Four a four-bit adder the generate and propagate terms for each stage are $G_0 = A_0 \bullet B_0 \quad P_0 = A_0 \oplus B_0$

$$G_1 = A_1 \bullet B_1 \quad P_1 = A_1 \oplus B_1$$

$$G_2 = A_2 \bullet B_2 \quad P_2 = A_2 \oplus B_2$$

$$G_3 = A_3 \bullet B_3 \quad P_3 = A_3 \oplus B_3$$

- while the carries for the various stages are

$$C_0 = P_0 \bullet C_{-1} + G_0$$

$$C_1 = P_1 \bullet C_0 + G_1$$

$$C_2 = P_2 \bullet C_1 + G_2$$

$$C_3 = P_3 \bullet C_2 + G_3$$

Carry Look-Ahead Circuit

- Substituting for C_0 in the C_1 equation etc leads to the following equations: $C_1 = P_1 P_0 C_{-1} + P_1 G_0 + G_1$

$$C_2 = P_2 (P_1 P_0 C_{-1} + P_1 G_0 + G_1) + G_2$$

$$C_3 = P_3 (P_2 (P_1 P_0 C_{-1} + P_1 G_0 + G_1)) + G_3$$

- And the sum

$$S_0 = A_0 \oplus B_0 \oplus C_{-1} = P_0 \oplus C_{-1}$$

$$S_1 = P_1 \oplus C_0$$

$$S_2 = P_2 \oplus C_1$$

$$S_3 = P_3 \oplus C_2$$

- Since the number of levels of logic required when a large number of bits has to be added does not increase then the Carry Look-Ahead adder will provide a faster addition time

Binary Multiplication

- Paper and Pen method

- which is implemented using 9 AND gates, 3 FA and 3 HA

	A_2	A_1	A_0

			A_2	A_1	A_0
			B_2	B_1	B_0
		$A_2 B_0$	$A_1 B_0$	$A_0 B_0$	
	$A_2 B_1$	$A_1 B_1$	$A_0 B_1$		
$A_2 B_2$	$A_1 B_2$	$A_0 B_2$			
	C'_3	C'_2			
C_4	C'_3	C'_2	C_1		
P_5	P_4	P_3	P_2	P_1	P_0
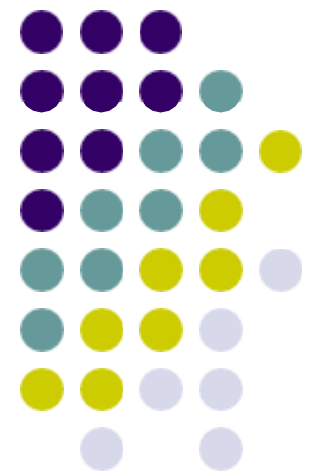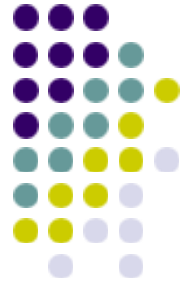
Electric Motors

Objective

To outline and provide relevant
information on the following

- The Various Components of an Electric Motor
- How an Electric Motor Works
- Function Within The Reciprocating Saw

What Are The Components of An Electric Motor
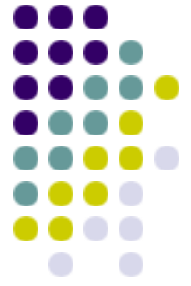
- Axle
- Commutator
- Armature
- Field Magnet
- DC Power Supply
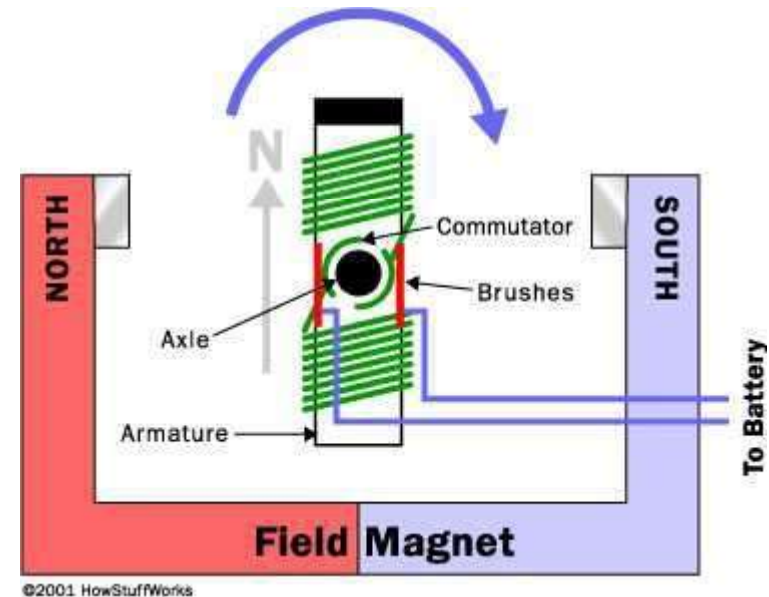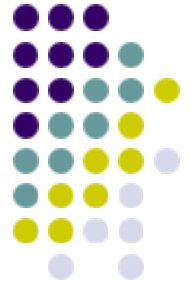
Axle, Armature and Commutator

- The axle contains the armature and commutator

- The armature consists of a set of electromagnets

- An electromagnet is a set of thin metal plates stacked together.

- Thin copper wire is coiled around each of the plates

- Each end of the wire is soldered onto the plate and then wired to the commutator.

- The commutator is a pair of plates attached to the axle.

- These plates provide the two connections for the coil of the electromagnet.

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Commutator contacts

Armature coil terminals

Armature

http://electronics.howstuffworks.com/motor5.htm
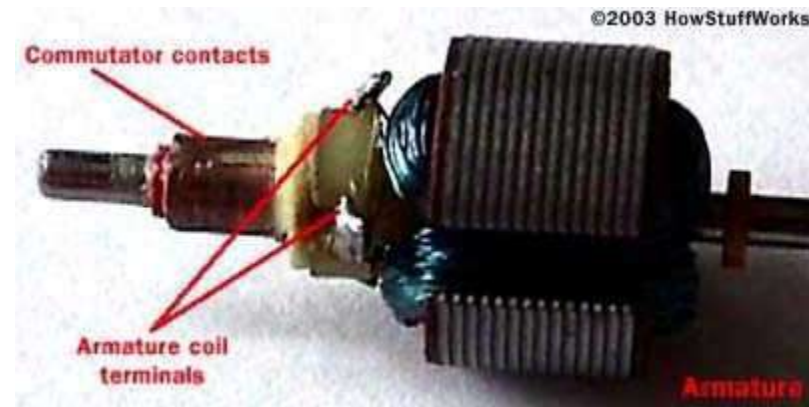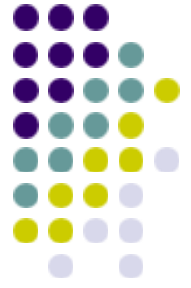
Field Magnet

- Consists of the motor housing and two curved permanent magnets

http://electronics.howstuffworks.com/motor4.htm

How Does An Electric Motor Work

SOUTH   NORTH

N   S

Battery

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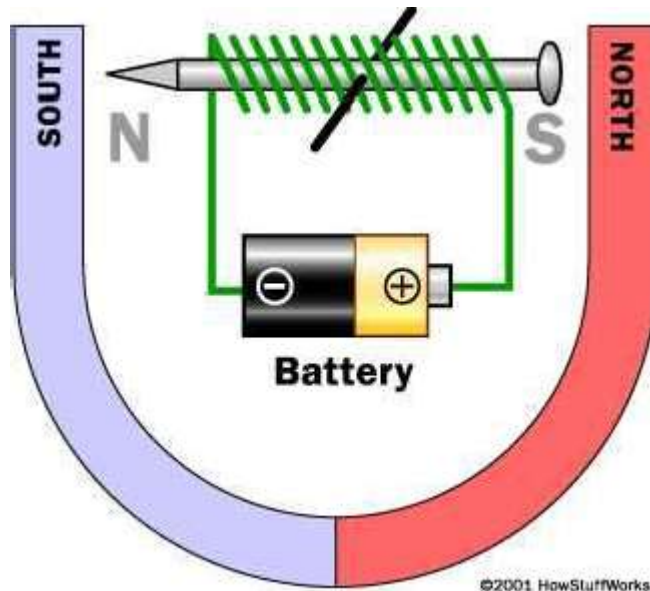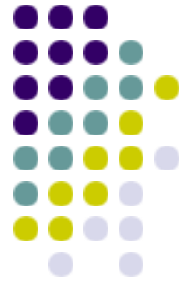
- A battery is used to magnetize the coils.

- Creates a magnetic field traveling north to south outside the coil

- North end of the coil is attracted the south end of the magnet

- Vice-versa for the south end of the coil

- This attraction causes the axel to make half a rotation

http://electronics.howstuffworks.com/motor4.htm

- In an electric motor the armature takes the place of the nail

- As the armature passes through the horizontal position, the current flips.

- The magnetic dipole is flipped, which is caused by a reverse in electron flow

- The commutator causes the reverse of electron flow

- The process continues indefinitely

When **electric current** passes through a coil in a **magnetic field**, the **magnetic force** produces a **torque** which turns the DC motor

S

F

I

B

N

I

Electric current supplied externally through a **commutator**

Magnetic force
F=ILB
acts perpendicular to both wire and magnetic field

F

R Nave
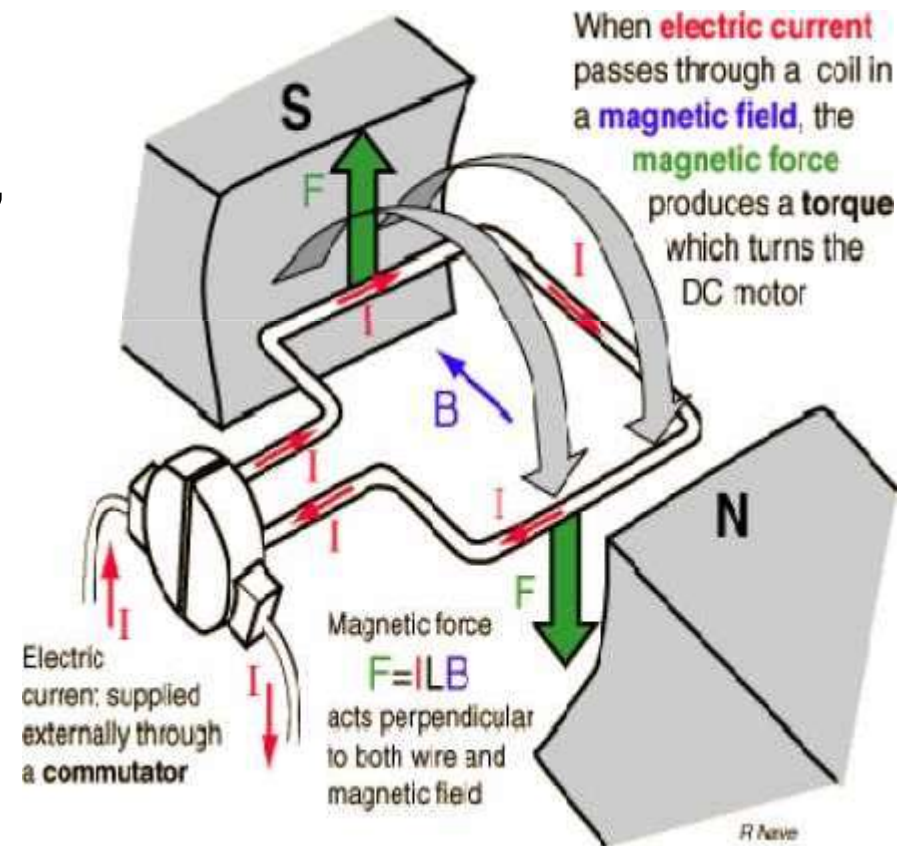
Function Within The Reciprocating Saw
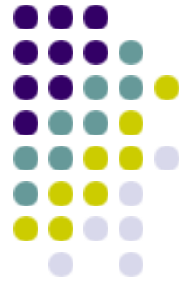
- The electric motor converts the power of the battery into mechanical energy

- The motor does work to create rotational motion

- The rotational motion is transferred into linear motion to be used for the tool's primary purpose.

Air pollution occurs when harmful or excessive quantities of substances including gases, particulates, and biological molecules are introduced into Earth's atmosphere. It may cause diseases, allergies and even death to humans; it may also cause harm to other living organisms such as animals and food crops, and may damage the natural or built environment. Both human activity and natural processes can generate air pollution.

Indoor air pollution and poor urban air quality are listed as two of the world's worst toxic pollution problems in the 2008 Blacksmith Institute World's Worst Polluted Places report. According to the 2014 World Health Organization report, air pollution in 2012 caused the deaths of around 7 million people worldwide an estimate roughly echoed by one from the International Energy .

Pollutants

An air pollutant is a material in the air that can have adverse effects on humans an the ecosystem. The substance can be solid particles, liquid droplets, or gases. A pollutant can be of natural origin or man-made. Pollutants are classified as primary or secondary. Primary pollutants are usually produced by processes such as ash from a volcanic eruption. Other examples include carbon monoxide gas from motor vehicle exhausts or sulphur dioxide released from the factories. Secondary pollutants are not emitted directly. Rather, they form in the air when primary pollutants react or interact. Ground level ozone is a prominent example of secondary pollutants. Some pollutants may be both primary and secondary: they are both emitted directly and formed from other primary pollutants.

Before flue-gas desulphurization was installed, the emissions from this power plant in New Mexico contained excessive amounts of sulphur dioxide.
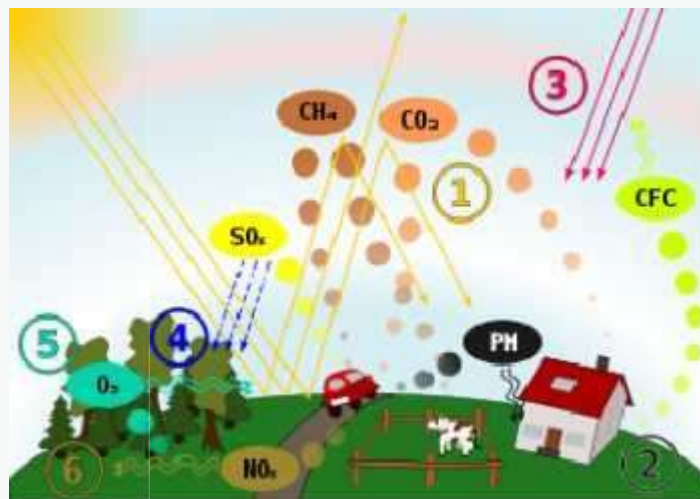
Schematic drawing, causes and effects of air pollution: (1) greenhouse effect, (2) particulate contamination, (3) increased UV radiation, (4) acid rain, (5) increased ground-level ozone concentration, (6) increased levels of nitrogen oxides.

Thermal oxidizers are air pollution abatement options for hazardous air pollutants (HAPs), volatile organic compounds (VOCs), and odorous emissions.

Substances emitted into the atmosphere by human activity include:

- Carbon dioxide (CO_2) – Because of its role as a greenhouse gas it has been described as "the leading pollutant"[5] and "the worst climate pollution".[6] Carbon dioxide is a natural component of the atmosphere, essential for plant life and given off by the human respiratory system.[7] This question of terminology has practical effects, for example as determining whether the U.S. Clean Air Act is deemed to regulate CO_2 emissions.[8] CO_2 currently forms about 410 parts per million (ppm) of earth's atmosphere, compared to about 280 ppm in pre-industrial times,[9] and billions of metric tons of CO_2 are emitted annually by burning of fossil fuels.[10] CO_2 increase in earth's atmosphere has been accelerating.[11]
- Sulphur oxides (SO_x) – particularly sulphur dioxide, a chemical compound with the formula SO_2. SO2 is produced by volcanoes and in various industrial processes. Coal and petroleum often contain sulphur compounds, and their combustion generates sulphur dioxide. Further oxidation of SO_2, usually in the presence of a catalyst such as NO_2, forms H_2SO_4, and thus acid rain.[2] This is one of the causes for concern over the environmental impact of the use of these fuels as power sources.
- Nitrogen oxides (NO_x) – Nitrogen oxides, particularly nitrogen dioxide, are expelled from high temperature combustion, and are also produced during thunderstorms by electric discharge. They can be seen as a brown haze dome above or a plume downwind of cities. Nitrogen dioxide is a chemical compound with the formula NO_2. It is one of several nitrogen oxides. One of the most prominent air pollutants, this reddish-brown toxic gas has a characteristic sharp, biting odor.
- Carbon monoxide (CO) – CO is a colorless, odorless, toxic yet non-irritating gas. It is a product of combustion of fuel such as natural gas, coal or wood. Vehicular exhaust contributes to the majority of carbon monoxide let into our atmosphere. It creates a smog type formation in the air that has been linked to many lung diseases and disruptions to the natural environment and animals. In 2013, more than half of the carbon monoxide emitted into our atmosphere was from vehicle traffic and burning one gallon of gas will often emit over 20 pounds of carbon monoxide into the air.[12]
- Volatile organic compounds (VOC) – VOCs are a well-known outdoor air pollutant. They are categorized as either methane (CH_4) or non-methane (NMVOCs). Methane is an extremely efficient greenhouse gas which contributes to enhanced global warming. Other hydrocarbon VOCs are also significant greenhouse gases because of their role in creating ozone and

prolonging the life of methane in the atmosphere. This effect varies depending on local air quality. The aromatic NMVOCs benzene, toluene and xylene are suspected carcinogens and may lead to leukemia with prolonged exposure. 1,3-butadiene is another dangerous compound often associated with industrial use.

- Particulates, alternatively referred to as particulate matter (PM), atmospheric particulate matter, or fine particles, are tiny particles of solid or liquid suspended in a gas. In contrast, aerosol refers to combined particles and gas. Some particulates occur naturally, originating from volcanoes, dust storms, forest and grassland fires, living vegetation, and sea spray. Human activities, such as the burning of fossil fuels in vehicles, power plants and various industrial processes also generate significant amounts of aerosols. Averaged worldwide, anthropogenic aerosols—those made by human activities—currently account for approximately 10 percent of our atmosphere. Increased levels of fine particles in the air are linked to health hazards such as heart disease,[13] altered lung function and lung cancer. Particulates are related to respiratory infections and can be particularly harmful to those already suffering from conditions like asthma.[14]
- Persistent free radicals connected to airborne fine particles are linked to cardiopulmonary disease.[15][16]
- Toxic metals, such as lead and mercury, especially their compounds.
- Chlorofluorocarbons (CFCs) – harmful to the ozone layer; emitted from products are currently banned from use. These are gases which are released from air conditioners, refrigerators, aerosol sprays, etc. On release into the air, CFCs rise to the stratosphere. Here they come in contact with other gases and damage the ozone layer. This allows harmful ultraviolet rays to reach the earth's surface. This can lead to skin cancer, eye disease and can even cause damage to plants.
- Ammonia (NH_3) – emitted from agricultural processes. Ammonia is a compound with the formula NH_3. It is normally encountered as a gas with a characteristic pungent odor. Ammonia contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to foodstuffs and fertilizers. Ammonia, either directly or indirectly, is also a building block for the synthesis of many pharmaceuticals. Although in wide use, ammonia is both caustic and hazardous. In the atmosphere, ammonia reacts with oxides of nitrogen and sulphur to form secondary particles.[17]
- Odours — such as from garbage, sewage, and industrial processes
- Radioactive pollutants – produced by nuclear explosions, nuclear events, war explosives, and natural processes such as the radioactive decay of radon.

Secondary pollutants include:

- Particulates created from gaseous primary pollutants and compounds in photochemical smog. Smog is a kind of air pollution. Classic smog results from large amounts of coal burning in an area caused by a mixture of smoke and sulphur dioxide. Modern smog does not usually come from coal but from vehicular and industrial emissions that are acted on in the atmosphere by ultraviolet light from the sun to form secondary pollutants that also combine with the primary emissions to form photochemical smog.
- Ground level ozone (O_3) formed from NO_x and VOCs. Ozone (O_3) is a key constituent of the troposphere. It is also an important constituent of certain regions of the stratosphere commonly known as the Ozone layer. Photochemical and chemical reactions involving it drive many of the chemical processes that occur in the atmosphere by day and by night. At abnormally high concentrations brought about by human activities (largely the combustion of fossil fuel), it is a pollutant and a constituent of smog.
- Peroxyacetyl nitrate ($C_2H_3NO_5$) – similarly formed from NO_x and VOCs.

Minor air pollutants include:

- A large number of minor hazardous air pollutants. Some of these are regulated in USA under the Clean Air Act and in Europe under the Air Framework Directive
- A variety of persistent organic pollutants, which can attach to particulates

Persistent organic pollutants (POPs) are organic compounds that are resistant to environmental degradation through chemical, biological, and photolytic processes. Because of this, they have been observed to persist in the environment, to be capable of long-range transport, bio accumulate in human and animal tissue, bio magnify in food chains, and to have potentially significant impacts on human health and the environment.

Boundary layer concept

u_∞

$u = 0.99u_\infty \approx u_\infty$

Nominal Limit of
Boundary Layer

Transition
Region (short)

Turbulent

δ

u

y

Laminar

Leading Edge

Transition
Point

Viscous
Sublayer

Buffer
Zone

Graph of velocity u
against distance y from
surface at point x

x
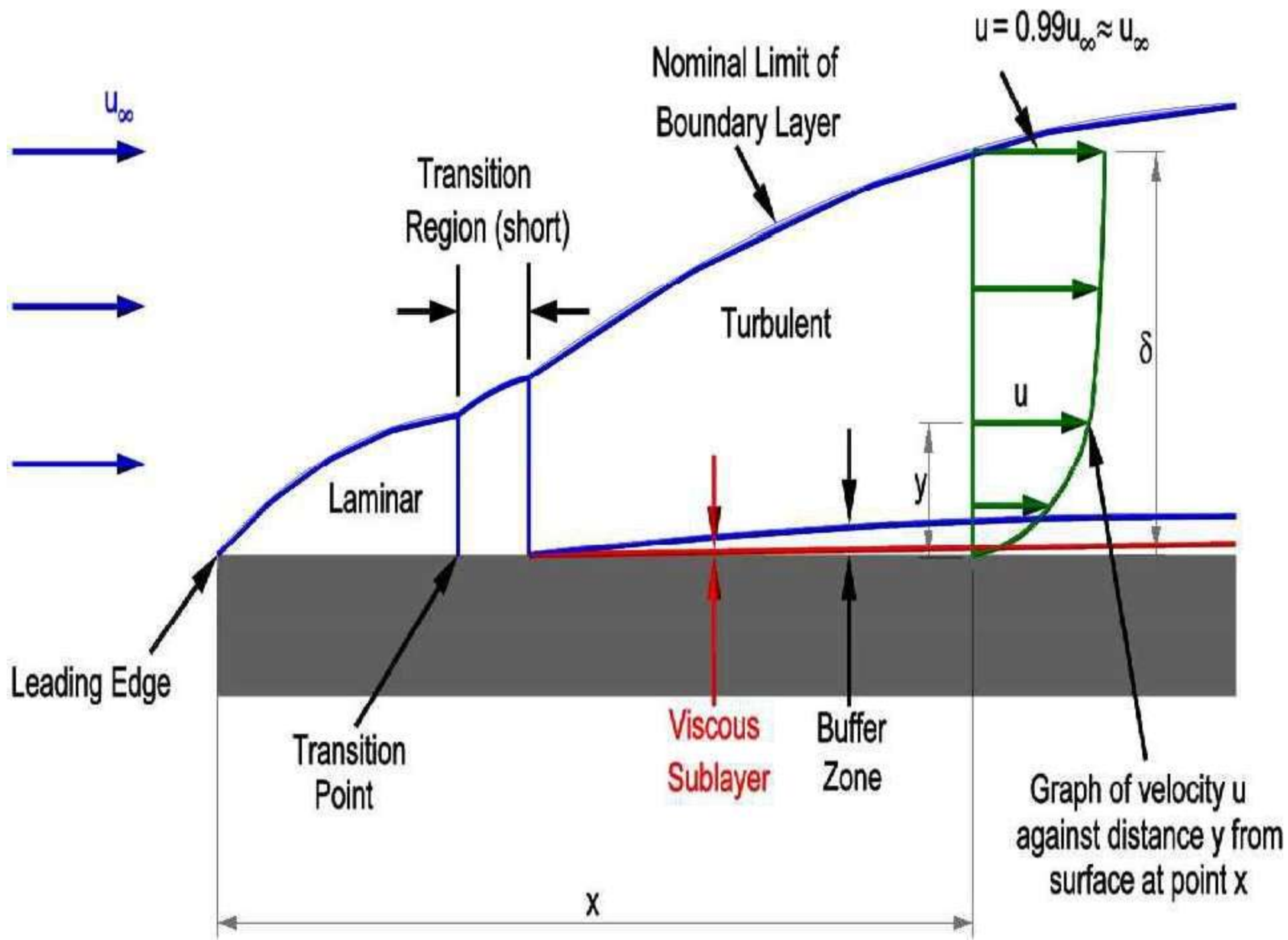
Laminar Boundary Layer Flow

- The laminar boundary layer is a very smooth flow, while the turbulent boundary layer contains swirls or "eddies."

- The laminar flow creates less skin friction drag than the turbulent flow, but is less stable.

- Boundary layer flow over a wing surface begins as a smooth laminar flow. As the flow continues back from the leading edge, the laminar boundary layer increases in thickness.

Turbulent Boundary Layer Flow

- At some distance back from the leading edge, the smooth laminar flow breaks down and transitions to a turbulent flow.

- From a drag standpoint, it is advisable to have the transition from laminar to turbulent flow as far aft on the wing as possible, or have a large amount of the wing surface within the laminar portion of the boundary layer.

- The low energy laminar flow, however, tends to break down more suddenly than the turbulent layer.
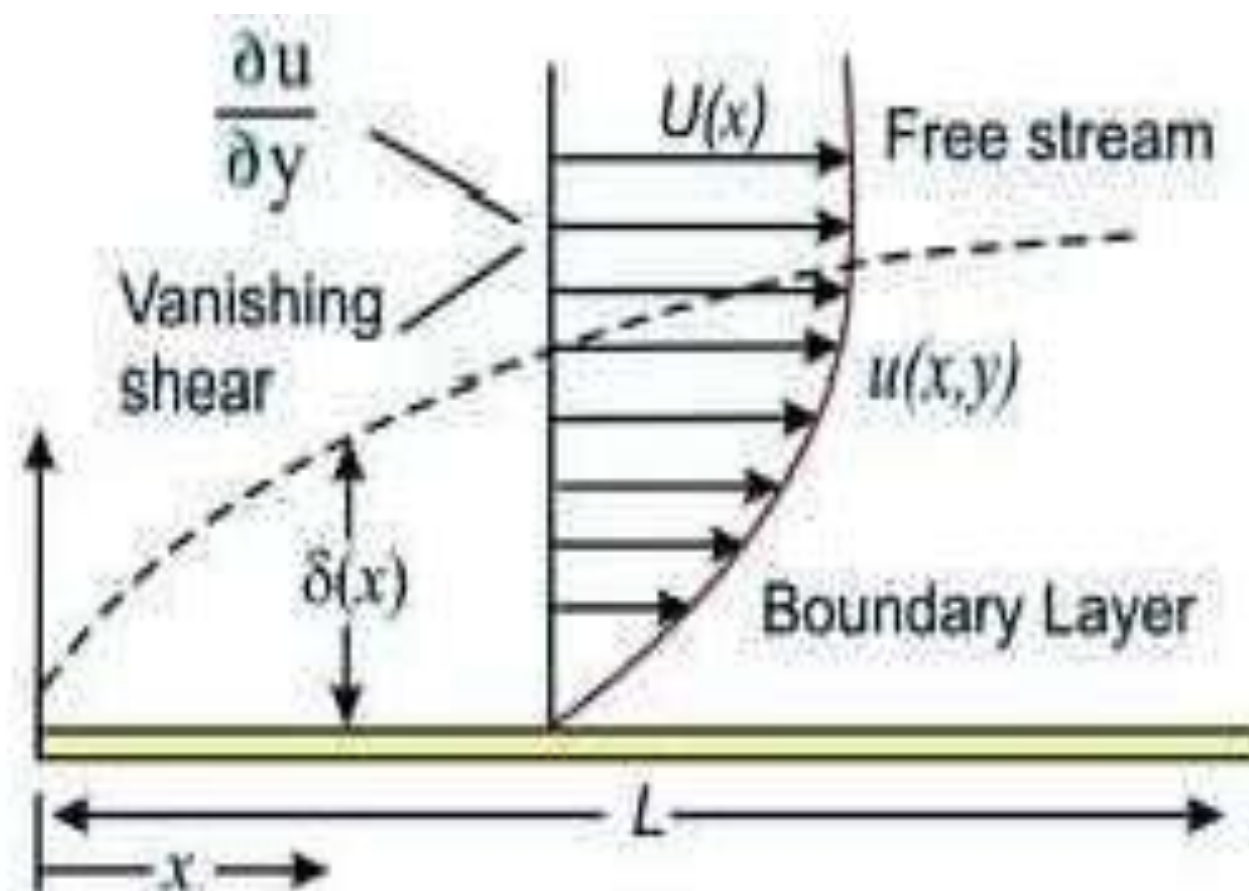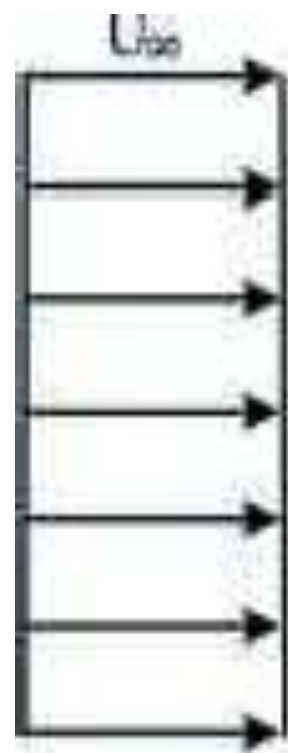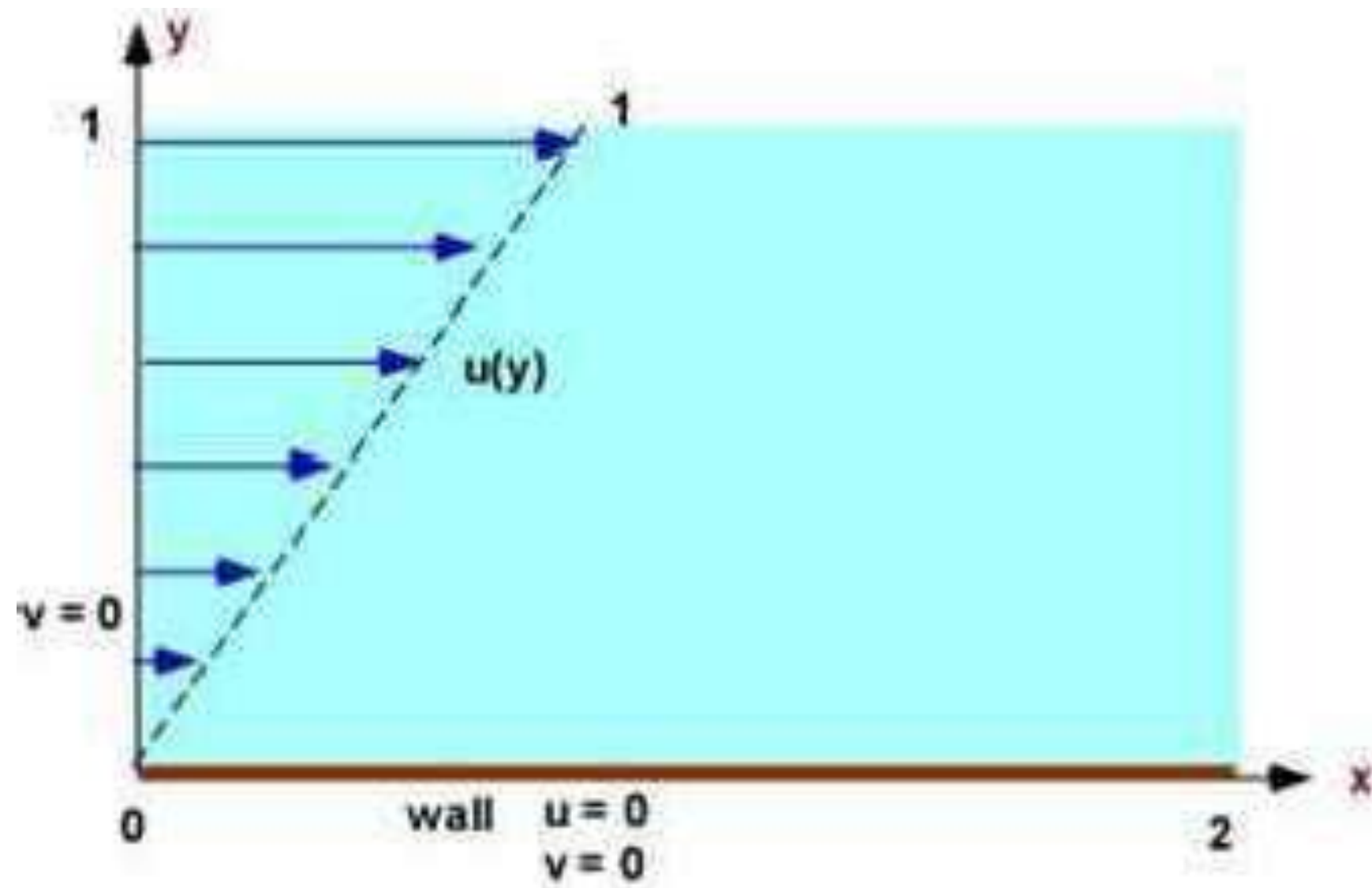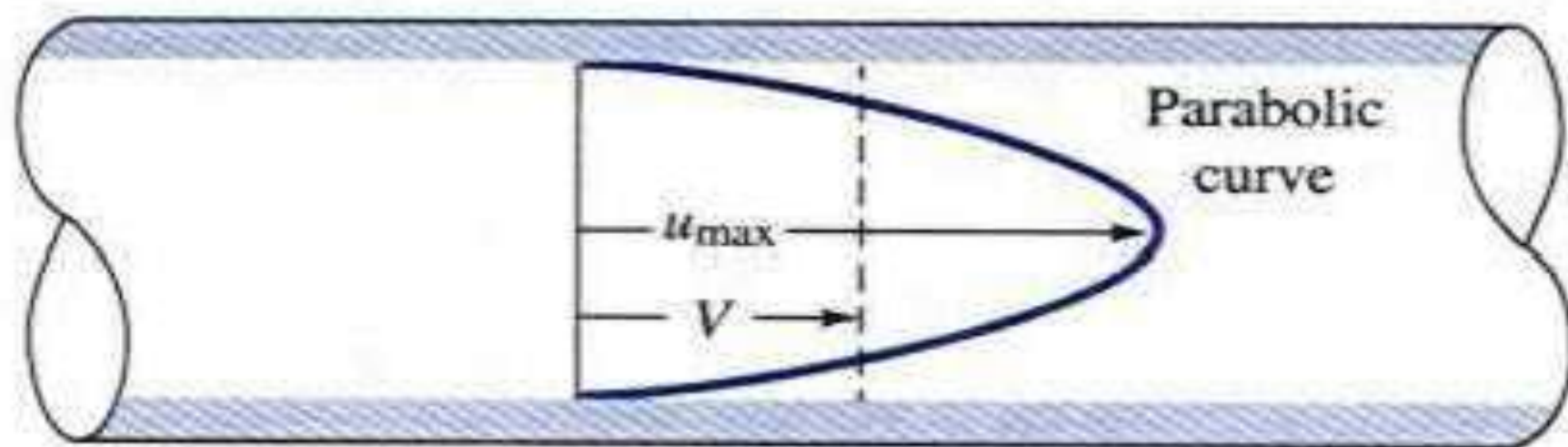
(a)
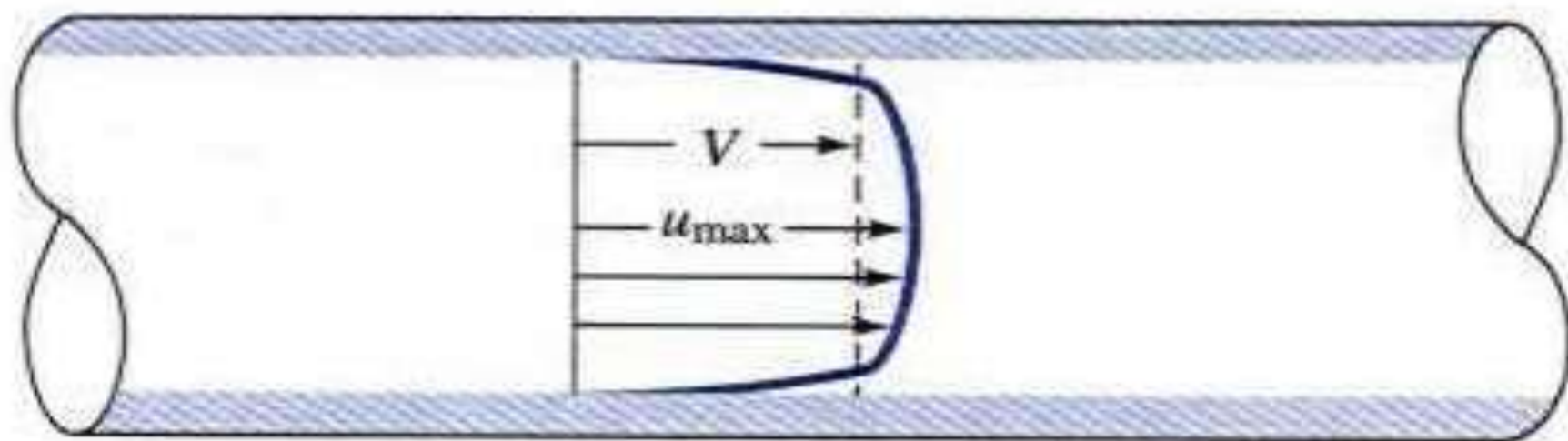
(b)

Flow through the pipes in series

- Pipes in series is defined as the pipes of different lengths and different diameters connected end to end to form a pipe line.

L_1, L_2, L_3 = length of pipes 1,2 and 3

d_1, d_2, d_3 = diameter of pipes 1,2,3

v_1, v_2, v_3 = velocity of flow through pipes 1,2,3

f_1, f_2, f_3 = coefficient of frictions for pipes 1,2,3

H = difference of water level in the two tanks

The discharge passing through the pipe is same.

$$Q = A_1 V_1 = A_2 V_2 = A_3 V_3$$

- The difference in liquid surface levels is equal to the sum of the total head loss in the pipes

Parallel pipe system

- Consider a main pipe which divide into two or more branches as shown in figure
  Again join together downstream to form a single pipe then the branch pipes are said to be connected in parallel. The discharge through the main is increased by connecting pipes in parallel

the rate of flow in the main pipe is equal to the sum of rate of flow through branch pipes.

hence

$$Q = Q_1 + Q_2$$

- In this arrangement loss of head for each pipe is same

  Loss of head for branch pipe1=loss of head for branch pipe 2

Moody diagram

Moody Diagram that can be used to estimate friction coefficients

- The Moody friction factor - *λ (or f)* - is used in the Darcy-Weisbach major loss equation

- If the flow is transient - *2300 < Re < 4000* - the flow varies between laminar and turbulent flow and the friction coefficient is not possible to determine.

- The friction factor can usually be interpolated between the laminar value at *Re = 2300* and the turbulent value at *Re = 4000*

• Moody diagram

Total energy gradient line

PIPE ENTRY LOSS $\quad 0.5\dfrac{V_1^2}{2g}$

PIPE FRICTION LOSS $\quad 4f\dfrac{L_1}{d_1}\dfrac{V_1^2}{2g}$

$\dfrac{V_1^2}{2g}$

CONTRACTION LOSS

TOTAL ENERGY LINE $\quad \left(0.25\dfrac{V_2^2}{2g}\right.\quad 4f\dfrac{l_2}{d_2}\dfrac{V_2^2}{2g}$

$\dfrac{V_2^2}{2g}$

HYDRAULIC GRADIENT

ENLARGEMENT LOSS $\quad \dfrac{(V_2-V_3)^2}{2g}$

$\left(\dfrac{V_3^2}{2g}\right)$

$4f\dfrac{l_3}{d_3}\dfrac{V_3^2}{2g}$

$\dfrac{V_3^2}{2g}$ "ENLARGEMENT INTO RESERVOIR $\quad \left(\dfrac{(V_3-0)^2}{2g}\right.$

AVAILABLE HEAD

AVAILABLE HEAD

WATER LEVEL IN LOWER TANK

$V_1 \quad L_1 \quad V_2$

$l_2 \quad V_3$

L_3

THE SUM OF THE LOSSES = THE AVAILABLE HEAD
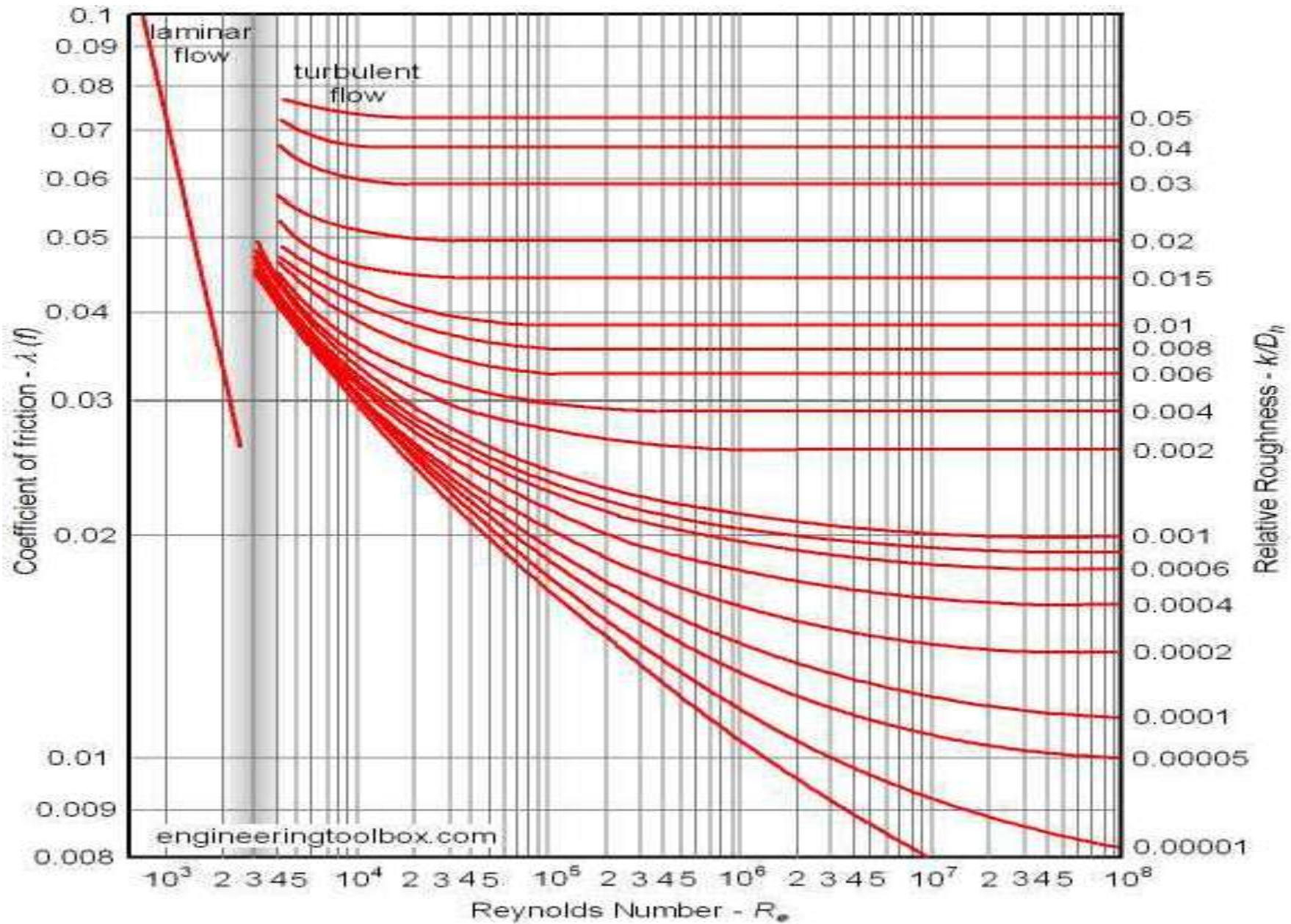
NOT TO SCALE
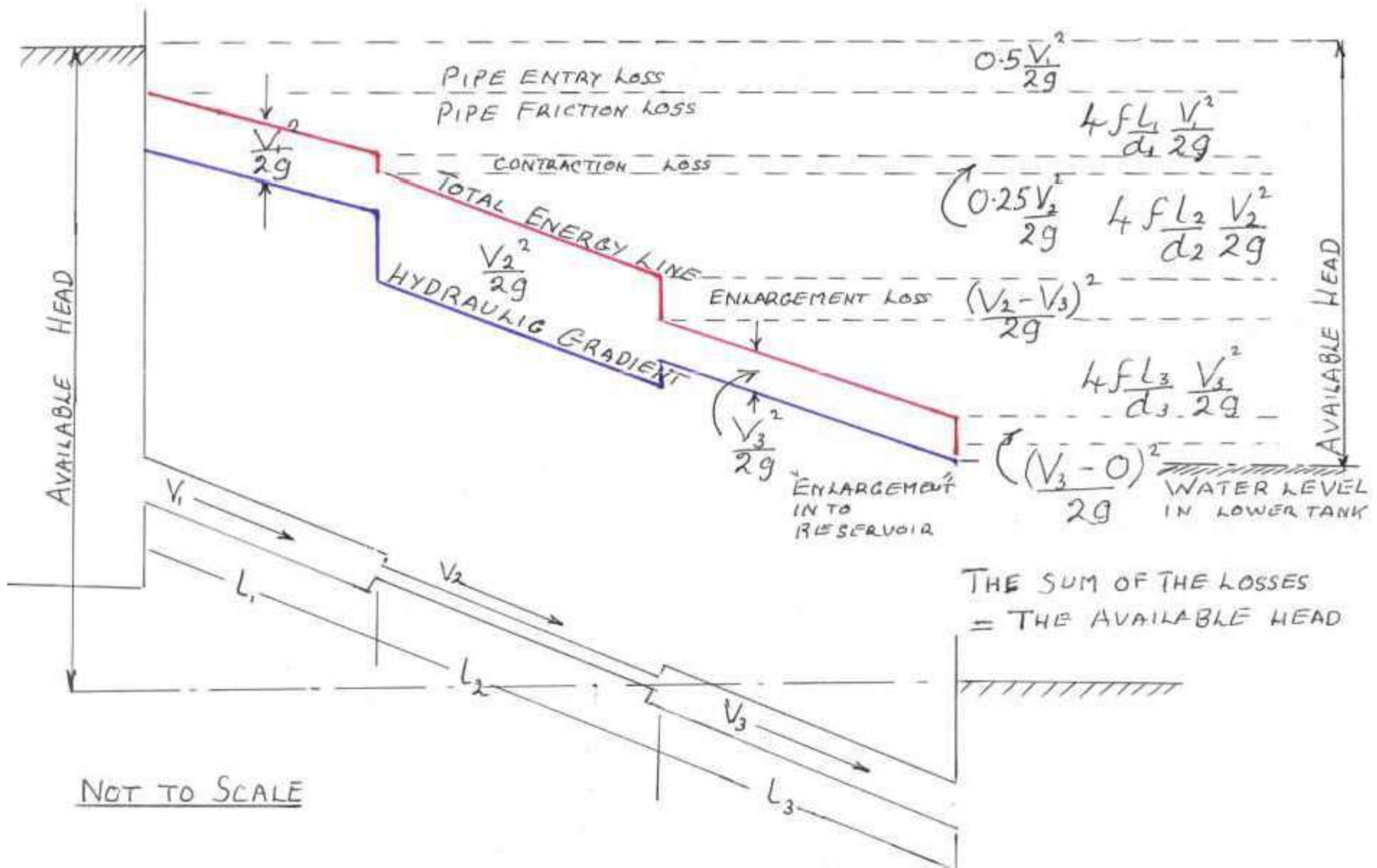
- **Total energy gradient** line is equal to sum of pressure head ,velocity head and datum head

  EL = H = p / W + v2 / 2 g + h = constant along a streamline

where

(EL) Energy Line

- For a fluid flow without any losses due to friction (major losses) or components (minor losses) - the energy line would be at a constant level. In a practical world the energy line decreases along the flow due to losses.

- A turbine in the flow reduces the energy line and a pump or fan in the line increases the energy line

Hydraulic Grade Line (HGL)

- Hydraulic gradient line is the sum of pressure head and datum head

$$HGL = p / W + h$$

where

The hydraulic grade line lies one velocity head below the energy line.

Gate type

As important as selecting the optimal gate size and location is the choice of the type of gate.
Gate types can be divided between manually and automatically trimmed gates.
Manually trimmed gates
Manually trimmed gates are those that require an operator to separate parts from runners
during a secondary operation. The reasons for using manually trimmed gates are:
The gate is too bulky to be sheared from the part as the tool is opened.
Some shear-sensitive materials (e.g., PVC) should not be exposed to the high shear
rates inherent to the design of automatically trimmed gates.

 Simultaneous flow distribution across a wide front to achieve specific orientation of
fibers of molecules often precludes automatic gate trimming.
Gate types trimmed from the cavity manually include:
Sprue gate
Edge gate
Tab gate
Overlap gate
Fan gate
Film gate
Diaphragm gate
External ring
Spoke or multipoint gate
Automatically trimmed gates
Automatically trimmed gates incorporate features in the tool to break or shear the gate as the
molding tool is opened to eject the part. Automatically trimmed gates should be used to:
Avoid gate removal as a secondary operation.
Maintain consistent cycle times for all shots.
Minimize gate scars.
Gate types trimmed from the cavity automatically include:
Pin gate
Submarine (tunnel) gates
Hot runner gates
Valve gates

4.1 Sprue gate
Recommended for single cavity molds or for parts requiring symmetrical filling. This type of
gate is suitable for thick sections because holding pressure is more effective. A short sprue is
favored, enabling rapid mold filling and low-pressure losses. A cold slug well should be
included opposite the gate. The disadvantage of using this type of gate is the gate mark left on

the part surface after the runner (or sprue) is trimmed off. Freeze-off is controlled by the part thickness rather than determined the gate thickness. Typically, the part shrinkage near the sprue gate will be low; shrinkage in the sprue gate will be high. This results in high tensile stresses near the gate.

Dimensions

The starting sprue diameter is controlled by the machine nozzle. The sprue diameter here must be about 0.5 mm larger than the nozzle exit diameter. Standard sprue bushings have a taper of 2.4 degrees, opening toward the part. Therefore, the sprue length will control the diameter of the gate where it meets the part; the diameter should be at least 1.5 mm larger than or approximately twice the thickness of the part at that point. The junction of sprue and part should be radiused to prevent stress cracking

A smaller taper angle (a minimum of one degree) risks not releasing the sprue from the sprue bushing on ejection.

A larger taper wastes material and extends cooling time.

Non-standard sprue tapers will be more expensive, with little gain.

4.2 Edge gate

The edge or side gate is suitable for medium and thick sections and can be used on multicavity two plate tools. The gate is located on the parting line and the part fills from the side, top or bottom.

Dimensions

The typical gate size is 80% to 100% of the part thickness up to 3.5 mm and 1.0 to 12 mm wide. The gate land should be no more than 1.0 mm in length, with 0.5 mm being the optimum.

4.3 Tab gate

A tab gate is typically employed for flat and thin parts, to reduce the shear stress in the cavity. The high shear stress generated around the gate is confined to the auxiliary tab, which is trimmed off after molding. A tab gate is often used for molding P.

Dimensions

The minimum tab width is 6 mm. The minimum tab thickness is 75% of the depth of the cavity.

4.4 Overlap gate

An overlap gate is similar to an edge gate, except the gate overlaps the wall or surfaces. This type of gate is typically used to eliminate jetting.

Dimensions

The typical gate size is 10% to 80% of the part thickness and 1.0 to 12 mm wide. The gate land should be no more than 1.0 mm in length, with 0.5 mm being the optimum.

4.5 Fan gate

A fan gate is a wide edge gate with variable thickness. This type is often used for thicksectioned moldings and enables slow injection without freeze-off, which is favored for low stress moldings or where warpage and dimensional stability are main concerns. The gate

should taper in both width and thickness, to maintain a constant cross sectional area. This will ensure that:

The melt velocity will be constant.

The entire width is being used for the flow.

The pressure is the same across the entire width.

Dimensions

As with other manually trimmed gates, the maximum thickness should be no more than 80% of the part thickness. The gate width varies typically from 6 mm up to 25% of the cavity length.

4.6 Film or flash gate

A film or flash gate consists of a straight runner and a gate land across either the entire length or a portion of the cavity. It is used for long flat thin walled parts and provides even filling. Shrinkage will be more uniform which is important especially for fiber reinforced thermoplastics and where warpage must be kept to a minimum.

Dimensions

The gate size is small, typically 0.25mm to 0.5mm thick. The land area (gate length) must also be kept small, approximately 0.5 to 1.0 mm long.

4.7 Diaphragm gate

A diaphragm gate is often used for gating cylindrical or round parts that have an open inside diameter. It is used for single cavity molds that have a small to medium internal diameter. It is used when concentricity is important and the presence of a weld line is not acceptable.

Dimensions

Typical gate thickness is 0.25 to 1.5 mm.

4.8 Internal ring gate.

4.9 External ring gate

This gate is used for cylindrical or round parts in a multicavity mould or when a diaphragm gate is not practical. Material enters the external ring from one side forming a weld line on the opposite side of the runner this weld line is not typically transferred to the part.

Dimensions

Typical gate thickness is 0.25 to 1.5 mm.

10 Spoke gate or multipoint gate

This kind of gate is used for cylindrical parts and offers easy de-gating and material savings. Disadvantages are the possibility of weld lines and the fact that perfect roundness is unlikely.

Dimensions

Typical gate size ranges from 0.8 to 5 mm diameter.

4.11 Pin gates

Pin gates are only feasible with a 3-plate tool because it must be ejected separately from the part in the opposite direction The gate must be weak enough to break off without damaging the part. This type of gate is most suitable for use with thin sections. The design is particularly useful when multiple gates per part are needed to assure symmetric filling or where long flow

paths must be reduced to assure packing to all areas of the part.

Dimensions

Gate diameters for unreinforced thermoplastics range from 0.8 up to 6 mm. Smaller gates may induce high shear and thus thermal degradation. Reinforced thermoplastics require slightly larger gates > 1 mm The maximal land length should be 1 mm. Advised gate dimensions can be found in the table below.

Dimensions of gates (* wall thickness larger than 5 mm should be avoided).

4.12 Submarine (tunnel) gates

A submarine gate is used in two-plate mold construction. An angled, tapered tunnel is machined from the end of the runner to the cavity, just below the parting line. As the parts and runners are ejected, the gate is sheared at the part. The tunnel can be located either in the moving mould half or in the fixed half. A sub-gate is often located into the side of an ejector pin on the non-visible side of the part when appearance is important. To degate, the tunnel requires a good taper and must be free to bend.

Dimensions

Typical gate sizes 0.8 mm to 1.5 mm, for glass reinforced materials sizes could be larger.

A variation of the tunnel gate design is the curved tunnel gate where the tunnel is machined in the movable mold half. This is not suitable for reinforced materials.

4.13 Curved tunnel gate.

4.14 Hot runner gates

Hot runner gates are also known as sprueless gating. The nozzle of a runnerless mold is extended forward to the part and the material is injected through a pinpoint gate. The face of the nozzle is part of the cavity surface; this can cause appearance problems (matt appearance and rippled surface). The nozzle diameter should therefore be kept as small as possible. Most suitable for thin walled parts with short cycle times, this avoid freezing of the nozzle.

4.15 Valve gates

The valve gate adds a valve rod to the hot runner gate. The valve can be activated to close the gate just before the material near the gate freezes. This allows a larger gate diameter and smoothes over the gate scar. Since the valve rod controls the packing cycle, better control of the packing cycle is maintained with more consistent quality.

Why Molds are Expensive

Introduction:

The simple answer is that Injection Molds are expensive because they are very complex mechanical systems. Molds require: Engineering and design, special materials, machinery and highly skilled personnel to manufacture, assemble and test them.

The injection molding process is one where molten plastic material is forced into a mold cavity under high pressure. The mold cavity is an exact hollow negative of the part to be

produced. In order for the part to be released, the mold must open at the widest place on the part. The molten plastic pressure during injection ranges from 5,000 to over 20,000 psi. This pressure multiplied by the area of the part gives rise to huge forces seeking to open the mold. The mold must be constructed to withstand the very high clamping forces exerted by the injection molding machine to contain this pressure

The injection molding process is capable of rapidly producing large quantities of parts with very high precision. Tolerances of a few thousandths of an inch are routinely achieved. With the right combination of material, part design and mold construction, even sub one thousandth inch tolerances can be achieved for small features.

The cost of injection molds can range from a few thousand dollars to hundreds of thousands of dollars.

5.1.1.2 Materials:

The materials used to construct injection molds range from aluminum to hardened steel:
Aluminum for simple low production prototypes.

The relative low strength of aluminum that makes it quicker to fabricate into molds likewise limits its useful life. Aluminum molds are typically intended to produce from a few thousand to a few hundred thousand parts with relatively simple features.

Prehardened tool steel for moderate production, more complex molds.

Prehardened tool steel molds are much stronger and more durable, yet still soft enough to be worked by conventional machining processes such as milling and turning. Prehardened tool steel molds are typically intended to produce from one hundred thousand to five hundred thousand parts, and can have a wide array of features such as slides and more intricate shapes that might break in an aluminum mold.

Hardened tool steel for high production, long life molds.

Hardened tool steel molds are the most durable and expensive because part way through fabrication their components are heat treated to achieve a hardness greater than can be machined. From that point on, the fabrication must continue using grinding and EDM processes.

Hardened steel molds are intended to produce one million or more parts. Their hardness enables them to resist wear from their own operation and the abrasion of the plastic material, particularly glass fiber reinforced materials. Hybrid construction is very common, where steel parts are used in an aluminum mold to add strength to a slender feature, or parts of a steel mold are hardened to prevent wear at a rotating or sliding mold feature.

5.1.1.3 Molds:

Single cavity molds offer the lowest tooling costs and highest precision at the penalty of higher unit costs. Multi-cavity molds are utilized to increase capacity and lower unit costs. Family molds, multi-cavity molds with different items together, offer both the lowest mold cost and low unit cost. However, they present other problems of matching the process conditions for each part and balancing supply when the product mix or yield at a later manufacturing step varies.

5.1.1.4 Engineering and Design:

The design of injection molds begins with a review of part specifications including:

Aesthetics: color, clarity, high gloss, matte, special texture, etc. Material: strength, toughness, hardness, chemical and environmental resistance Interaction with mating parts: fits and tolerances Demand and unit cost goals

From this review process the mold design concept is evolved and decisions are made resulting in a mold specification:

Single, multiple cavity or family molds The grade of mold: aluminum, prehardened tool steel or hardened tool steel Material flow considerations Parting lines and gates Finish: high gloss, texturing, embedded text and graphics, etc. Accuracy and tolerances Cooling passages Ejection system Runners or runnerless system design

The next step is the actual design of the mold. Highly skilled designers using very complex and expensive computer software programs perform this. The design tasks include:

Modeling of the products and mold components in 3D. Mold flow analysis CNC tool path design and calculation Mold materials procurement list

Early in the design process, materials and components are ordered so that manufacturing can commence as soon as possible.

5.1.1.5 Manufacturing:

Once the design is completed manufacturing begins. Mold making involves many steps, most of which are very exacting work requiring highly skilled moldmakers. One mistake can ruin or cause major repair expense to a work piece that has undergone a series of manufacturing steps over several weeks. The processes employed in mold making include:

o Milling and turning
o Heat-treating
o Grinding and honing
o Electrical discharge machining
o Polishing and texturing

To save cost, common mold components are purchased from suppliers. Frequently, outside services are required from subcontractors, which use specialty equipment such as thread grinding, etc.

When all of the parts are completed the next step is to fit, assemble and test the mold. All of the mold component parts must fit together precisely to achieve an aesthetic result on the product and for the mold to not wear out rapidly or break. The mold must be fluid tight to contain the molten plastic. Yet, at the same time the mold must have venting features added to allow the air to escape. The behavior of the plastic material when molded has been anticipated, however there can be some variance in the actual result. The mold must be tested to insure the products are correct and that the mold is performing properly. Where high accuracy is required, the mold may intentionally be made "metal safe" with the final adjustments coming after the first molding trial.

5.1.1.6 Conclusion:

As can be seen from the above, the engineering and creation of injection molds is a time consuming process. The work is demanding in terms of knowledge, skills and exacting attention to details. This will always be expensive, however this expense must be viewed in terms of what is achieved: Unsurpassed sophistication in part design and aesthetic appearance with low cost mass production.

WHAT IS MAINTENANCE ?

- Maintenance involves fixing any sort of mechanical or electrical device which has become out of order or broken.

- It also includes performing routine actions which keep device in working order or prevent trouble from arising.

WHAT DOES MAINTANANCE DEPARTMENT DO IN COMPANY ?

- Maintenance department implements some maintenance operations to produce products according to specific criteria.

WHAT IS THIS CRITERIA?

- Before this department implements maintenance operations, they can be categorized by whether the product remains the property of the customer, service is being offered, or whether the product is bought by the reprocessing organization and sold to any customer wishing to make the purchase.

MAINTENANCE TYPES:

1. Preventive Maintenance:
2. Corrective Maintenance:

PREVENTIVE MAINTENANCE:

-      Preventive maintenance can be described as maintenance of equipment or systems before fault occurs.

CORRECTIVE MAINTEANANCE:

-    Corrective maintenance is probably the most commonly used approach, but it is easy to see its limitations. When equipment fails, it often leads to downtime in production. In most cases it is costly business. Also, if the equipment needs to be replaced, the cost of replacing it alone can be substantial. It is also important to consider health, safety and environment issues related to malfunctioning equipment.

DIFFERENCE BETWEEN PREVENTIVE AND CORRECTIVE MAINTANANCE:

- While preventive maintenance is generally considered to be worthwhile, there are risks such as equipment failure or human error involved when performing preventive maintenance, just as in any maintenance operation.

- Preventive maintenance as scheduled overhaul or scheduled replacement provides two of the three proactive failure management policies available to the maintenance engineer.

To Make It Simple:

-       Preventive maintenance is conducted to keep equipment working or extend the life of the equipment.
-       Corrective maintenance, sometimes called "repair" is conducted to get equipment working again.

BRANCH OF MAINTENANCE:

- Condition-Based Maintenance
- Predictive Maintenance
- Reliability-Centered Maintenance
- Value Driven Maintenance

CONDITION-BASED MAINTENANCE:

- Shortly described, this maintenance is performed after one or more indicators show that equipment is going to fail or that equipment performance is deteriorating.

- CBM was introduced to try to maintain the correct equipment at the right time. CBM is based on using real-time data to prioritize and optimize maintenance resources.

PREDICTIVE MAINTENANCE:

- Techniques help to determine the condition of in-service equipment in order to predict when maintenance should be performed. This approach offers cost savings over routine or time –based predictive maintenance, because tasks are performed only when warranted.

RELIABILITY-CENTERED MAINTENANCE:

- It is generally used to achieve improvements in fields such as the establishment of safe minimum levels of maintenance, changes to operating procedures strategies and the establishment of capital maintenance regimes and plans.

- Successful implementation of RCM will lead to increase in cost effectiveness, machine uptime. And a greater understanding of the level of risk that the organization is presently managing.

VALUE DRIVEN MAINTENANCE:

-     A cash flow is the difference between income and expenditure. It is not the difference between turnover and costs, because this is easy to manipulate through accounting. There are companies that use highly creative lease, depreciation and reservation techniques to keep book profits artificially high or low, this doesn't always contribute to shareholder value. Recent stock market scandals are a painful but revealing illustration of what sometimes happens as a result of this.

The second part of the definition concerns the knowledge the value of a cash flow is time-related, given the term "present value". Future cash flows must be corrected or discounted to today. Managing by value necessitates maximizing future cash flows. Managing by value obliges companies constantly to search for new free cash flows. It is no longer enough for a company to go on doing what it is already doing. Today, it's all about creating value

Materials used for Dies Moulds

Every mold designer must have a basic understanding of the various types of materials used in mold making . The mold designer has many aspects to consider . He must know processing conditions and production requirements . The mold to be fabricated must be correct to produce parts economically and tough to withstand the hard use to which it will be subjected . The cost of the material which goes into the mold is the least important consideration but the houses of labor and expensive equipment used in the construction of mould parts represent an important investment that will be lost of the design is poor or the materials unsuitable . In view of the above the greatest care and consideration must be given to the selection of materials used in mold building .

Steel is the most common material used in making of the molds other materials not be commonly used are Beryllium copper , Aluminums , bronze , Kristie (zinc alloy) , brass , Epoxies and phenol and wood .

1) Steel : In reference to the mold building steel may be defined as an alloy which has properties that move it useful as a math from which to form the main body of tools . Steel is made from iron and elements such as carbon , manganese , chromium , nickel , cobalt , unfasten , vanadium and molybdenum etc. are added singly or in combination in order to impart desired qualities to the metal .

Effect of alloy of elements in steels used for mold making :

element	Effect
Carbon	Increases strength and brittleness , lowers corrosion resistance and conductivity .
Manganese	Deoxidizes , increases strength , ductility , wear resistance .
Silicon	Di oxidizes , increases hardness .
Nickel	Increase toughness , strength and through hardness but lowers thermal and electrical conductivity .
Chromium	Carbide former , increase hardness ,resistance to wear and corrosion , lowers conductivity .
Molybdenum	Increase heat resistance , expands heat treatment range , raises creep strength .
Vanadium	De oxidizer , forms hard carbides , raises fatigue strength .
Tungsten	Forms extremely hard carbides , increases hardness and resistance to wear and temperature , helps to maintain shop edges .
Sulphur	Increase mach inability but lowers corrosion resistance and weld ability and interferes with texturing and plating .

There are four general classes of steels used by the mold maker .

1) **Plate steels -** Plate steel is a low carbon steel such as AVSI 1020 , produced in relatively increasive process , where in cleanliness is loss important than high volume and low cost . Use of this material is restricted to non – critical components e.g. the frames of molds . After car busing or case hardening it can also be used to make cavities and plumages for cheap qualities of molds . Plate steels have low core strength because they are prone to structural faults such as pipe , seams , pits and other defects .

Mold plates are usually made from plate steel , while knockout bars or cold rolled steals of the mold has to be used in corrosive atmosphere , an all stainless construction must be considered machinery steel is of the same general class as the AISI 1020 plate steel . The difference is that machinery steel is hot rolled into flat rolled product , square bars or round rods . For many applications such bars can be used without any special other than surface grinding on both sides to ensure flatness .

Typical composition of steel for moulds :

Elements in %

AISI Type	C	Mn	P	S
1020	0.20	0.45	0.04	0.05
1030	0.30	0.75	0.04	0.05
1040	0.40	0.75	0.04	0.05
1095	0.95	0.40	0.04	0.05

2) **Tool Steel -** Tool steel was the first material widely used in making the molds of good qulity .
There are three types of tools in use –

1) Water hardening
2) Oil hardening
3) Air hardening

Tool steels have first fair mach inability and are not suitable for hobbing after hardening a block of tool steel will have almost the same hardness strength out its body but may lack toughness . As a result the mold may be brittle and tend to break rather than yield when excess pressure is applied . The initial cost of tool steel is high and it is sometimes the preffered material for injection molds because it does not or deform as easily as some other steels water hardening tool steel may be used when maximum hardness is desired . Water hardening tool steels are not recommended for use with plastic moulds . Oil hardening tool steel and even better air hardening tool steels are recommended because they perform more predictably in applications where distortion must be held to a minimum .

Typical composition of tool steels for moulds :

Elements in percent

AISI Type	C	Mn	Si	Cr	Ni	Mo	V	Others
S1	0.50	0.70	0.75	3.25	-	-	0.2	w 2.5
A2	1.00	2.00	0.35	5.00	-	-	-	-
D2	1.50	-	-	12.00	-	1.0	1.0	-
H13	0.35	0.40	1.00	5.00	0.30	1.4	1.0	-
L6	0.75	0.75	-	0.90	1.75	0.35	-	-
P2	0.07	-	-	2.00	-	0.20	-	-
P20	0.35	0.80	0.50	1.70	0.30	0.45	-	-
P21	0.20	0.30	0.30	0.30	4.25	0.45	0.2	Al. 1.2

Alloy Steels - The alloy steels differ. From tool steels in several ways . Their carbon content is reduced and various other elements are added to modify their properties . Typical composition of alloy steels used in mold making is given below .

AISI Type	C	Mn	Si	Cr	Mo	Others
1330	0.3	1.75	0.25	-	-	-
4130	0.3	0.50	0.25	0.9	0.2	-
4340	0.4	0.70	0.25	0.8	0.25	2.0 Ni
8630	0.3	0.80	0.25	0.5	0.20	0.7 Ni

The addition of phosphorus and sulphur is restricted to 0.035 and 0.04% respectively .

Stainless Steel - While there are many alloys classed as stainless steel , only a few are to be considered for use in high pressure molds . For a desirable balance of hardenbility , corrosion resistance and thermal conductively , the AISI type in the 400 refries are generally proffered of these , type 420 is the most popular . It contains 12 to 14% cr. And can be satisfactorily heat treated to develop a through hardness of 48-50 RC . It is used where corrosion and resisting are problems such as processing as vinyl's particularly in lurid conditions . Type 414 is a preharded steel having a hardness of HRC 30-35 . It does not require further heat treatment after the mold is finished . It is suitable for injection mold where pressures are relatively low . It is the recommended material for molding corrosine materials where rusting is a problem . It does not conductivity of ss is lower than non ss .

Typical composition of stainless mold steels :

Type	C	Mn	Si	Ni	Cr.
T 410	0.15	1.00	1.00	-	12.0
T 414	0.05	1.00	1.00	2.00	12.0
T 420	0.25	1.00	1.00	-	13.0
T 440	0.60/120	1.00	1.00	-	17.5

Precipitation hardening & mar aging steels : These are relatively new types of steels being used as mold steels . They are hardened by procedures completely different from the heating/quenching tempering sequence associated with the conventional mold steels . Precipitation hardening alloys are delivered in the soft , solution treated conditional in which they machine easily , they are hardenal by slow and gentle heating to a temp. as low as 480^0 c . Hardness is controlled by the length of time at which the alloy is held at the hardening temp. The main advantages of precipitation hardening alloys are –

1) Good Mach inability
2) Superior polish ability and ease of texturing .
3) Controlled heat treatment .
4) Avoidance of thermal shock .
5) Good weld ability and reaper ability .

Composition of precipitation hardening steels -

Universal No.	C	Mn	Si	Cr	Ni	Cu	Others
UNS S 15500	0.07	1.0	1.0	15.0	5.0	3.5	0.30 Nb
UNS S 17400	0.07	1.0	1.0	17.0	4.5	4.0	0.30 Nb
UNS S 17700	0.09	1.0	1.0	17.0	7.0	-	1.00 Al.

The material cost of precipitation hardening alloys is 2-5 times the cost of a good quality p 20 alloy However since the material cost of the mold , this is not a very important factor .

Maraging steels are an advanced and expensive class of precipition hardening steel . In addition to exceptional fracture toughness and other advantages of precipitation hardening steels , maraging steels can be safely hardened to HRC 70 at which hardness they devlop a strength of 3,00,000 PSI .

Typical composition of maraging steels :

Elements

	C	Ni	C	Mo	Ti	All	Cr
350 type 18% Nickel Maraging Steel	.02	17.5	12.0	4.8	1.5	.1	25
300 „ 18% „ „ „	.03	18.5	9.0	4.8	.6	-	-
250 „ 18% „ „ „	0.03	18.25	7.75	4.8	.4	.1	-
200 „ 18% „ „ „	0.03	18.25	7.50	4.25	.2	.1	-
220 „ 12% Chromium „ „	0.02	10.00	-	-	.35	1.3	12%

Mold steel requirements - There are certain qualities which are essential for a steel to be used in building of molds – These include

1) **Cleanliness -** A good mold steel must be clean . It should not contain non-metal ling inclusions which will cause pitting during polishing .
2) **Soundness -** The steel must be dense an free from voids and porosity .
3) **Structure uniformity -** It must be uniform structure and free from segregations analysis . Its properties should be substantially the same both along and across the direction of rolling .
4) **Mach inability -** Steels which can be machined easily and uniformly are needed for economical mold construction . Extreme softness is as undesirable as extreme hardness .
5) **Hob ability -** Hibbing steels must be very soft when annealed and be clean and ductile as well . In got iron and low alloy steels are easiest to hob . The higher alloy content steels offer some difficulty but give the best results in service .
6) **Harden ability -** During the heat treating process , good mold steels must acquire surface and a tough strong core .
7) **Strength , toughness & Fracture Toughness -** Molds require a hard surface and a very tough core . The larger the projected area of the mold , the greater will be the core strength needed to resist collapse , distortion or cracking due to brittleness .
8) **Heat Treating safety -** An important characteristic of a good mold steel is its ability to be hardened satisfactorily in a wide range of section thickness and by a variety of hardening methods while still producing uniform results .
9) **Polish ability or finish -** All mold steels must reading take a mirror like finish , althengh a dull surface is sometimes selected as a final finish .
10) **Wear Resistance -** Wear resistance is a fundamental requirement of a good general purpose mold steel . Glass and mineral filled composites cause maximum tool wear and therefore steels used for such composites should offer max. resistance to wear or abrasion .

Steels for injection molds :

Steel AISI	**Applications**
P 20	suitable for all types and sizes of machine cut molds . Usually used in the prehardened condition RC 30-35 . This should be carburized and hardened for low viscosity & glass filled plastics and for usage in excess of 1,00,000 Pcs per cavity .
H 13.	Used for large & small molds when toughness strength are required . Good dimensional stability during hardening . Hardness up to Rc 52.
A 2	for small and medium size molds when higher hardness is required as for molding abasing materials .

D 2	for small molds when abrasion becomes a problem. Also for molds operating at temps. Up to 400^0 c.
420 stainless	for molding corrosive resins. Hardens up to Rc-48-52.
SAE 4140	usually used for holds and shoes can be used for molds where a high finish is not necessary usually used the prehardened condition HRC – 28-32.
M2 HSS	used if operating temps are above 600^0 c, but not higher than 700^0 c and mold hardness must be higher than 60 RC.

Precipitation hardening :

Mar aging steels : For large molds or molds containing deep cuts and heavy sections, to avoid stresses and brittleness associated with quenching and tempering, also for mold components which require exceptional hardness and fracture toughness.

Steels for compression & Transfer molds :

Steel (AISI)	**Application**
P 20	Must be carburized of 0.030-0.065% deep, depending upon size. Surface hardness RC – 60. Core hardness RC 45-50.
H 13	Good for large compression molds if nitride after heat treating to RC 48.
SAE 4145	Often used for holdness and chases can be carburized to RC 60.
S 1	For small & medium sized molds. Tougher than A2 but not as stable, dimensionally in hardening. It may be oil hardened use at RC 53-56.
S 7	For medium and large molds has good combination of toughness and stability sections thinner than 2" will air harden otherwise oil harden to RC 53-56.

Precipitation hardening :

Mar aging steels : For large molds and molds containing deep cuts and heavy sections to avoid stresses and brittleness associated with quenching & tempering. Also for mold components which require exceptional hardness and for fracture toughness.

NON – FERROUS METAL MOLDS : Several types of non ferrous metals are used for molds, especially for short runs or where the pressures or wear conditions are not so severe, or where the metal has some special characteristic such as high thermal conductivity, ease of casting etc. The most commonly used metal non-ferrous alloys are –

1) **Beryllium Copper Alloys :** Many different alloys containing beryllium and copper are in use. Selection depends upon the desired balance between hardness, strength, cast ability, conductivity and resistance to wear and corrosion as well as on the particular technique used for mold making. Certain alloys are used for making cores and mandrels rather than molds.

In general, the alloys with 1.7% or more beryllium provide better fluidity and therefore better reproducibility. They have less tendency to form dross thus making possible to cast them at a lower temp. Higher beryllium concentration results in better reproduction, but the cost increases.

The c 82400 alloys are most common in use. C 82600 alloys can be used where lower pattern precision is required.

Alloys with less than 1.7% be content are generally used only for mold cores and mandrels, Where high fidelity of reproduction and very high strength are not required. Such use of Be Cu alloys results in lower mold material cost and

There may be some difficulty in their disposal in an environmentally acceptable manner.

Be – Cu Alloys : Properties & Applications

Type	composition	others	Thermal	HRC.	Characteristic & applications
	(Balance cu		Conductivity		
	Be Co		(BTU/ft/w/		
			Of at f)		

C 172000	2.0	0.5	-	Co	40	Good strength & wear Resistance with good
		elec.&				Thermal conductivity .
C 17510	0.6	2.5	-	145	22	High thermal & elect. Conductivity but lower hardness used where max. heating cooling rates are report .
C 82400	1.7	0.3	-	58	37	Good strength , hardness Corrosion resistance & conductivity .
C 82510	2.0	0.5	0.3 Si	56	41	Similar to 82400 but with Better cast ability .
C 82600 improved	2.3	0.5	0.3 Si	54	44	As 82400 but with Resistance to wear used in pressure & ceramic cashings .
C 96700 resistance	1.2	-	30.0 Ni	21	50	Highest corrosion and strength & cast ability , but lower thermal conductivity , Resists flame retardants , blowing Agents and other corrosive chemicals contained in molding resins .

2) **Aluminum :** All alloys injection mold are mainly used for short run production or for proto type fabrication . They are however used extensively for low pressure applications such as rotational offers the advantages of light weight , ease of machining , high thermal conductivity and moderate costs . Most commonly used alloys for making of molds are 7075 T6, 6061 or 245 alloys . Alloys 7075 T6 is representative of the group . It contains 5.6% Zn , 2.5% mg , 1.6% Cu and 0.25% Cr . Al alloy molds have given good service for production runs up to 2.50,000 cycles . Anodizing increases the alloys wear resistance .

3) **Zinc Alloys :** Several alloys of zinc have been used for casting molds especially for pre production proto types for injection molding . They are easier to handle , can be cost at 475^0 c and yet they develop surface hardness and compressive strength equal to some of Al. alloys . The use of a steel frame is recommended if the mold is used in any high pressure application . Typical composition of zinc alloy is zn – 92% , cu – 3.5% , Al- 4.0% , mf 0.04% .

4) **Nickel :** In general electroformed Nickel is used to produce molds such as pen barrel cavities and similar parts which might be very difficult to fabricate by normal machining . In some cases , the cavity is built up to a thickness of approve 1/6" using a hard nickel deposit and then the mold is deposit faster . In some cases the hard nickel is rain forced by a copper deposit which builds up even faster . Nickel molds are also produced by a vapor deposition technique which results in better tolerances , more uniformity of shell thickness , lither strength and better heat transfer .

5) **Al-Bronze and Nickel Aluminum Bronze :** This is a family of copper based alloys . The grades used in the mold making typically contain about 80% cu , 12% Al , and 5% iron . To increase the strength of the alloy about 5% Ni is added by reducing Cu & Al contents . This also raises the corrosion resistance while maintaining good ductility and fracture toughness . The Al bronze alloys have been used widely in applications such as wear plates , slides , moveable bushings and / or plunges in contact with steel .

6) **Powdered Metal Components :** Small cavities can be produced by compressing finely powdered metals or mixture of such powders held together by the binder materials . The powder mix is molded around a master from which the cavity is formed .

In this process different metals and binds are mixed together at room temperature and then compacted to form hard and strong shapes such as injection moulding cavities . This process is known as mechanical alloying . The powdered mix may contain super hard particles such as tungsten or titanium carbides for better wear resistance or nickel if toughness and resistance to corrosion are rigid . It may also contain soft particle such as alloys of copper to impart lubricity .

Some powders require heat treatment and HIP treatment (HOP isocratic pressing) Where as in some cases a chemical action is employed followed by sintering to remove any residue binder .

Nonmetallic mold materials : There are a number of non-metallic materials which are also used to produce molds . In general these materials are used where the pressures are not high such as casting , rotational molding , non-structural foam , thermo forming etc. The non-metallic mold materials are of two types –

1) **The elastomeric or flexible materials :** These include room temperature mechanizing silicons in many different hardness , use them resins , vinyl plastically , gelatin , polysulfide and various rubber latches . The mold is made by casting or brushing the material around a master and then hardening to form a mold . The main advantage of using the elastomeric materials is that the parts can be made with under cuts and still se removed from the mold . the disadvantage is that only plastic casting can be made using such molds since any pressure will cause deformation . A special characteristic of the silicon RTV molds is that usually mold releasing agent is not rigid even when casting of epoxies or Pus is done .

2) **The Rigid Materials :** The rigid non-metallic's include such materials as plaster of pass , wood , glass fiber reinforced plastics such as epoxies and polyesters . A mold release agents is required in these types of molds . Cast epoxies reinforced with metal powder can be made strong enough to be used as an injection mold for small quotation of parts , if very high pressure are not employed and temps. Are kept below 200-230^{0}c . Backing up the mold with a metal frame is recommended .
The main advantages of using non-metallic molds are -

1) In most cases the cost is considerably less then a similar metal mold .
2) Prod time is usually much less than making a metal mold by machining , EDM or electroforming .
3) The wt. is usually much less than a metal mold .
4) Repair work is simple and can be done quickly .
5) These molds are much more corrosive resistant then metal molds .
6) Transparent molds can be made and for some applications such molds allow better control of the process .
   The disadvantages are –
   Lower temp. resistance , Lower thermal conductivity and Lower pressure resistance as compared to metal molds .

General Design Consideration for Various

Types of Molds & dies

The designing of mold and dies should be given a lot of careful attention . It is important to recognize that the forces involved resulting from high injection pressures in case of injection molds are very large and their effects on cavity strength must be carefully analyzed . The temp. of molding and its influence on cavity configuration must also be taken into account . Once the general design concept has been established , a detailed analysis of strength requirements should be done . After completion of this process , one should proceed with dimension and proportions of vital components . Mold design should include calculations for runner size , position of gates strength that will assure safe and sates factory performance of the costly tools and so on .

A mold should be designed to be changed with min. down time of the m/c . If should change time is small lesser inventories may be kept leading to profitability .

Designing a mold requires that a logical sequence be followed and the basic information be obtained about the part , the material to be molded and the equipment to be utilized .

1) **Part Design :** The part design should be analyzed to determine the location of parting line , the acceptable gate location and the type of ejection to be used to remove the part . There may be some part design features that require special design consideration in the mold design . Such features are molded threads , side cores , undercuts etc. Problem areas such as critical dimensions , minimal draft specification etc. should be identified .

2) **Mold Configuration :** The anticipated volume of parts to be produced by the mold will determine no. of cavities to be included in the mold and the type of the mold to be built.

3) **Machine Selection :** The design of the mold will also depend upon the type of the M/C. for an injection mold , following data about the M/C should be available—
   a) Clamp force (Tons)
   b) Injection capacity (gms/ oj)
   c) Injection Pressure (PSI/Newton/M^2)
   d) Platen size hxv (in , cm)
   e) Distance between tie rods hxv (in , cm)
   f) Clamp stroke max. (in , cm)
   g) Min. Mold height (in , cm) .
   The weight of the shot and the required clamp tonnage based on the projected area of the part must be calculated .

4) **Material :** Physical properties of the plastic malt to be molded must be known . The flow characteristics , mold shrinkage , corrosiveness , and wear characteristics of the material must be considered .

5) **Mold Layout :** When the above information has been collected , a rough design of the mold can be made . The size of the cavity and core components can be estimated and the size of the mold base to be utilized can be selected .

6) **Gating :** A choice must be made for the type of material distribution system from the barred to the cavity to be used . The conventional multicavity mold utilize a sprue and a parting line runner system . Other choices which are dictated by part configuration , economics etc. are three plate , back gated , insulated runner , hot manifold or lot runner .

7) Part ejection : The method by which a part will be ejected is lactated by the part design , the size of the mold the M/C. and the degree of automation to be utilized in the molding operation . The choice of ejector pins , ejector sleeves , stripper plate or air assisted ejection is determined by the part design .

Some Considerations for Compression Molds :-

1) Mold which are made with cavities or plumages in a section require especially good backing and hardened back up plates are recommended .
2) Loose pins used in molds may stick , therefore provision should be made for the addition of an ejector pin behind the loose pin .
3) When ejector pins but against the opposite half of the mold , use hardened strips under the pins to prevent sinking .
4) A solid part will shrink more than a part having thin walls , therefore additional shrinkage allowance must be made .
5) Removable plate molds must be designed with stop blocks between the top and bottom so the mold can not be fully closed when the plate is out .

6) All feather edges must be eliminated in mold designs . Molded threads must be designed without feather edges if low cost operation is desired . Feather edges will require frequent mold replacements because of breakages .

7) The determination of bulk factor and shrinkage are of prime importance in the design of a compression mold .

8) The product design must be studied carefully to make sure that the selected design is moldable .

General concepts of die design : Designing dies requires an accurate knowledge of flow characteristics of the particular plastic material to be processed . The designer must determine the precise shape of flow channels in the die and the exact shape of the exit orifice . The designer must know how plastics flow under pressure . One important factor to be considered is die swell . The amount of die swell will vary from one material to the another and will also vary with changes in the operating conditions for the extruder . Depending upon the material and the melt conditions , die swell will range from less than 5% to over 100% of the orifice dimensions . The basic relationship used for die design is the fellow will vary as the cube of the channel depth (D) and inversely as the channel length (L) with any given upstream pressure .

BASIC CONCEPTS OF DESIGN

Before the design of any part is begun , the usual procedure is to first determine the function of the part and the environment in which it is to operate . This environmental survey should include the thermal conditions high and low temps. and the mechanical stresses on the part tensile load , impact , compression etc. In some types of parts the Major factors may be electrical stresses high voltages or frequencies , dielectric losses etc. Some parts may combine thermal stresses with chemical stresses such as strong acids , solvents , oils , high lucidity etc. Operational time must also be considered .

The next step is usually to prepare a list of the requirements of the part from the stand point of user acceptance . Such a list may include items such as colour , transparency , specific gravity and cost . The list should also include hard to define items such as feel of the part etc. After all the requirements have been determined , the next step is to decide on the material . In selecting the material , the most important factor should be used as the first screening guide . For example if a transparent article is to be made , the list of probable materials is considerably shortened . The final choice is usually a material which will give the optimum performance at the lowest cost . In practice usually a compromise is made in the selection of material .

The next step for the designer is to make the selection of fabrication process . In many cases the choice is dictated by the no. of parts or the material chosen . In other cases the fabrication process is dictated by the type of part or sometimes the type of machine available .

Regardless of the type of part or the overall design , there are certain fundamental design rules which are applicable to almost all types of parts . There include avoidance of stress concentrators , proper use of ribs and fillets , hole spacing etc.

SHRIN KAGE :- Shrinkage is the amount by which a molded product is smaller than the size of the cavity space , where in it was produced by injecting plastic under high pressure injection and at high temperatures . It is expressed as MM/MM Dr in % . There is a definite relationship between pressure (P) , volume (V) and temp. (T) . This relationship is different for various plastics . Any and all conditions that affect temp. pressure and timing will affect shrinkage .

- When a volume of plastic is heated , it expands . When it cools to the original temp. , it will contract to the original volume .
- When a plastic is compressed , its volume is reduced . When the pressure is reduced to original pressure , it will turn to its original volume .

Shrinkage depends on the following variables –

1) The plastic material :- different materials have different heat expansion values . But even materials with the same chemical and physical specifications may have significant differences in heat expansion and therefore in shrinkage .
2) Product geometry :- This applies mainly to variations in wall thickness and the shape of surfaces , ribs etc .
3) Mold design :- The designer must take shrinkage into account , particularly in the waling layout within the mold , the geometry of runners and gates and the uniformity of heating in hot runners etc.
4) Type of molding machine :- Injection speed , available injection pressure , accuracy of time , temp. and pressure controls etc. , all affect shrinkage .
5) Condition of molding M/C . & Mold :- The condition of molding M/C . & Mold may also affect the shrinkage . An old or neglected M/C . may have unreliable controls or a worn check valve etc. A mold which has not been properly maintained may have corroded or plugged waling lines .
6) Molding conditions :- This includes the M/C . set up , mold cooling temperatures , cycle time elements , injection and hold pressures etc. When hot plastic is injected into the cavity , the pressure in the cavity is relatively low until the cavity is filled . After the molten plastic has filled up the cavity , pressure builds up rapidly . This compresses the plastic in the cavity space . The pressure in the cavity is , therefore , a major factor affecting mold shrinkage , Normally this pressure is maintained until the gate freezes or is closed sealing off the material in the cavity . From this time on wards , the pressure within the cavity will drop as the plastic cools and shrinks . Therefore at constant mold and melt temps. Variations in injection pressure and timing of sealing of the gate are the most important factors affecting variations in shrinkage . If the component is ejected in fairly hot condition it will shrink more than the component ejected at lower temp. Thickness of the product also affect shrinkage . as a rule a thick walled product will shrink more than one with a smaller wall thickness . Therefore confiscation of heavy and thin walls adjacent to each other should be avoided , provided deformation is not required in the end product .

Shrinkage Formula :- The diagram and variables defined below are used in calculating shrinkage factors .

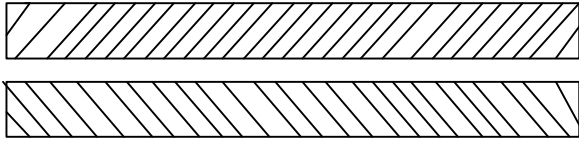$Dc = Dpt (Dp*s) + (Dp*s^2)$

Or $Dc = Dp (I+S+S^2)$

Because S is usually very small , S^2 can be ignored and the formula is simplified to

$Dc = Dp (I+S)$

Where Dc = cavity and core steel dimension

Dp = Product dimension &

S = shrinkage factor (MM/MM or %)

Shrinkage may also be defined as –

(A) Axial shrinkage - It is the shrinkage , Which occurs in the direction of flow of plastic .

(B) Radial shrinkage – It is the shrinkage which is in the direction perpendicular to the flow .
This may be important when product tolerances are very tight and the plastic shows considerable difference in the shrinkage in these two directions .

APPROXIMATE SHRINKAGE VALUES FOR VARIOUS MOLDING MATERIALS :-

MATL	SHRINKAGE
ABS	0.005 – 0.007
Acetal Axially	0.021 – 0.026
Acetal radically	0.018 – 0.020
Acrylic	0.004 – 0.007
EVA	0.007 – 0.020
Nylon 6	0.006 – 0.014
Nylon 66 Axially	0.012 – 0.033
Radically	0.020 – 0.028
Poly carbonate	0.006 – 0.008
PE	0.015 – 0.050
PE , 30% glass filled	0.014 – 0.045
PET bottle grade	0.005 – 0.012
PP	0.012 – 0.022
PS	0.002 – 0.006
PS 30% glass filled	0.0005 – 0.0010
PVC	0.003 – 0.008
PVC 30% glass filled	0.001 – 0.002

FLASH LINE OR PARTING LINE :- Parting line or flash line considerations depend on the function that the part is to perform with most products the P/L is in an obvious location . However in other products the P/L is not so simple and requires considerable thought . Following points should be considered –

1) Ejection :- An important consideration in selecting the parting line is to ensure that the product will stay on the side which will have the ejection mechanism .

2) Shut-offs, offset P/L :- If there are openings in the sides of a product , which do allow the product to pull off but which will require shut off areas between core and cavity , then to prevent sliding motion of a shut off area between cavity and core , this area must be at an angle . Such an angle (a) Prevents flashing and (b) reduces wear .

3) Strength of P/L :- After establishing the P/L , it is necessary to check the strength of the area where cavity and core will touch . If strength is inefficient either the area should be increased or supports should be added to take some of the clamping force .

4) Matching of P/L :- P/L should be produced to provide flash free matching of the mating surfaces . Usually the P/L is ground on both cavity and core side .

UNDER CUTS :- Under cuts are indentations or projections on the wall of a plastic part which interfere with simple ejection from a two part mould . Under cuts should be avoided whenever possible . The unnecessarily complicate the mould design and considerably increase the cost .

Special split moulds are required for ejection of components having under cuts and retracting mechanisms etc may be needed .

Designs with internal undercuts may be machined after moulding of the components at less cost than the cost which may be incurred if the component is moulded with under cuts . This is particularly true of external undercuts .

WALL THICKNESS :- The first rule of good design is to use a uniform wall thickness whenever and wherever possible . A thick section , next to thin sections will cool last and shrink more away from the mold , resulting in a sink mark . The differential cooling will also result in internal stresses , warpage or distortion and may sometime cause cracking . If a non uniform wall thickness can not be avoided then the different wall sizes should be gradually blended as shown in the figure below .

The wall thickness should however not vary by more than a ratio of 3:1 if possible . In addition to uniform thickness it is desirable to design parts with wall sections that are well within normal molding capability , which in turn depends upon the machine , mold and material to be molded . It should also be kept in mind that higher wall thickness will result in longer cycle times because of slow rates of cooling .

IMPRESSION :- The injection mould is an assembly of parts containing within it an impression into which plastic material is injected and cooled . It is the impression which gives the moulding its form . The impression may therefore be defined as that part of the mold which imparts shape to the molding . The impression is generally formed by two mould members –

1) The cavity – it is the female portion of the mould and it gives the moulding its external form .
2) The core – It is the male portion of the mold and it forms the internal shape of the moulding .

Cavity & core Plates :- A basic mould consists of two plates . In to one plate , the cavity is sunk which shapes the outside form of the moulding and is therefore known as cavity plate . Similarly the core which projects from the core plate forms the inside shape of the moulding . When the mould is closed , the two plates come together forming a space between the cavity & core , which is called the impression .

Types of core & cavity :- There are two alternative ways by which the cavity and core can be incorporated into the mould , namely the integer method and the insert method . Another method by which the cavity can be incorporated is by means of split inserts or splits .

1) Integer Cavity & Core Plates :- When the cavity or core is machined from a large plate or block of steel or is cost in one piece and used without bolstering as one of the mould plates . It is termed an integer cavity plate or integer core plate . This design is preferred for single impression moulds because of the strength smaller size and lower cost characteristics . It is not used as much for multi impression moulds .

Normally two types of process are used for preparing integer type cavity and core . These are

a) A direct machining operation on a rough steel forming or blank using the conventional machine tools or

b)   The precision investment casting technique in which a master pattern is made of the cavity and core . the pattern is then used to prepare a costing of the cavity or core by a special process . A 4.25% Ni – Cr – Mo steel (BS- 970-835 M 30) is normally specified for integer mould plates which are to made by the direct machining method . The precision investment casting method utilizes a high chrome steel .

2)   INSERTS :- Core & Cavity :- For moulds containing intricate impressions and for multi impression moulds , It may not be satisfactory to machine the cavity and core plates from single blocks of steel . The machining sequences and operation would be very complicated and costly . The insert bolster assembly method is used for this type of moulds . The method consists of machining the impression out of small blocks of steel . these machined components are known as core inserts or cavity inserts depending upon their use either in core or in cavity . These are then inserted and securely fitted into holds in a plate of steel called a bolster . The holes are either sunk part way or are machined right though the bolster plate . The inserts are mostly circular or rectangular in shape .

Advantages & Disadvantages of integer and insert bolster method :-

Both the integer and the insert bolster methods have their advantages depending upon the size , the shape of the moulding , the complexity of the mould , no. of impressions in the mould etc. The comparison of the advantages and disadvantages is discussed below –

1) Cost :- The total cost of a mold includes – (a) the cost of the mold material and (b) the cost of matching & fitting . The integer method requires the whole mould plate to be made of expansive mould steel , where as the insert – bolster method needs only parts , which form the impression to be made of mould steel and the bolster is made from considerably cheaper mild steel . However the machining & fitting of a single impression integer type mould is less costly in time and in no. of operations as compared with the insert – bolster combination .

2) No. of Impressions :- The difficulty in machining and aligning the cavities and cores in an integer type mould increases with the no. of impressions in the mould . Therefore for multi impression moulds it is usually preferable to use insert – bolster system .

3) Multi impression Mould alignment :- The non uniformity and non- conformity of the cores & cavities in a multi impression mould can be corrected more easily in an insert – bolster system as compared to integer type mould .

4) Mould size :- The fabrication of an integer type mould requires that very heavy steel blocks are to be handled during the manufacturing stage , where as in the case of an insert – bolster system , the smaller blocks will have to handled , for individual impressions which is much easier .

5) Heat Treatment :- It is often desirable to heat treat that part of the mould which contains the impression to given a hard , wear resisting surface . During this heat treatment , these is a possibility that the steel may distort . This possibility reduces for smaller blocks of steel . From this point of view , insert type moulds are preferable .

6) Replacement of damaged parts :- with the insert bolster type system , it is possible to repair a damaged impression while continuing to operate the mould with the remaining impressions , resulting in minimum interruption to prod[4] .

7) Cooling system :-   It is easier for an integer mould .

8) Conclusion :- For single impression moulds the integer design is to be preferred irrespective of whether the component form is a simple or a complex one . The resulting mould will be stronger , smaller & less costly . For multi impression moulds , the insert – bolster system is most commonly used for the ease of manufacture , mould alignment and resulting lower mould costs .

BOLSTERS

When the cores and the cavities are incorporated into a mould design as inserts , they must be securely retained in the mould . This is achieved by fitting the inserts into a bolster , which when fitted with suitable guiding arrangements , ensures that alignment of the cavities and cores is maintained . The fundamental requirements of a bolster are –

1) It must provide a suitable pocket into which an insert can be fitted .
2) It must provide some means for securing the insert after it is fitted in position .
3) It must have sufficient strength to withstand the applied moulding forces .

The bolster is normally made from mild steel plate to the BS 970-040 A 15 specification . In certain cases , a medium carbon steel (BS – 970-080-M 40) is also used .

Types of bolster :- Following are the main types of bolsters :-

1) Solid bolster :- Solid bolster is suitable for use with both rectangular and circular inserts . This is made by squaring up a block of steel . Then by a direct machining operation , a pocket is sunk in to the top surface to a predetermined depth . The shape of the pocket is either rectangular or circular to suit the shape of the mould inserts .

2) Strip type bolster :- in this type of bolsters , the poet is made by machining slot completely through the bolster block . Steel strips are then fitted at either end of the slot to complete a frame for the inserts . To prevent the strips from moving under possible side thrust , a projection extends from the underside of the strip and this fits into a mating recess in the bolster with socket – headed screws . These types of bolsters can be used only for rectangular inserts . The advantage of this type of bolsters is that all the important surfaces are ground and the subsequent fitting of the insert is simplified .

3) Frame type bolster :- This bolster consist of two parts , namely a frame and backing plate . The frame is made by machining an aperture of the required shape completely through the bolster plate . The bottom of the insert is supported by a backing plate secure to the frame with a no. of socket headed screw . The inserts them selves may be secured either in the same manner by screws through the backing plate or alternatively by the use of flanged inserts . This type of inserts are particularly useful for small inserts .

4) Chase bolster :-   This type of bolsters are used with split inserts . When splits inserts are to be incorporated in the mould design it is necessary for one of the bolsters to lock the splits in their closed position . chase bolsters are of two types :-

   a) The open channel :- This is used for shallow rectangular splits and is mad by machining a channel across the width of the bolster plate . The sides of the channel are stopped or angles . The stopping sides or faces are usually faced with hardened area strip made from a carburized low carbon steel .

   b) Enclosed chase bolster :- This is used for deep splits It is machined from a solid block and the pocket which is to accommodate the splits may be a tapered circular or a tapered rectangular form .

5) Bolster plate :- Inserts can be mounted directly into a plane bolster plate . This system provides no side support and the walls of the inserts must be of sufficient thickness to withstand the applied moulding pressure without undue defection . the inserts must also be securely screwed and dowelled in position to prevent misalignment .

Mould alignment :- mould alignment is one of the most important area in fabrication and operation of a mold . If the mould haves are not perfectly aligned , it will not be possible to produce quality components . Moreover the leader pins and bushes will be subjected to excessive wear , reducing their life .

During the fabrication , the aligning is done after the core and cavity have been semi finished . This is achieved by clamping the two mould halves together in correct position and boring guide halves together both the plates . Guide pillers and bushes are then fitted into the plates . The two mould plates are again brought together to check the perfect alignment of core and cavity . A dummy moulding is often made at this stage , using wax , so that the wall sections of the mold can be checked .

During the injection moulding operation the mold halves are normally hold in place by using mold clamps .

Dowel or leader pins :- The dowel or leader pins or the guide pillers are used to ensure the alignment of mould halves during operation . This is necessary for mouldling an even called product . The guide pillers pins are incorporated on one mould plate . Which then enter corresponding guide bushes in other mould plate as the mould closes . The size of guide pillers should be such that they maintain alignment inspective of the applied moulding force .

A guide piller is designed so that the working diameter is smaller then the fitting diameter D by a min. of 7mm. This introduces a shoulder into the piller , where it emerges from the mould plate so that the fitting diameter of the guide piller can be made the same as the guide bust . Thus the holes of same dia can be bored and ground thought both mould plates , when clamped together . Thus allows perfect alignment .

The piller is normally machined from a low carbon steel (BS- 970 – 050-M 15) which is then case hardened . Save times carburized Nickel-chrome steel (BS-970-835 M 15) is used for better bending resistance . The normal size range of guide pillers is between 10mm to 38mm working diameter . Some very large moulds may require guide pillers outside this range .

Size range of guide pillers :-

Working diameter(d)		Size of mould	
MM	In	(MM)	(In)
10	3/5	100*100	4*4
13	½	100*150	4*6
16	5/8	150*200	6*8
19	¾	200*250	8*10
22	7/8	250*300	10*12
25	1	300*400	12*16
32	1 ¼	400*600	16*24
38	1½	600*700	24*28

Register Ring :- The registering or the locating ring , is a flat circular member normally fitted on the front face of the mould . It is purpose is to locate the mould in its correct position on the injection moulding machine plastic .

When the mould is mounted on the machine . the front mounted register ring fits into a circular hole which is accurately machined in the injection platen on the cylinder nozzle axis . This ensures that the small aperture in the nozzle is in direct alignment with the sprue bush hole .

Since the sprue bush is the connecting member between the machine nozzle and the mould face , this alignment of nozzle aperture and sprue bush hole permits an uninterrupted flow of material from the cylinder , through the nozzle and sprue hole into the mould runner system . The register ring infect forms a direct connection between the sprue bush and the hole in the injection platen of the machine .

As the register ring is permanently attached to the mould , correct alignment follows automatically whenever the mould is set up on the machine and no adjustment by the setter is therefore necessary .

The register rings may be of various designs as shown in the fingers below :-

Attachment of mould to platen :- There are two ways by which the mould halves may be attached to the platen of the injection moulding machine .

1) Direct Bolting Method :- In principle , holes are provided in each mould half to correspond with the holes tapped in the machines platen . Bolts are then used to directly secure the mould to the platen . Now a days machine manufactures adopt a standard hole layout and therefore a mold design for one machine can normally be fitted to another of similar size . Various alternative direct bolting design can be chosen as shown in the figures below .

2) Indirect Bolting Method :- With this design the attachment of the mould to the machine is by means of a clamp plate . It is used when it is not possible to use the direct bolting method . The indirect bolting assembly consists of three parts , namely the clamp plate , the bolt and the packing piece . There are two alternative designs –

   a) The front plate incorporates a projection (or flange) and a clamping force is applied to this by the bolt via the clamp plate .

   b) A slot can be machined through the mould plate and the clamping force applied in identical manner .

Since large clamping forces are provided by M/C Mfrs, and it is likely that if small land widths are adopted , the effective land area will be insufficient to withstand the applied forces and the relatwely narrow steel projection will deform . To overcome this possible hazard , the land area is increased by insuring that other area of the mould face are left proud in places unlikely to be affected by flash such as the corns of the mould .

Venting :- When the plastic material elves an impression , all the air inside should be displaces otherwise moulding defects such as discoloration sink marks , incomplete filling etc. will develop . Therefore it is recommended that vents be provided in the mould to allow air (and other gases when present) to escape freely . The vent is normally a shallow slot , not more than 0.05MM deep by 3MM wide , machined in the land . Positions where the vent is likely to be required are –

1) At the point where flow paths are likely to meet .
2) At the point further most from the gate on symmetrical mouldings and
3) At the bottom of projections .
   The vent is normally machined into the mould plate once the mould has been tried out to determine its best location .

FEED SYSTEM

It is necessary to provide a flow way in the injection mould to connect the nozzle to each impression . This flow way is termed as the feed system . Normally the feed system comprises a sprue , runner and gate . The material passes through the sprue , main runner , branch runners and gate before entering the impression . It is desirable to keep the distance that the material has to travel down to a minimum to reduce pressure and heat losses .

SPRUE :- During the injection process , plastic matl. is delivered to the nozzle of the machine as a melt , It is then transferred to the impression through a passage . In the simplest case this passage is a tapered hole within a bush . The material in this passage is termed the sprue , and the bush is called a sprue bush . Therefore sprue bush is the connecting member between the machine nozzle and the mould face and provides a suitable aperture through which the matl. can travel on its way to the impressions or to start of the runner system in multi impression moulds . Sprue bush is normally made from a 1 ½ % nickel chrome steel (BS 970-817 – M 40) and should always be hardened .

RUNNER :- The runner is a channel machined into the mould plate to connect the sprue with the entrance (gate) to the impression . In the basic two plate mould the runner is positioned on the parting surface while in more complex designs the runner may be positioned below the parting surface . The wall of the runner channel must be smooth to prevent any restriction to flow . Also as the runner has to be removed with the moulding , there must be no machine marks left which would land to retain the runner in the mould plate . There are some considerations for the designer to keep in mind during designing of a runner for a particular mould .

1) The shape of the cross section of the runner –

The cross sectional shape of the runner used in a mould is usually one of the four forms – (a) fully round (b) trapezoidal (c) modified trapezoidal and (d) hexagonal (fig.) The criteria of efficient runner design is that the runner should provide a maximum cross sectional area from the stand point of pressure transfer and a minimum contact on the periphery from the stand point of heat transfer . The runner efficiency is therefore defined as .

Runner efficiency = $\dfrac{\text{Cross sectional area}}{\text{Periphery of runner}}$

Efficiencies of various types of runners are finer below –

It can be observed from the table that the round and square type of runners are the two most satisfactory designs from the stand point of efficiency . The square runner however becomes undesirable because it cannot be ejected easily . In practice , an angle of 10^0 is incorporated on the runner wall , thus modifying the square to the trapezoidal section . The volume of the trapezoidal runner is approximately 25% greater then that of a round runner with corresponding dimensions (W=D) .

The hexagonal runner is basically a double trapezoidal runner , where he two halves of the trapezium meet at the parting surface . The cross sectional area of this type of runner is about 82% of that of corresponding round runner .

The choice of runner is also influenced by the question whether positive ejection of the runner system is possible . This can be used in two plate moulds only and is not practicable for multiplate moulds . Here the basic trapezoidal type runner is specified . Hence we can say that for simple two plate moulds which have flat parting surface the fully round runner or hexagonal runner is to be preferred for moulds which have complex parting surface , the semicircular , trapezoidal or modified trapezoidal runner should be used .

2) Runner size :- Following factors should be considered for deciding the size of the runner –
a) The wall section and volume of moulding .

b) The distance of the impression from the sprue .
c) Runner cooling considerations .
d) The range of mould maker's cutter available , and
e) The plastics materials to be used .

The cross sectional area of the runner must be sufficient to permit the melt to pass through and fill the impression before the runner freezes and for packing pressure to be applied for shrinkage compensation of required . Runners below 2MM dia are not normally used . The longer the melt has to travel along the runner , the greater is the resistance to flow . Hence longer the runner distance , bigger should be the cross sectional area . If cooling of the runner system is very fast , larger cross sectional area will have to be provided . If size of the cross sectional area of the runner is such that it is in between two sizes of the cutters available with the mould maker, then the designer should opt for the longer cutter size .

Type of the plastic material to be processed also affects the size of the runner . A less viscous and smooth plastic melt will need smaller cross section than a more viscous and more abrasive material such as FR Ps. The following formula is used to find the size of the runner or branch runner mouldings weighing up to 200gms. and with wall sections less then 3MM.

$$D =$$

Where,   D = Runner dia (MM)
             W = Weight of moulding (gm)
             L   =   Length of runner (MM)

For rigid PVCs and acrylics , the calculated dia of the runner is increased by 25% . The runner should not be below 2MM dia nor above 10 or 13MM dia wherever applicable and the calculated size . The cross sectional area of the main runner should be equal to or in excess of the area of the branch runners . This relationship is ignored when the max. dia is reached . Intersection of secondary runners with the main runner should be filleted with a 3MM radius on the sprue side of the intersection . All main runners in a given mould should be equal in diameter , while the diameter of all secondary runners should be at least 0.7MM less than the diameter of the main runner .

RUNNER DIAMETERS FOR UNIFILLED MATERIALS

MATL.	RUNNER DIA.		
	Indult.		MM.
ABS, SAN	3/16	-	3/8
ACETAL	1/8	-	3/8
ACRYLIC	5/16	-	3/8
NYCON	1/16	-	3/8
P.C	3/16	-	3/8
POLYESTER(TP)(UNFILLED)	1/8	-	5/16
Reinforced	3/16	-	3/8
Poly ethylene LD – HD	1/16	-	3/8
PP	3/16	-	3/8
PS (All Types)	1/8	-	3/8
PVC (Plastic used)	1/8	-	3/8
Rigid	¼	-	5/16

Weights of runner systems for matl. density 1gm/cm^3.

RUNNER DIA	Wf. (gm) per cm length of runner .	
	ROUND.	**TRAPEZOIDAL**
2	0.0314	0.0366
3	0.0707	0.0823
4	0.1256	0.1463
5	0.1963	0.2286
6	0.2826	0.3292
12	1.1304	1.3167
15	1.7663	2.0574
18	2.5434	2.9626

RUNNER LAYOUT :-   The layout of the runner system depends upon the following factors –
a)   The no. of impressions .

b) The shape of the mouldings .
c) The type of the mould . (Two plate or multi plate mould)
d) The type of gate .

There are two main considerations for designing a runner layout –
1) The runner length should always be kept to a min. and
2) The runner system should be balanced .

Various types of balanced runner systems are shown in the fig. below –

BALANCING OF RUNNERS :-   Runner balancing means that the distance the plastic material travels from the sprue to the gate should be the same for each moulding . This system ensures that all the impressions will fill uniformly and without interception provided the gate lands and the gate areas are identical .
The melt should arrive at all gates with the same pressure & temp. so that all products within one mould have uniform characteristics .
        To achieve balancing it is preferred to arrange the runners symmetrically from the point of entry of plastic all the way to each gate . This is fairly easy with some layouts but becomes difficult with a large no. of cavities even through the geometry of the product is symmetrical because of the following reasons .
-    The flow of plastics through the channels changes at every point of division into branch channels and depends on the amount of redirection of the melt at the point of change .
-    The flow depends upon the accuracy of machining and finish inside the channel.
-    There may be temperature differences within the runner due to uneven heating and cooling of the steel runner ding the runner .
-    There are machining tolerances of the gate .
-    Uneven venting can affect the filling of cavity.
-    Some resins are flow sensitive to changes in direction and generally will not flow evenly around several bends in a runner system .
-    The phenomenon of the "plastic memory" can also affect the flow within the runners .

GATES

The gate is a channel or orifice connecting the runner with the impression . It has a small cross sectional area when compared with the rest of the feed system . The cross sectional area is small because of following reasons .

1) The gate freezes soon after the impression is filled so that the injection plunger can be with drawn without the probability of void being created in the moulding by sunk back.
2) It allows for simple degating .
3) After degating only a small witness mark remains.
4) Better control of the filling of multi-impressions can be achieved.
5) Packing the material impression with material in excess of that required to compensate for shrinkage is minimized . The optimum size of a gate will depend on the following factors .
    a) The follow characteristics of the matl. to be moulded .
    b) The wall section of the moulding .
    c) The volume of the material to be injected into the impression.
    d) The temp. of the melt and
    e) The temp. of the mould .

Posting of the Gate :- Ideally the position of the gate should be such that there these is an even flow of melt in the impression so that it is filled uniform ally and the advancing melt front spreads out and reaches the various impression extremities at the same time . In this way two or more advancing fronts would really meet to form a weld line . Such an ideal position for gate is possible in certain shopped moulding such as those with circular cross sections . Another reason for central gating for slender cone like components such that pen caps is that side gating may cause defection of the core . This results in a thinner wall section one side thus adding another weakness to that of the weld line .

For thin walled rectangular mouldings off centre multipoint gating or film gating is used it should be positioned so that the melt flow immediately meet a restriction .

GATE BALANCING :- It is often necessary to balance the gates of a multimpression mould to ensure that the impressions fill simultaneous . This method is adopted when the preferred

balanced runner system can not be used to achieve balanced filling it is necessary to cause the greater restriction to the flow of the melt to those impressions closet to the sprue to progressively reduce the restriction as the distance from the sprue increases . These are two ways of varying the restriction –

a) By varying the land length and
b) By varying the cross sectional area of the gate . Following formula can be used to calculate the gate size for impressions of different shot weights for round gates–

$$D_2 = d_1 \left(\frac{w_2}{w_1}\right)^{1/4}$$

For rectangular gates –

$$T_2 = t_1 \left(\frac{w_2}{w_1}\right)^{1/3}$$

Where –

D_1 = The gate dia of first cavity (cm)
D_2 = " "   "   second " (cm)
T_1 = depth of the gate in first cavity
T_2 = "   " " "   " second "
W_1 = wt. of first cavity component (gm)
W_2 = "   " second "   "   "

Types of Gate :- The type of gate must be chosen carefully to obtain optimum filling conditions . The choice normally depends upon the plastic material , types of mould , types of enjection of gate and permissible visibility of gate marks on the products . The types of gate commonly used are – sprue gate , edge gate , overlap gate , fan gate , dia pram gate , ring gate , film gate , pin gate and subsurface gate .

1) Sprue gate :- when the moulding is directly fed from a sprue , the feed section is termed a sprue gate . The main disadvantage with this type of gate is that it leaves a large gate mark on the moulding . the size of this mark depends on – (a) The dia at the small end of the sprue (b) The sprue ingle and (c) The sprue length . The gate mark can be minimized by keeping the dimensions of the above factors to a min .

Sprue sizes for PS.

Wt. of moulding (gm)	Min. sprue dia (mm)
10	3.5
10-20	4.5
20-40	5.5
40-150	6.5
150-300	7.5

For other materials the sprue dia should be multihued by following factors –

Acrylic	2.0
Plasticized PVC	0.8
Nylon	0.8
Cellulose acetate	1.0
Polyethylene	0.5

2) Rectangular gate :- This is a general purpose gate and in it's simplest form it is a rectangular channel machined in one mould plate to connect the runner to the impression . Following are the main advantages of this type of gate–
   1) The cross sectional form is simple and cheap to machine .
   2) Close accuracy in the gate dimensions can be achieved .
   3) The gate dimensions can be quickly and easily modified .
   4) The filling rate of the impression can be controlled relatively indepently of the gate real time .
   5) All commonly used materials can be moulded through the type of gate .

The main disadvantage of this type of gate is however that after gate removal a witness mark is left on the visible surface of the moulding .

Gate size :-

OUTLINE

- Micro pumps
- Micro valves
- Micro mixers
- Keypoints (conclusion)

MICROPUMPS

GENERAL TYPES OF MICROPUMPS

- BUBBLE PUMPS
- DIFUSSER PUMPS
- MEMBRANE PUMPS (most common)
- ROTARY PUMPS
- ELECTROHYDRODYNAMIC PUMPS
- ELECTROOSMOTIC/ ELECTROPHORETIC PUMPS
- ULTRASONIC PUMPS
- OPTICAL PUMPS

BUBBLE/DIFUSSER PUMP

■ The formation and collapse of a bubble in the liquid is used to drive the flow of the liquid

■ Allows for a valve-less diffuser design

■ Greatly enhances mixing of the constituent phases

■ Flow rate in the range of 4-5 µL/sec for 250-400Hz
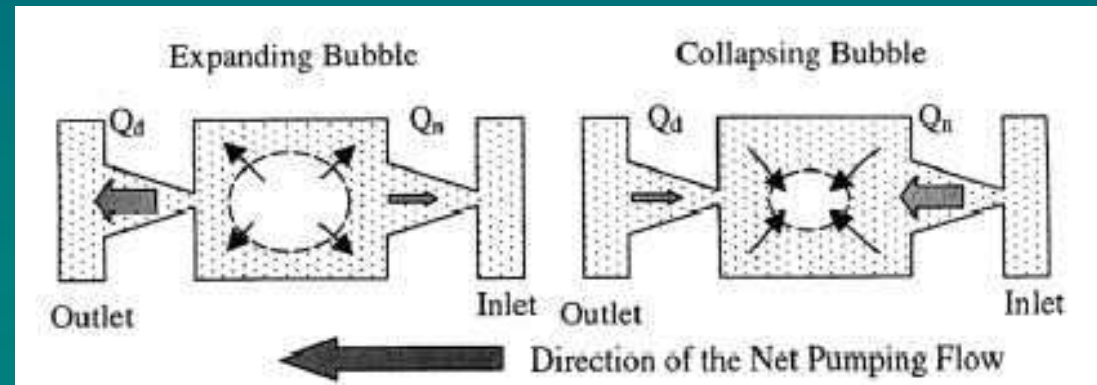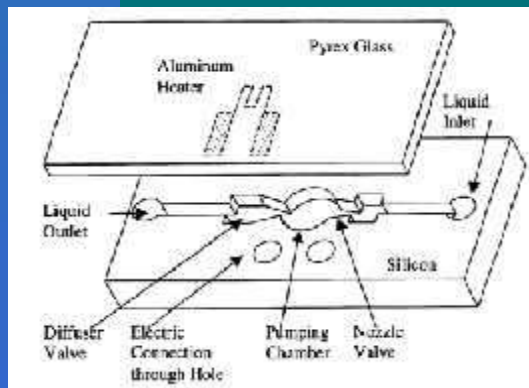
MEMBRANE PUMPS

- **Method of displacing the membrane**
  - Magnetically
  - Electrostatically
  - With a piezoelectric
  - Thermally (SMA and thermopneumatically)
- **Sensitive to blockage by particulates in the fluid**
- **Flow rate in the range of 100-10000 µL/sec**

http://ej.iop.org/links/60/IYwveEquvuX,ovtuKcQOMw/jm8218.pdf   http://www.ajou.ac.kr/~mems/proj-1-1.htm
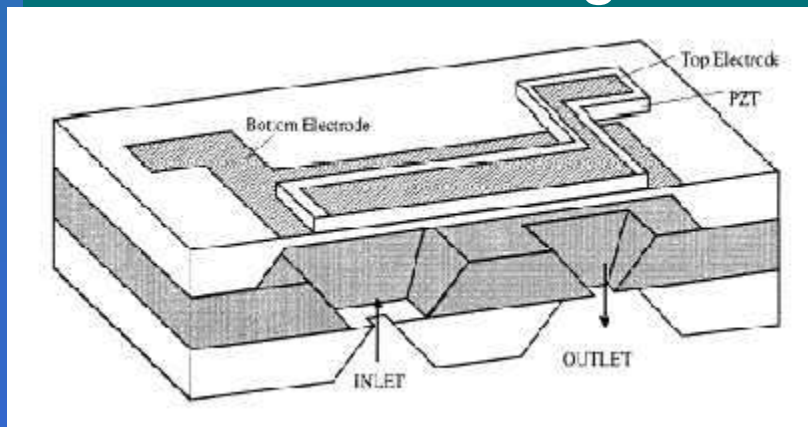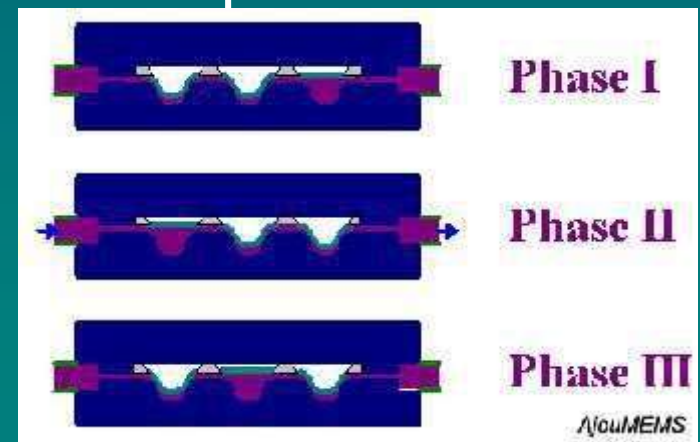
ROTARY PUMPS

- Very rare and not commonly researched
- Extremely complicated fabrication process
- High susceptibility to failure
- Very precise control of the fluid flow and direction
- Good for transporting high impurity liquids

Figure 1. Basic concept of a jet-type rotary micropump.

(c)
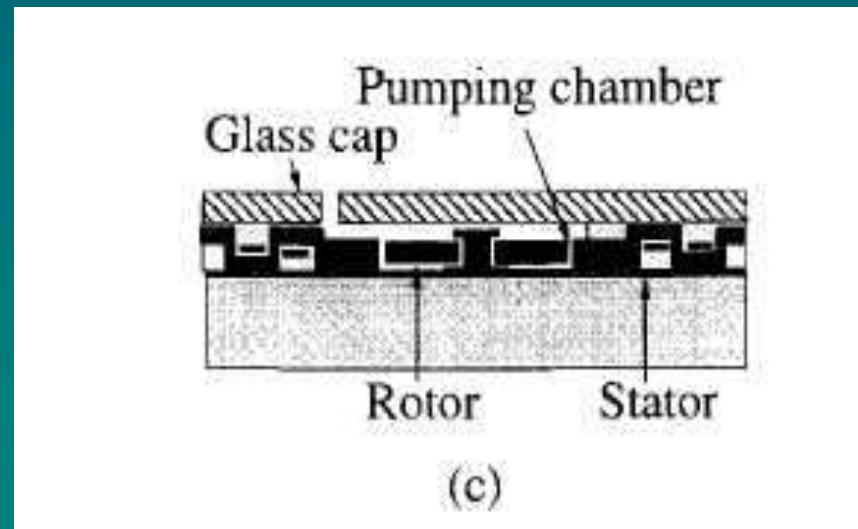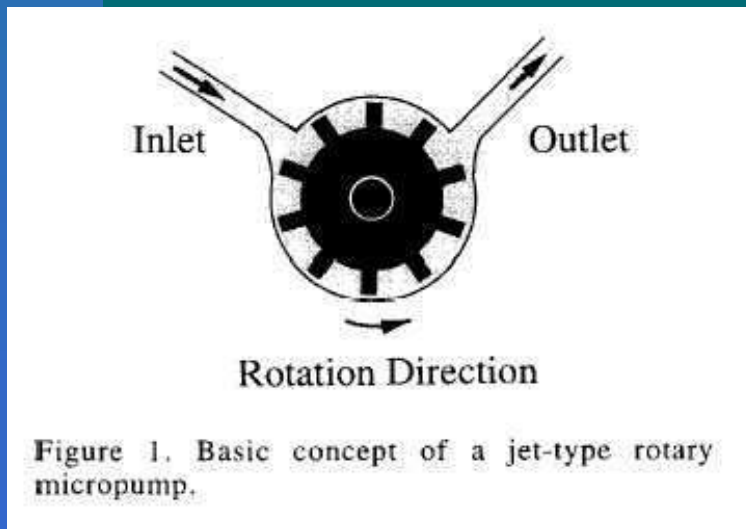
ELECTROHYDRODYNAMIC PUMPS

- Uses an applied electric field on the fluid to be pumped to induce charge and also to electrostatically move the induced charges
- Not suitable for the delivery of most biological fluids, as a very specific fluid conductivity is required
- Extremely high voltages are required to move the fluids (~700volts)
- Has an equivalent magnetohydrodynamic pump

ELECTROOSMOTIC/ ELECTROPHORETIC PUMPS

- Electrophoretic pumping relies on the presence of ions in the fluid
  - The ions are manipulated through the application of an electric field and flow is induced
- Electroosmotic flow relies on the presence of ions on the surfaces of the fluidic channel
  Example- between glass and organic fluids
  - An applied electric field allows for the movement of the bulk fluid
- Flow rate on the order of 15 µL/sec
- No moving parts
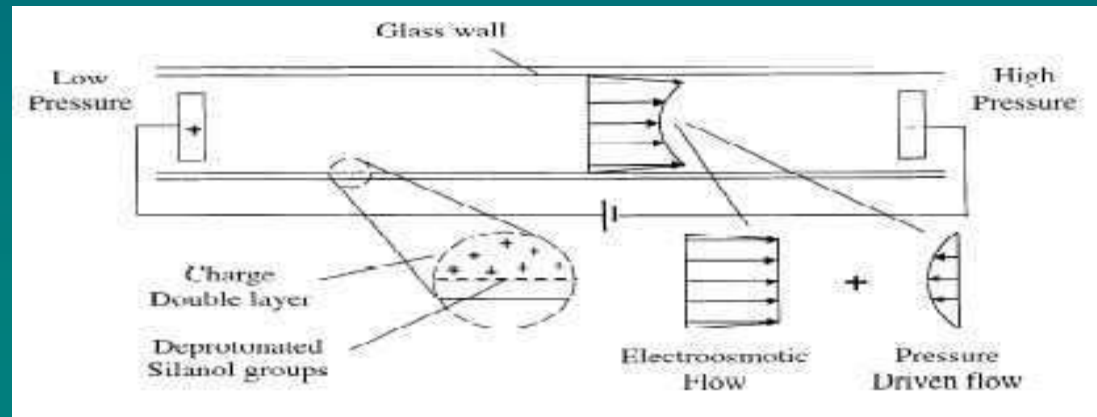
ULTRASONIC/OPTICAL PUMPS

- ■ Ultrasonic pumps use piezoelectric networks to actuate on a cyclical basis to produce predictable fluid motion
  - – Most applicable to mixing, not pumping
- ■ In optical pumps, heat is introduced to the fluid by way of optical absorption
  - – Gradients in the fluids heat result in viscosity and surface tension gradients, which in turn lead to fluid flow by way of the thermocapillary effect
  - – Most applicable to mixing, not pumping

VALVES

VALVE CLASSIFICATION

- Non-moving valve
- Passive valves
- Actuated valves

NON_MOVING VALVES

■ Diffuser Valve

– Provides directional resistance

Figure 5: Configuration of micro-pump.

http://www.cr.org/publications/MSM2001/html/T67.02.html
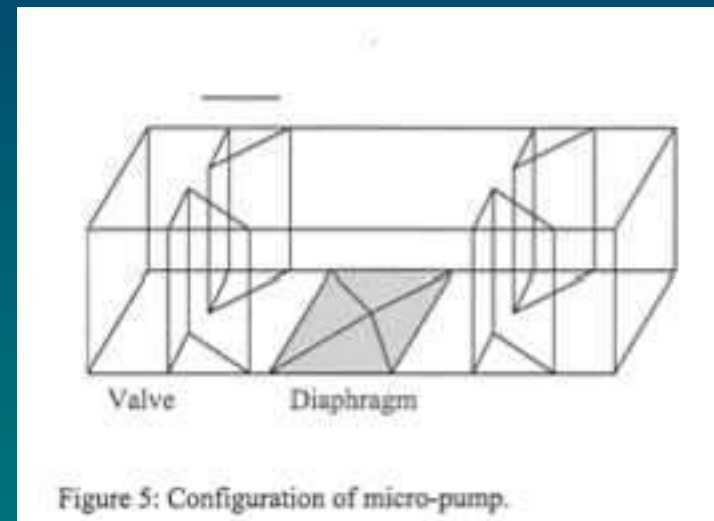
PASSIVE VALVES

■ Cantilever

■ Disc

■ Membrane

Shoji, Journal of micromechanics and microengineering 1994
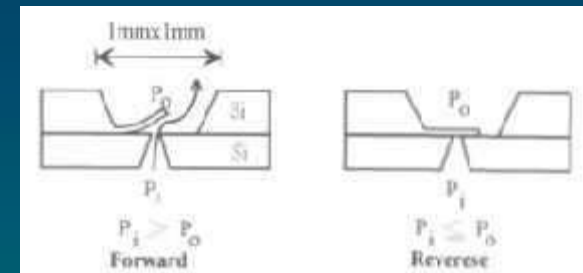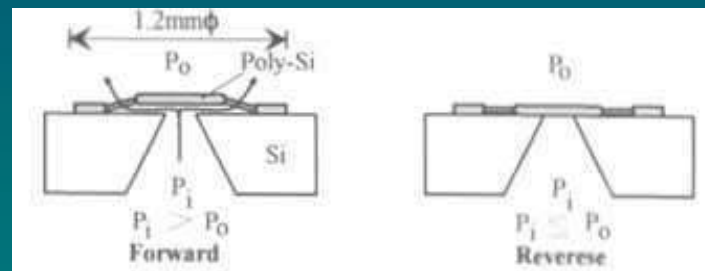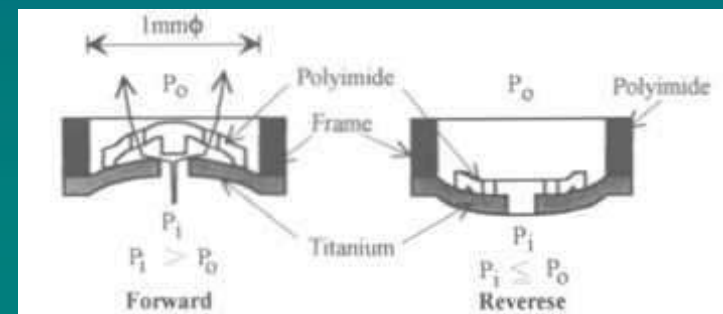
PASSIVE VALVES (con't)

■ Piston

piston

http://www.ca.sandia.gov/microchem/microfluidics/valves/valves1.html
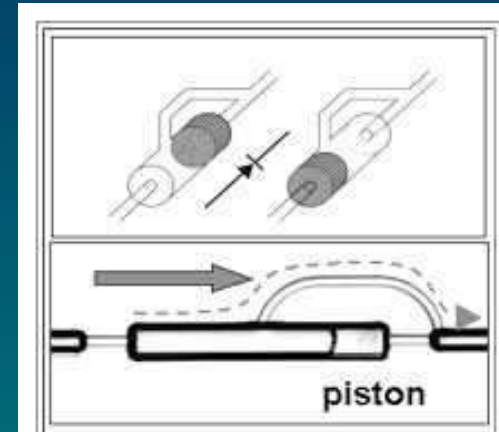
■ Gas controlled

Quake, Science 2000

ACTIVE VALVES

■ Valve types based on actuation
- Electromagnetic
- Piezoelectric
- Pneumatic
- Shape memory alloy
- Thermopneumatic
- Chemical

MICROMIXERS

Definition: The controlled micro-mixing of two or more fluids

GENERAL TYPES OF MIXERS

- Laminating Mixers

- Plume Mixers

- Active Mixers
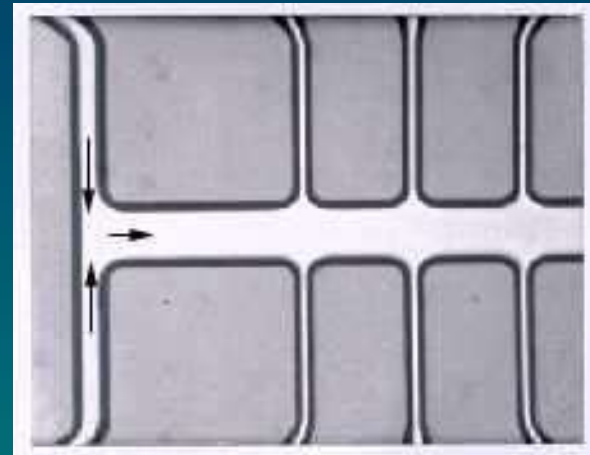
Micrograph of Silicon-glass -- Copyright, Meinhart, Bayt 1998

http://www.engineering.ucsb.edu/~nari/mycurrentresearch.htm

LAMINATING MIXERS

■ At the microscopic scale the use of laminating mixers is try to "laminate" two or more fluids together to increase the contact area and enhance diffusion (0.5 to 12 μl/min)
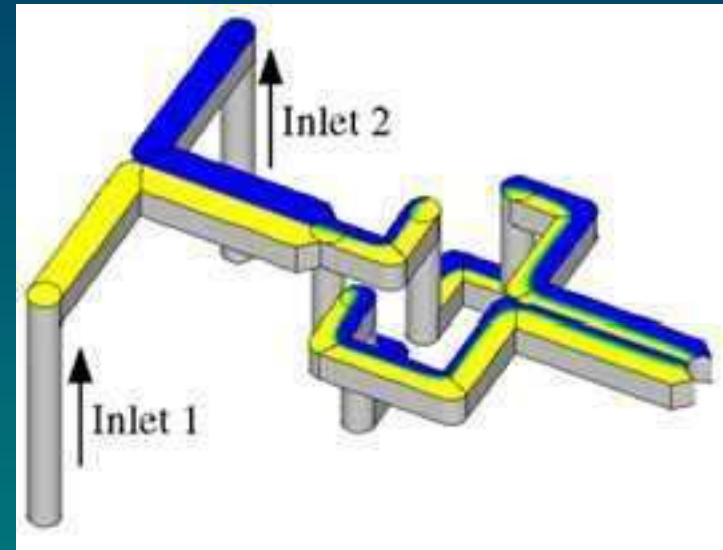
Two fluids entering the inlet ports laminate at the first horizontal junction, producing two side-by-side fluid streams. Successive vertical separation and horizontal reuniting of fluid streams increases the number of laminates with each stage and, thus, the contact area between the two fluids.

http://transducers.stanford.edu/stl/Projects/fluidic-charact.html

PLUME MIXERS

- Takes advantage of the behavior of a fluid leaving a narrow nozzle (15μm)
- Generates a small plume which increases the contact area of two liquids
- Homogeneous mixing in 1.2 secs in a 0.5 μl volume at a 45 μl/min flow rate

ACTIVE MIXERS

- The use of external energy
  - Ultrasonic traveling wave pumps moving fluids in a circulating path

  - Bubble pumps – two large pumps used to generate push & pull forces

KEY POINTS

- Membrane pumps are the most common type of micro pumping device currently fabricated
- An attempt is being made to phase out check valves and other mechanisms that slow down the frequency response of the pumping system.
  - Drive toward diffuser valves
    - More flow loss, but increase in frequency.
- Pumps with non-moving parts are preferred due to higher reliability, etc.
- Bubble, electroosmotic, and electrophoretic pumps tend to be the direction in bio-micro fluidics applications.

KEY POINTS (con't)

- Passive valves are commonly used because they are easier to fabricate and are smaller that actuated valves

- The easier and cheaper the valve is to fabricate the more likely it will be used

- Chemically reactive valves are ideal for bio-microfluidics because they are easy to make, they are small and they behave as an active valve

KEY POINTS (con't)

- Laminating Mixers – to laminate fluids together
- Plume Mixers – plume is generated to increase contact area of two liquids
- Active Mixers – uses external energy to mix fluids

Lecture 13: Petrochemicals: Overview

13.1 Introduction

- In this lecture, we present a brief overview of petrochemical technologies and discuss upon the general topology of the petrochemical process technologies.
- Petrochemicals refers to all those compounds that can be derived from the petroleum refinery products
- Typical feedstocks to petrochemical processes include
  - o C1 Compounds: Methane & Synthesis gas
  - o C2 Compounds: Ethylene and Acetylene
  - o C3 Compounds: Propylene
  - o C4 Compounds: Butanes and Butenes
  - o Aromatic Compounds: Benzene
- It can be seen that petrochemicals are produced from simple compounds such as methane, ethylene and acetylene but not multicomponent products such as naphtha, gas oil etc.
- **13.1.1 Definition :** These are the chemicals that are made from petroleum and natural gas. Petroleum and natural gas are made up of hydrocarbon molecules, which comprises of one or more carbon atoms, to which hydrogen atoms are attached.
- About 5 % of the oil and gas consumed each year is needed to make all the petrochemical products. Petrochemicals play an important role on our food, clothing, shelter and leisure. Because of low cost and easy availability, oil and natural gas are considered to be the main sources of raw materials for most petrochemicals.

13.1.2 Classification: Petrochemicals can be broadly classified into three categories-

a. Light Petrochemicals: These are mainly used as bottled fuel and raw materials for other organic chemicals. The lightest of these -- methane, ethane and ethylene -- are gaseous at room temperature.The next lightest fractions comprise petroleum ether and light naphtha with boiling points between 80 and 190 degrees Fahrenheit.

b. Medium Petrochemicals: Hydrocarbons with $6 - 12$ carbon atoms are called "gasoline", which are mainly used as automobile fuels. Octane, with eight carbons, is a particularly good automobile fuel, and is considered to be of high quality. Kerosene contains 12 to 15 carbons and is used in aviation fuels, and also as solvents for heating and lighting.

c. Heavy Petrochemicals: These can be generally categorized as diesel oil, heating oil and lubricating oil for engines and machinery. They contain around 15 and 18 carbon atoms with boiling points between 570 and 750 degrees Fahrenheit. The heaviest fractions of all are called "bitumens" and are used to surface roads or for waterproofing.

Bitumens can also be broken down into lighter hydrocarbons using a process called "cracking."

13.2 Process Topology

- Reactors: Reactors are the most important units in petrochemical processes. Petrochemicals are manufactured by following simple reactions using relatively purer feedstocks. Therefore, reaction chemistry for petrochemicals manufacture is very well established from significant amount of research in this field. Essentially all petrochemical processes need to heavily depend upon chemical transformation to first product the purification.
- Separation: With distillation being the most important unit operation to separate the unreacted feed and generated petrochemical product, the separation processes also play a major role in the process flow sheet. Where multiple series parallel reactions are involved, the separation process assumes a distillation sequence to separate all products from the feed. A characteristic feed recycle will be also existent in the process topology. Apart from this, other separation technologies used in petrochemical processing units include phase separators, gravity settling units and absorption columns. Therefore, the underlying physical principle behind all these separation technologies is well exploited to achieve the desired separation.
- Dependence on Reaction pathway: A petrochemical can be produced in several ways from the same feedstock. This is based on the research conducted in the process chemistry. For instance, phenol can be produced using the following pathways
    o Peroxidation of Cumene followed by hydrolysis of the peroxide
    o Two stage oxidation of Toluene
    o Chlorination of Benzene and hydrolysis of chloro-benzene
    o Direct oxidation of Benzene
- We can observe that in the above reaction schemes, there are two reaction pathways for phenol from benzene i.e., either chlorination of benzene or oxidation of benzene. Therefore, choosing the most appropriate technology for production is a trivial task.
- Complexity in pathway: In the above Cumene example case, it is interesting to note that toluene hydrodealkylation produces benzene which can be used to produce phenol. Therefore, fundamentally toluene is required for the generation of various petrochemicals such as benzene and phenol. In other words, there is no hard and fast rule to say that a petrochemical is manufactured using a suggested route or a suggested intermediate petrochemical. Intermediate petrochemicals play a greater role in consolidating the manufacture of other downstream petrochemicals.

13.3 Summary of petrochemical processes presented in the course

We next present a summary of the petrochemical processes that would be presented in the course

- Lecture 13
  o Methanol from Synthesis gas route
- Lecture 14
  o Formaldehyde from Methanol
  o Chloromethanes from methane
- Lecture 15
  o Ethylene and acetylene production via steam cracking of hydrocarbons
- Lecture 16
  o Vinyl chloride from ethylene using two step process
- Lecture 17
  o Ethanolamine from ethylene
- Lecture 18
  o Isopropanol from Propylene
  o Cumene from propylene
- Lecture 19
  o Acrylonitrile from propylene
  o Oxo process for converting olefins and synthesis gas to aldehydes and alcohols
- Lecture 20
  o Butadiene from Butane
  o Hydrodealkylation of Toluene
- Lecture 21
  o Phenol from Cumene
  o Phenol from Toluene Oxidation
- Lecture 22
  o Styrene from Benzene
  o Pthalic anhydride from o-xylene
- Lecture 23
  o Maleic anhydride from Benzene
  o DDT manufacture from Benzene

13.4 Manufacture of Methanol from Synthesis Gas

13.4.1 Introduction

- Synthesis gas is $H_2 + CO$
- When synthesis gas is subjected to high pressure and moderate temperature conditions, it converts to methanol.
- Followed by this, the methanol is separated using a series of phase separators and distillation columns.
- The process technology is relatively simple

13.4.2 Reactions

- Desired: $CO + 2H_2 \rightarrow CH_3OH$
- Side reactions: $CO + 3H_2 \rightarrow CH_4 + H_2O$
          $2CO + 2H_2 \rightarrow CH_4 + CO_2$
- All above reactions are exothermic
- Undesired reaction: $zCO + aH_2 \rightarrow$ alchohols + hydrocarbons
- Catalyst: Mixed catalyst made of oxides of Zn, Cr, Mn, Al.

13.4.3 Process Technology (Figure 13.1)
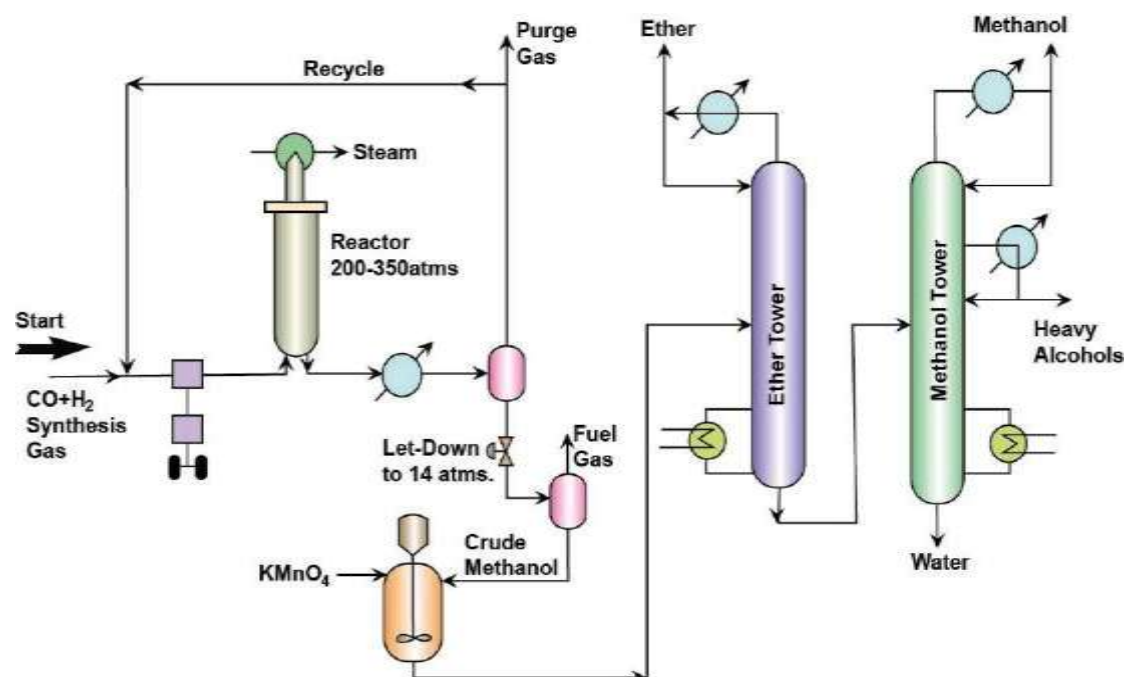
Figure 13.1 Flow sheet of manufacture of Methanol from Synthesis Gas

- H_2 and CO adjusted to molar ratio of 2.25
- The mixture is compressed to $200 - 350$ atms
- Recycle gas (Unreacted feed) is also mixed and sent to the compressor
- Then eventually the mixture is fed to a reactor. Steam is circulated in the heating tubes to maintain a temperature of $300 - 375 \,^{o}C$

- After reaction, the exit gases are cooled
- After cooling, phase separation is allowed. In this phase separation operation methanol and other high molecular weight compounds enter the liquid phase and unreacted feed is produced as the gas phase.
- The gas phase stream is purged to remove inert components and most of the gas stream is sent as a recycle to the reactor.
- The liquid stream is further depressurized to about 14 atms to enter a second phase separator that produces fuel gas as the gaseous product and the liquid stream bereft of the fuel gas components is rich of the methanol component.
- The liquid stream then enters a mixer fed with $KMNO_4$ so as to remove traces of impurities such as ketones, aldehydes etc.
- Eventually, the liquid stream enters a distillation column that separates dimethyl ether as a top product.
- The bottom product from the first distillation column enters a fractionator that produces methanol, other high molecular weight alcohols and water as three different products.

13.4.4 Technical questions

1. **Why pressure is not reduced for the first phase separator?**

Ans: Methanol is separated out in the liquid stream by just cooling the reactor product stream. Therefore, since the separation is achieved physically, there is no need to reduce the pressure of the stream. Also, if pressure is reduced, then again so much pressure needs to be provided using the compressor.

2. **Why the pressure is reduced to 14 atms for the phase separator?**

Ans: The second phase separator is required to remove dissolved fuel gas components in the liquid stream at higher pressure. If this is not done, then methane will remain in the liquid stream and fractionators will produce methane rich ethers which don't have value. Fuel gas on the other hand has value or it can be used as a fuel to generate steam in a boiler or furnace.

3. **Why two compressors are used in the process flowsheet but not one?**

Ans: The main compressor is the feed compressor where feed is compressed to 3000 – 5000 psi. The second compressor is for the recycle stream which is brought to the reactor inlet pressure conditions by taking into account the pressure losses in the reactor, cooler and phase separator.

4. How multiple products are obtained from a single distillation column?

Ans: This is an important question. Any distillation column consists of liquid reflux stream. A careful simulation of a distillation column using process simulators such as ASPEN or HYSYS or PRO II will give the liquid compositions at each tray. Using this information, one can exploit whether the intermediate liquid stream is having composition of any specific product. In such case, the liquid stream from the column can be taken out (as a pump around stream in the crude distillation column) and the balance could be cooled and sent back to a section above the distillation unit. Alternatively, without pump around also we can operate the column, but the basis of keeping pump around or not is based on the desired liquid reflux flow rates on the particular tray.

5. Can heat integration be carried out in the flowsheet?

Ans: Yes, the reactor product is at higher temperature and can be energy integrated with the feed stream after compression. This is also due to the fact that compression usually increases the temperature and feed stream can be subjected to further heating after compression.

6. From engineering perspective, what is the most difficult part in the process flow sheet

Ans: The design and operation of the high pressure reactor is the most difficult. To withstand such high pressure, thick walled reactor needs to be designed. Other materials of construction need to be as well looked into for safeguarding the long term shelf life of the reactor.

References:

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Shreve R. N., Austin G. T., Shreve's Chemical process industries, McGraw – Hill, 1984

Lecture 14: Formaldehyde and Chloromethanes

14.1 Introduction

- In this lecture, we present the production technology for formaldehyde and chloromethanes.
- Formaldehyde is produced from methanol
- Chloromethanes are produced from methane by chlorination route.

14.2 Formaldehyde production

14.2.1 Reactions

a) Oxidation: $CH_3OH + 0.5 O_2 \rightarrow HCHO + H_2O$
b) Pyrolysis: $CH_3OH \rightarrow HCHO + H_2$
c) Undesired reaction: $CH_3OH + 1.5 O_2 \rightarrow 2H_2O + CO_2$

In the above reactions, the first and third are exothermic reactions but the second reaction is endothermic. The reactions are carried out in vapour phase.

Catalyst: Silver or zinc oxide catalysts on wire gauge are used.

Operating temperature and pressure: Near about atmospheric pressure and $500 - 600 \, ^{\circ}C$

14.2.2 Process Technology (Figure 14.1):

- Air is sent for pre-heating using reactor outlet product and heat integration concept.
- Eventually heated air and methanol are fed to a methanol evaporator unit which enables the evaporation of methanol as well as mixing with air. The reactor inlet temperature is 54 $^{\circ}C$.
- The feed ratio is about $30 - 50$ % for CH_3OH: O_2
- After reaction, the product is a vapour mixture with temperature $450 - 900 \, ^{\circ}C$
- After reaction, the product gas is cooled with the heat integration concept and then eventually fed to the absorption tower.
- The absorbent in the absorption tower is water as well as formaldehyde rich water.
- Since formaldehyde rich water is produced in the absorption, a portion of the rich water absorbent solution from the absorber is partially recycled at a specific section of the absorber.
- From the absorber, HCHO + methanol rich water stream is obtained as the bottom product.
- The stream is sent to a light end stripper eventually to remove any light end compounds that got absorbed in the stream. The vapors from the light end unit consisting of light end compounds can be fed at the absorption unit at

specific location that matches with the composition of the vapors in the absorption column.

- Eventually, the light end stripper bottom product is fed to a distillation tower that produces methanol vapour as the top product and the bottom formaldehyde + water product (37 % formaldehyde concentration).
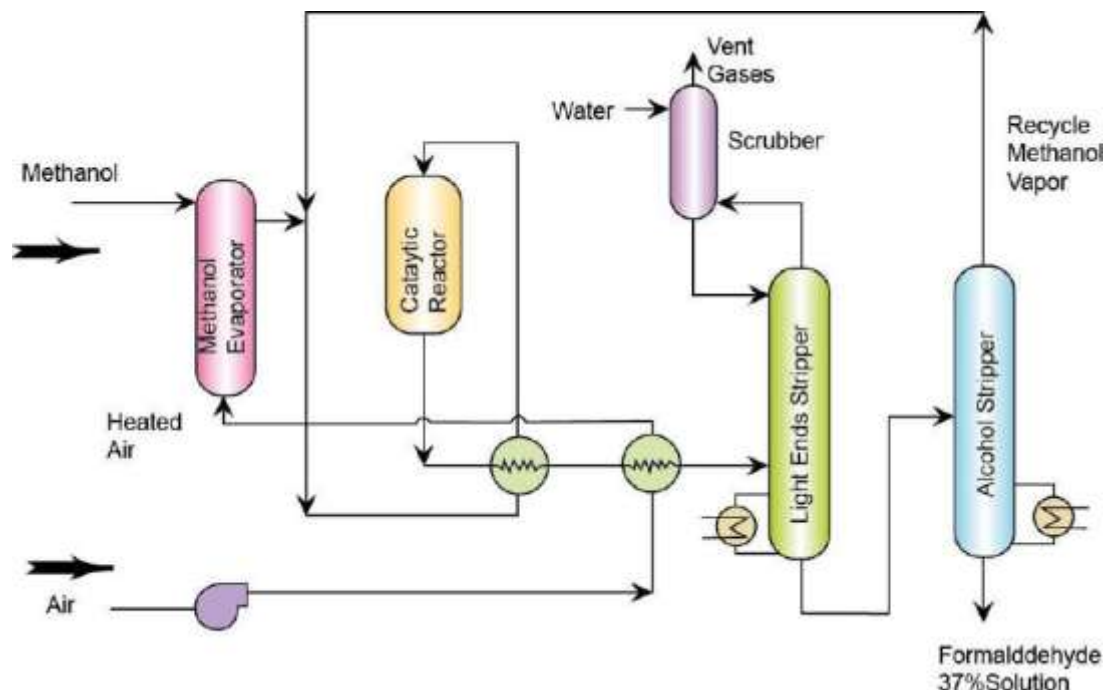
Figure 14.1 Flow sheet of Formaldehyde production

14.3 Technical questions

1. **Why water + HCHO + methanol stream is sent to a specific section of the absorber but not the top section of the absorber?**

Ans: This is to maximize the removal efficiency of both water and formaldehyde rich solution. If both are sent from the top, then formaldehyde rich solution will be dilute and not effective in extracting more HCHO + methanol from the gas phase stream.

2. **Explain Why light end stripper is used after absorber?**

Ans: Water + HCHO + Formaldehyde solution may absorb other light end compounds which are not desired for absorption. This is due to the basic feature of multicomponent absorption where absorption factors for various absorbing components is not biased sharply and other undesired components also get absorbed. Therefore, the light end stripper would take care of removing these unwanted components by gently heating the same.

3. **Suggest why pure formaldehyde is not produced in the process?**

Ans: Pure formaldehyde is not stable and tends to produce a trimer or polymer. Formaldehyde is stable in only water and therefore, 37% formaldehyde solution with 3 – 15 % methanol (stabilizer) is produced as formalin and sold.

4. **What type of process design is expected for the air preheater?**

Ans: Since we have a problem of vapour and air, we should use extended surface area heat exchanger or finned heat exchanger.

14.4 Chloromethanes

Chloromethanes namely methyl chloride (CH_3Cl), methylene chloride (CH_3Cl_2), Chloroform ($CHCl_3$) and Carbon Tetrachloride (CCl_4) are produced by direct chlorination of Cl_2 in a gas phase reaction without any catalyst.

14.4.1 Reactions

$CH_4 + Cl_2 \rightarrow CH_3Cl + H_2$

$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + H_2$

$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + H_2$

$CHCl_3 + H_2 \rightarrow CCl_4 + H_2$
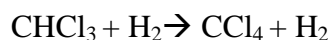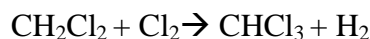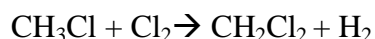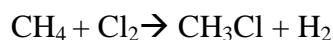
- The reactions are very exothermic.
- The feed molar ratio affects the product distribution. When CH_4/Cl_2 is about 1.8, then more CH_3Cl is produced. On the other hand, when CH_4 is chosen as a limiting reactant, more of CCl_4 is produced. Therefore, depending upon the product demand, the feed ratio is adjusted.

14.4.2 Process Technology

- Methane and Cl_2 are mixed and sent to a furnace
- The furnace has a jacket or shell and tube system to accommodate feed pre-heating to desired furnace inlet temperature (about 280 – 300 ^{o}C).
- To control temperature, N_2 is used as a diluent at times.
- Depending on the product distribution desired, the CH_4/Cl_2 ratio is chosen.
- The product gases enter an integrated heat exchanger that receives separated CH_4 (or a mixture of $CH_4 + N_2$) and gets cooled from the furnace exit temperature (about 400 ^{o}C).
- Eventually, the mixture enters an absorber where water is used as an absorbent and water absorbs the HCl to produce 32 % HCl.
- The trace amounts of HCl in the vapour phase are removed in a neutralizer fed with NaOH

- The gas eventually is compressed and sent to a partial condenser followed with a phase separator. The phase separator produces two streams namely a liquid stream consisting of the chlorides and the unreacted CH_4/N_2.
- The gaseous product enters a dryer to remove H_2O from the vapour stream using 98% H_2SO_4 as the absorbent for water from the vapour.
- The chloromethanes enter a distillation sequence. The distillation sequence consists of columns that sequentially separate CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4.
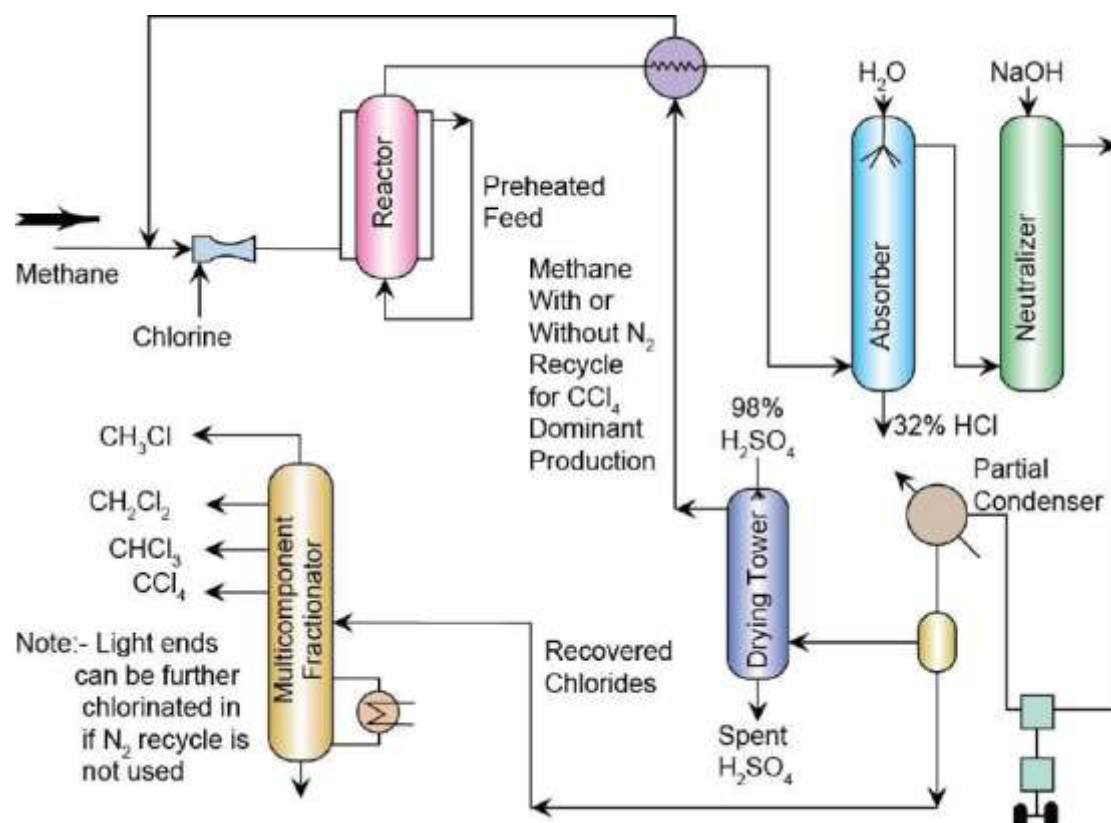
Figure 14.2 Flowsheet of Chloromethane production

14.4.3 Technical questions

1. Why compressor is used before partial condenser?

Ans: The compressor increases the pressure of the system which is beneficial to increase the boiling points of the mixtures. Note that the boiling points of chloromethanes are -97.7, -97.6, -63.5 and -22.6 $^{\circ}$C for CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 respectively. On the other hand, the boiling point is -161.6 $^{\circ}$C. For these boiling point mixtures, when the system pressure is increased substantially, the boiling points of the compounds increase and could reach close to those of the cooling water (20 – 30 $^{\circ}$C). Cooling water is required in the partial condenser and if it is not used, a refrigerant needs to be used which requires an additional refrigeration plant. Therefore, the system pressure is increased.

2. Why water is removed using the dryer?

Ans: Water enters the vapour system due in the absorption column where solvent loss to the vapour will be a common feature. Water molecule can react with the highly active intermediate chloromethanes to form oxychlorides, which are highly undesired.

3. Will there be any difficulty in separation by increasing boiling points of the chloromethanes in the distillation sequences?

Ans: Definitely yes. This is because the relative volatility of compounds atleast slightly increases with reducing pressure and viceversa. But due to cooling water criteria in the distillation sequences also, there is no other way economical than doing distillation at higher pressure.

4. Since the boiling point of CH_3Cl and CH_2Cl_2 are very close, what do you expect for the production of CH_3Cl from the first column?

Ans: It is indeed difficult to separate CH_3Cl and CH_2Cl_2 and therefore, good number of separation trays be used. Or structured packing be used to reduce the height of the first column.

5. When the reactions are highly exothermic, why is the feed pre-heated?

Ans: Irrespective of the reactions being exothermic or endothermic, the reaction rate always increases with temperature for non-equilibrium reactions. Therefore, feed is pre-heated to the desired temperature so as to fastly convert the reactants to products.

References:

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Shreve R. N., Austin G. T., Shreve's Chemical process industries, McGraw – Hill, 1984

Lecture 15: Hydrocarbon Steam Cracking for Petrochemicals

15.1 Introduction

In industrial processes, hydrocarbons are contacted with H_2O, depending upon the desired effect. When hydrocarbon vapors at very high pressures are contacted with water, water which has a very high latent heat of vaporization quenches the hydrocarbon vapors and transforms into steam. In such an operation, chemical transformations would not be dominant and energy lost from the hydrocarbons would be gained by water to generate steam. The quenching process refers to direct contact heat transfer operations and therefore has maximum energy transfer effeiciency. This is due to the fact that no heat transfer medium is used that would accompany heat losses. The steam cracking of hydrocarbons is an anti-quenching operation, and will involve the participation of water molecule in reactions in addition to teh cracking of the bnydriocarbond on their own. Since steam and the hydrocarbons react in the vapour phase the reaction products can be formed very fast. Therefore cracking of the hydrocarbons on their own as well as by steam in principle is very effective.

When steam cracking is carried out, in addition to the energy supplied by the direct contact of steam with the hydrocarbons, steam also takes part in the reaction to produce wider choices of hydrocarbon distribution along with the generation of H_2 and CO.

- Hydrocarbons such as Naphtha and LPG have lighter compounds.
- When they are subjected to steam pyrolysis, then good number of petrochemicals can be produced.
- These include primarily ethyelene and acetylene along with other compounds such as propylene, butadiene, aromatics (benzene, toluene and xylene) and heavy oil residues.
- The reaction is of paramount importance to India as India petrochemical market is dominated by this single process.

15.2 Reaction

$C_xH_y + H_2O + O_2 \rightarrow C_2H_4 + C_2H_6 + C_2H_2 + H_2 + CO + CO_2 + CH_4 + C_3H_6 + C_3H_8 + C_4H_{10} + C_4H_8 + C_6H_6 + C +$ Heavy oils
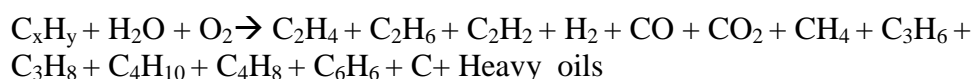
- The reaction is pretty complex as we produce about 10 to 12 compounds in one go
- The flowsheet will be reaction-separation-recycle system only in its topology. But the separation system will be pretty complex.
- Almost all basic principles of separation appears to be accommodated from a preliminary look.
- Important separation tasks: Elimination of CO and CO_2, Purification of all products such as ethylene, acetylene etc.

- The process can be easily understood if we follow the basic fundamental principles of process technology
- Typical feed stocks are Naphtha & LPG
- Reaction temperature is about $700 - 800\ ^oC$ (Vapor phase reaction).

15.3 Process technology (Figure 15.1)
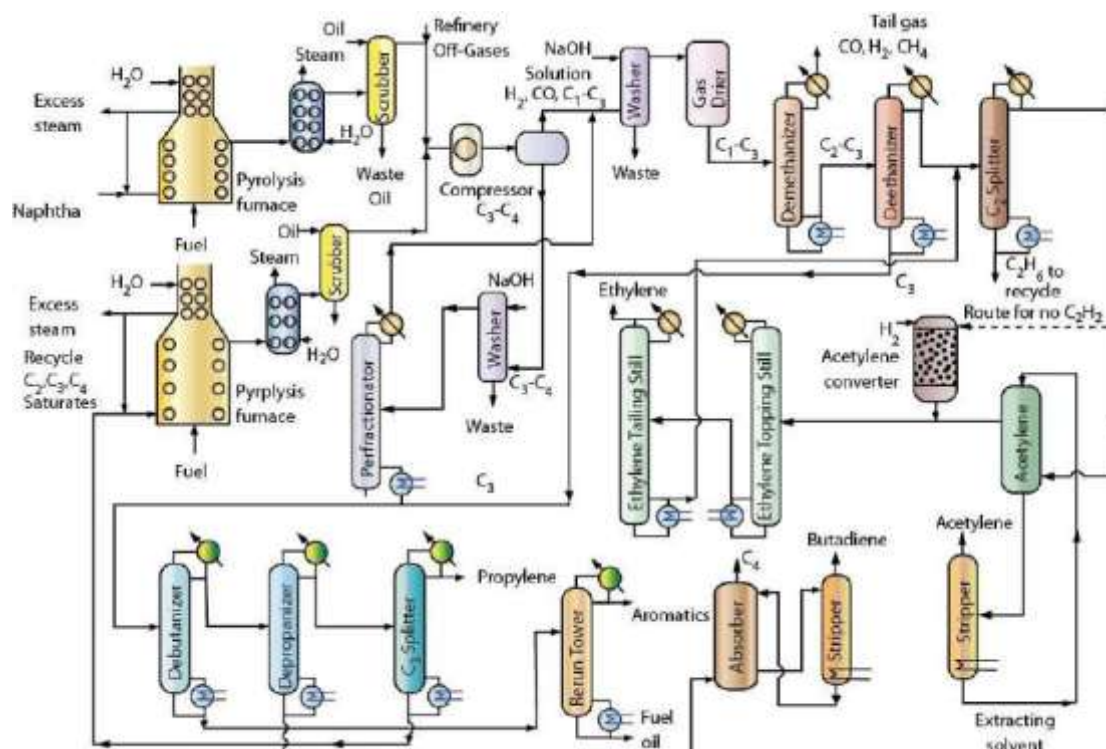
Figure 15.1 Flow sheet of Hydrocarbon Steam Cracking for Petrochemicals

- Naphtha/LPG saturates is mixed with superheated steam and fed to a furnace fuel gas + fuel oil as fuels to generate heat. The superheated steam is generated from the furnace itself using heat recovery boiler concept.
- The C_2-C_4 saturates are fed to a separate furnace fed with fuel gas + fuel oil as fuels to generate heat.
- In the furnace, apart from the steam cracking, steam is also generated. This is by using waste heat recovery concept where the combustion gases in the furnace.
- After pyrolysis reaction, the products from the furnace are sent to another heat recovery steam boiler to cool the product streams (from about $700 - 800\ ^oC$) and generate steam from water.
- After this operation, the product vapours enter a scrubber that is fed with gas oil as absorbent. The gas oil removes solids and heavy hydrocarbons.
- Separate set of waste heat recovery boiler and scrubbers are used for the LPG furnace and Naphtha steam cracking furnaces
- After scrubbing, both product gases from the scrubbers are mixed and fed to a compressor. The compressor increases the system pressure to 35 atms.

- The compressed vapour is fed to a phase separation that separates the feed into two stream namely the vapour phase stream and liquid phase stream. The vapour phase stream consists of H_2, CO, CO_2 C_1-C_3+ components in excess. The liquid phase stream consists of C_3 and C_4 compounds in excess.
- Subsequently, the vapour phase and liquid phase streams are subjected to separate processing.

  Gas stream processing:
  - CO_2 in the vapour phase stream is removed using NaOH scrubber. Subsequently gas is dried to consist of only H_2, CO, C_1-C_3 components only. This stream is then sent to a demethanizer which separates tail gas (CO + H_2 + CH_4) from a mixture of C_1-C_3 components. The C_2-C_3+ components enter a dethanizerwhich separates C_2 from C_3 components.
  - Here C_2 components refer to all kinds of C_2s namely ethylene, acetylene etc. Similarly, C_3 the excess of propylene, and propane.
  - The C2 components then enter a C2 splitter which separates ethane from ethylene and acetylene.
  - The ethylene and acetylene gas mixture is fed to absorption unit which is fed with an extracting solvent (such as N-methylpyrrolidinone) to extract Acetylene from a mixture of acetylene and ethylene.
  - The extractant then goes to a stripper that generates acetylene by stripping. The regenerated solvent is fed back to the absorber.
  - The ethylene stream is fed to a topping and tailing still to obtain high purity ethylene and a mixture of ethylene and acetylene as the top and bottom products. The mixture of ethylene and acetylene is sent back to the C2 splitter unit as its composition matches to that of the C2 splitter feed.
- Liquid stream processing
  - The liqiuid stream consists of C3,C4, aromatics and other heavy oil components is fed to a NaOH scrubber to remove CO_2
  - Eventually it is fed to a pre-fractionator. The pre-fractionator separates lighter components from the heavy components. The lighter components are mixed with the vapour phase stream and sent to the NaOH vapour phase scrubber unit.
  - The pre-fractionator bottom product is mixed with the deethanizer bottom product.
  - Eventually the liquid mixture enters a debutanizer that separates C3, C4 components from aromatics and fuel oil mixture. The bottom product eventually enters a distillation tower that separates aromatics and fuel oil as top and bottom products respectively.
  - The top product then enters a depropanizer that separates C3s from C4 components.
  - The C4 components then enter an extractive distillation unit that separates butane + butylenes from butadiene.   The   extractive

distillation unit consists of a distillation column coupled to a solvent stripper. The solvent stripper produces butadiene and pure solvent which is sent to the distillation column.

- o The C3 components enter a C3 splitter that separates propylene from propane + butane mixture. Thesaturates mixture is recycled to the saturates cracking furnace as a feed stream.

15.4 Technical questions

1. **Why two separate furnaces are used for C2-C4 saturates and Naphtha feed stocks?**

Ans: The purpose of steam cracking is to maximize ethylene and acetylene production. For this purpose if we mix C2-C4 saturates and naphtha and feed them to the same furnace, then we cannot maximize ethylene and acetylene production. The napntha steam cracker has its own operating conditions for maximizing ethylene and acetylene and so is the case for C2-C4 saturates.

2. **Why the product gases from naphtha and C2-C4 saturates steam cracker processed separately before mixing them and sending them to the compressor?**

Ans: Both crackers produce products with diverse compositions. Both cannot be fed to a single scrubber and remove the heavy hydrocarbons and oil components. While the scrubber associated to naphtha steam cracking needs to be remove significantly the oil and heavy hydrocarbons, this is not the case for steam cracker product vapour processing.

An alternate way of designing a single scrubber is to design a complex scrubber that has multiple feed entry points correspond to both product gases entering from various units. This refers to process intensification and would be encouraging.

3. **Why specifically the gases are compressed to 35 atm?**

Ans: The distribution of light and heavy components in vapour and liquid streams is critically dependent on the pressure. Therefore, the pressure of the system plays a critical role in the distribution of these key components.

4. **Why is it not possible to sharply split C3 components in the phase separator?**

Ans: This is the basic problem of the phase equilibrium factors associated to the intermediate components. Usually, phase equilibrium factors are highest for lighter components and lowest for the heavier components. But intermediate components such as C3s have phase equilibrium factors in between. Therefore, C3s get distributed between both vapour and liquid equally. This will be the case even with higher pressure and going for higher pressure is not economical as the pressurizing costs will be significantly.

5. Why a tailing and topping still is required for ethylene production?

Ans: The distillation column for separating ethylene from ethylene from C2 components needs to carry out a difficult separation. This is also due to the fact that the boiling points of C2 components is very close. Therefore, there needs to be two columns (indicating good number of trays).

6. Explain how extractive distillation enables the separation of butadiene?

Ans: Dimethyl formamide (solvent) is fed to the distillation column fed with butadiene, butane and butylenes. The solvent interacts differently with the components and therefore adjusts the relative volatility of the mixture which was close to 1 previously. Thereby, the solvent forms a high boiling mixture at the bottom with butadiene and thereby enables the difficult separation of butadiene from the C4 compounds. Thereby, the solvent + butadiene is fed to a stripper which removes butadiene from the DMF. One important issue here is that the solvent does not form an azeotrope with the butadiene and is therefore, easy to separate.

7. When acetylene is not required, what process modifications will exist to the technology?

Ans: When acetylene is not required, then the top product from C2 splitter (which is a mixture of acetylene and ethylene) is fed to a packed bed column and H_2 to convert the acetylene to ethylene. Eventually, one does not require the absorber-stripper technology for acetylene purification.

References:

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Shreve R. N., Austin G. T., Shreve's Chemical process industries, McGraw – Hill, 1984

Lecture 16: Vinyl Chloride from Ethylene

Introduction

- In this lecture we study the process technology involved in the production of Vinyl Chloride from Ethylene
- Vinyl chloride is produced in a two step process from ethylene
    - o Ethylene first reacts with Chlorine to produce Ethylene dichloride
    - o The purified Ethylene dichloride undergoes selective cracking to form vinyl chloride
- We first present the process technology associated to Ethylene Chloride

16.1 Ethylene dichloride

16.1.1 Reactions

- $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$
- Undesired products: Propylene dichloride and Polychloroethanes
- Reaction occurs in a liquid phase reactor with ethylene dichloride serving as the liquid medium and reactants reacting the liquid phase
- Catalyst is $FeCl_3$ or Ethylene dibromide

16.1.2 Process Technology (Figure 16.1)
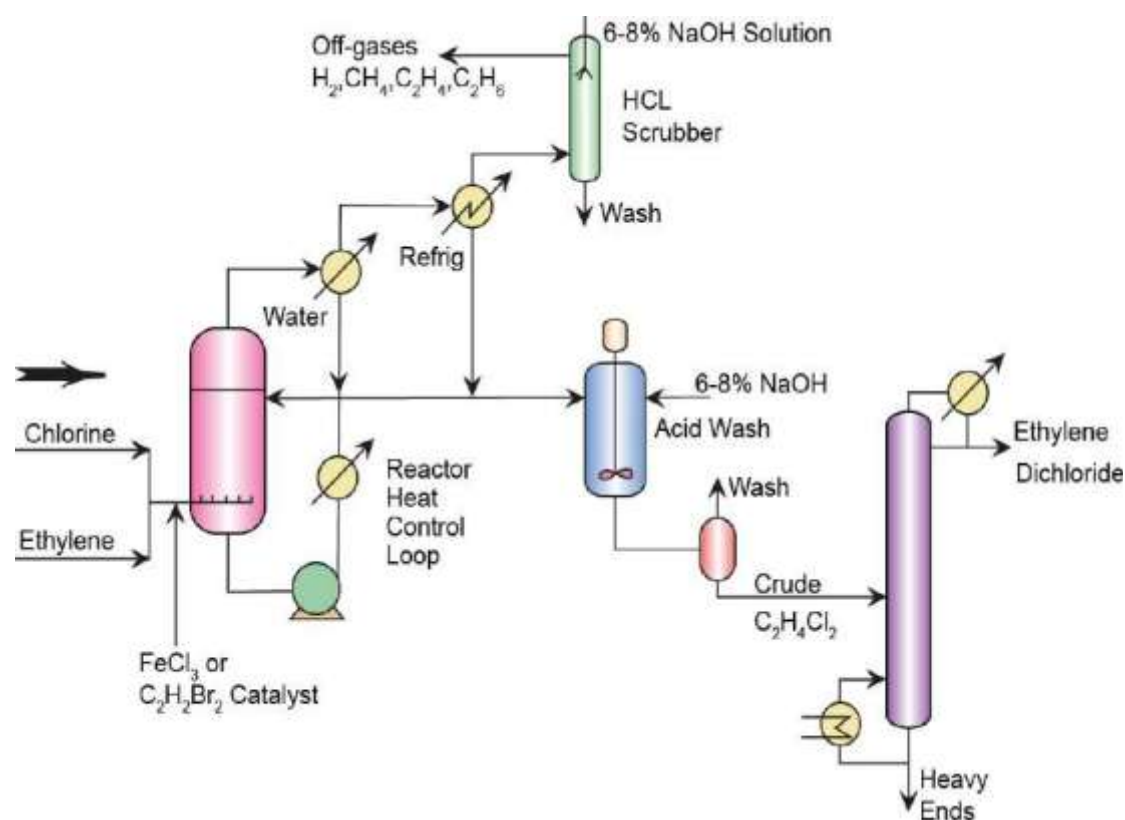
Figure 16.1 Flow sheet of production of ethylene dichloride

- C_2H_4 and Cl_2 are mixed and sent to the liquid phase reactor.
- Here, the feed mixture bubbles through the ethylene dichloride product medium
- Reactor operating conditions are 50 ^{o}C and 1.5 – 2 atms.
- The reaction is exothermic. Therefore, energy is removed using either cooling jacket or external heat exchanger
- To facilitate better conversion, circulating reactor designs are used.
- $FeCl_3$ traces are also added to serve as catalyst
- The vapour products are cooled to produce two products namely a vapour product and a liquid product. The liquid product is partially recycled back to the reactor to maintain the liquid medium concentration.
- The vapour product is sent to a refrigeration unit for further cooling which will further extract ethylene dichloride to liquid phase and makes the vapour phase bereft of the product.
- The liquid product is crude ethylene dichloride with traces of HCl. Therefore, acid wash is carried out first with dilute NaOH to obtain crude ethylene dichloride. A settling tank is allowed to separate the spent NaOH solution and crude $C_2H_4Cl_2$ (as well liquid).
- The crude ethylene dichloride eventually enters a distillation column that separates the ethylene dichloride from the other heavy end products.
- The vapour phase stream is sent to a dilute NaOH solution to remove HCl and produce the spent NaOH solution. The off gases consist of H_2, CH_4, C_2H_4 and C_2H_6.

16.1.3 Technical questions

1. **Provide an insight into the liquid phase guided gas phase reaction?**

Ans: The liquid phase acts as a resistance phase for the movement of various gases. The recirculator enables greater turbulence of the liquid phase stream. Thereby, using these mechanisms, the gases are allowed to react with one another and produce ethylene dichloride which gets dissolved in the liquid.

2. **Why a water condenser followed by refrigeration is used when the single refrigeration can serve the purpose of cooling?**

Ans: This is an important question. Allowing only refrigeration enhances process costs drastically. Therefore, water is used to carry out partial condensation and then refrigeration, even though in principle, water condensation can be bypassed and reactor operation and stream contacting can be further optimized.

3. **Why do we need a settling tank after the acid wash unit associated to the crude ethylene dichloride?**

Ans: Typically, we observe HCL removal from vapour streams. In such case, the unit used is a scrubber or absorber. The gas/vapour is fed to the absorption column and is obtained as a gas. When a liquid is allowed for scrubbing, it is possible to obtain emulsions of the organic phase in the aqueous phase. Therefore, provide gravity settling mechanism should exist so as to separate the crude ethylene dichloride from the mixture emanating from the acid wash tank.

16.2 Vinyl chloride production

16.2.1 Reaction

- $C_2H_4Cl_2 \rightarrow CH_2CHCl + HCl$
- Charcoal is used as the catalyst
- The reaction is a reversible gas phase reaction

16.2.2 Process Technology (Figure 16.2)
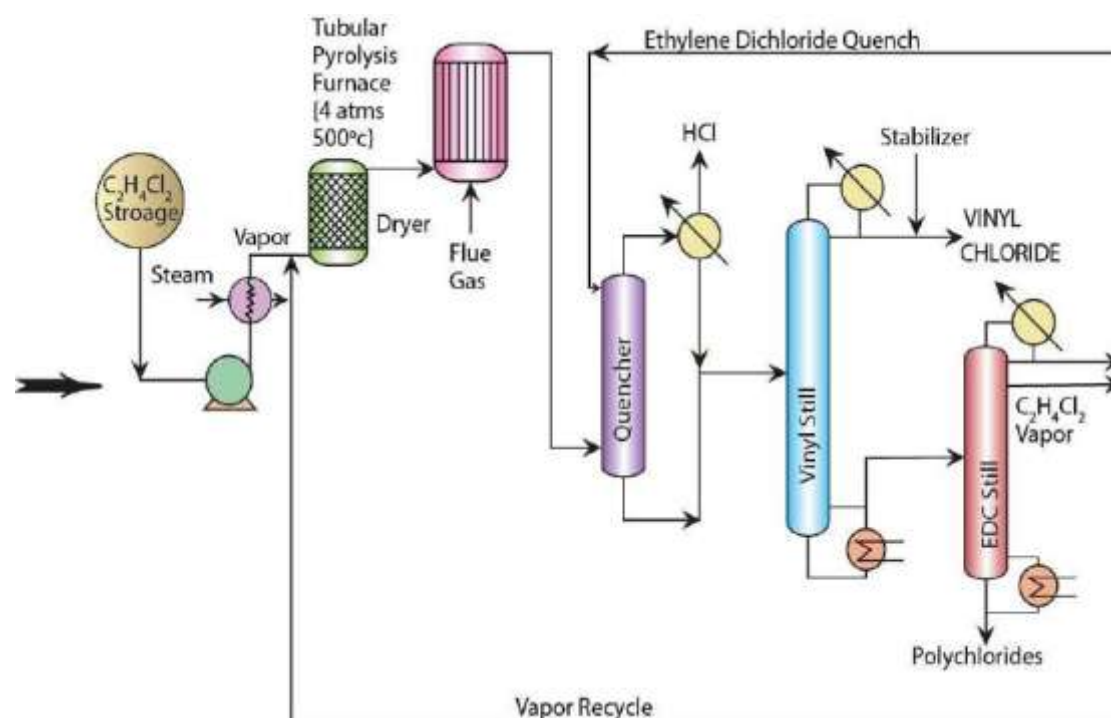
Figure 16.2 Flow sheet of production of vinyl chloride

- Ethylene dichloride is initially vaporized using a heat exchanger fed with process steam
- Ethylene vapors then enter a dryer that removes traces of water molecules
- After drying, the vapors enter a pyrolysis furnace operated at 4 atm and 500 ^{o}C. The furnace is similar to a shell and tube arrangement with the gases entering the tube side and hot flue gas goes past the tubes in the shell side.
- The product vapors eventually enter a quenching tower in which cold ethylene dichloride is used to quench the product gases and cool them.

- The gases from the quench tower then enter a partial condenser which produces HCl as a gas and the liquid stream consisting of vinyl chloride, unreacted ethylene dichloride and polychlorides.
- The liquid stream from the quench tower as well as the condenser is fed to the vinyl still which produces the vinyl chloride product. The product is stabilized using a stabilizer as vinyl chloride is highly reactive without stabilizer.
- The bottom product from the vinyl still is fed to a distillation column which separates the ethylene dichloride from the polychlorides. The ethylene dichloride vapors are recycled back to the cracking furnace and the ethylene dichloride liquid is sent to the quenching tower to serve as the quenching liquid.

16.2.3 Technical questions

1. **Why ethylene dichloride is dried before entering the cracking furnace?**

Ans: To avoid the formation of other compounds during cracking. Vinyl chloride cracking is a very selective cracking that we wish to happen. The selective cracking needs very clean feed stock.

2. **Why quenching is carried out?**

Ans: The selective cracking reaction is a reversible reaction. Therefore, by doing cold ethylene dichloride quenching, we are suppressing the backward reaction and ensuring that only vinyl chloride gets formed in good quantities.

3. **Can heat integration be carried out in the process?**

Ans: IN principle it can be done but in reality no. The reason is that if quenching is not done immediately, then vinyl chloride can get converted back to the ethylene dichloride. Therefore, though there is a hot stream available, heat integration cannot be done due to prevalent process conditions.

4. **Can a partial condenser be used in the last distillation column to serve for both quenching, distillation reflux and produce vapour for the ethylene dichloride?**

Ans: Yes, this arrangement will be excellent as all requirements in the process will be met by going for a partial condenser. But it all depends on the quenching tower requirements and hence if ethylene dichloride needs to be cooled more than its boiling point, then partial condenser will not serve the purpose.

5. **What is the effect of pressure on quenching. This question is interesting as the reaction occurs at 4 atm and quenching occurs at higher pressure?**

Ans: Quenching is an operation used for minimizing temperature. As such its not absorption where pressure plays an important role. As such, the effect of pressure will not be significant in the quenching operation.

References:

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

Lecture 17: Ethylene oxide and Ethanolamines

17.1 Introduction

- In this lecture, we discuss upon the process technology for ethylene oxide and ethanolamines.
- Ethylene oxide is produced by the oxidation of ethylene using air
- Ethanolamines are produced using the series reaction scheme of ethylene oxide with ammonia.
- Ethanolamines are significantly used as absorbents to remove CO_2 and H_2S from process gas streams.

17.2 Ethylene Oxide

17.2.1 Reactions

- $C_2H_4 + 0.5\ O_2 \rightarrow CH_2O.CH_2O$
- Ethylene to air ratio: 3 – 10 %
- Side reaction products: CO_2, H_2O
- Catalyst: Silver oxide on alumina
- Operating temperature and pressure: 250 – 300 $^{\circ}$C and 120 – 300 psi
- Supressing agent for side reactions: Ethylene dichloride
- Reaction is exothermic

17.2.2 Process technology (Figure 17.1)
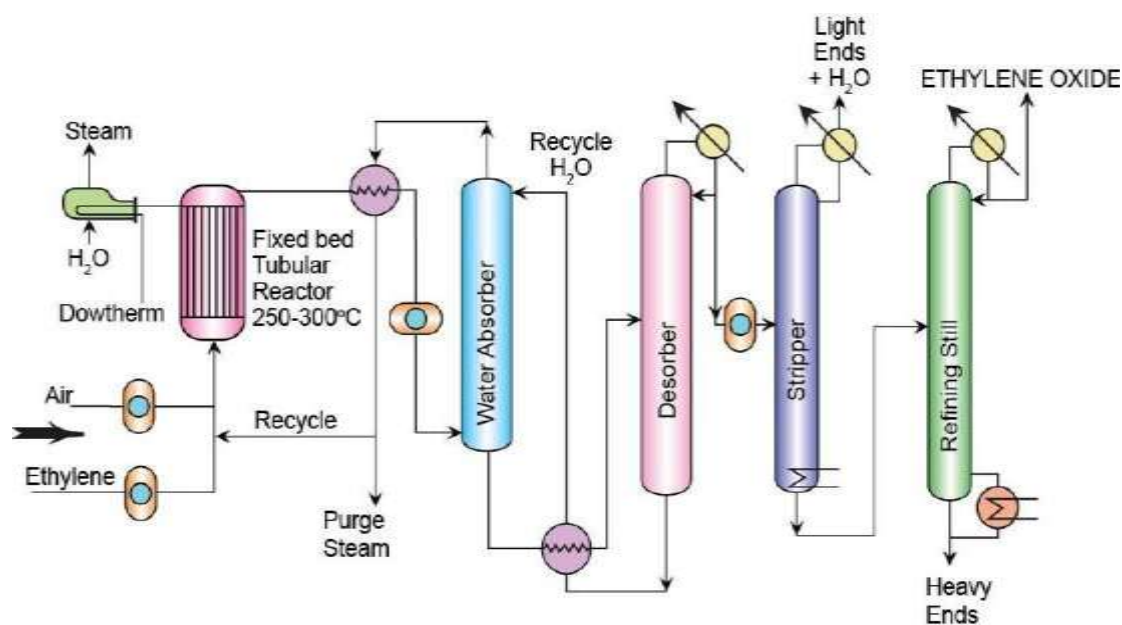
Figure 17.1 Flow sheet of production of ethylene oxide

- Air and ethylene are separate compressed and along with recycle stream are sent to the shell and tube reactor

- The reactor is fed on the shell side with Dowtherm fluid that serves to maintain the reaction temperature. A dowtherm fluid is a heat transfer fluid , which is a mixture of two very stable compounds, biphenyl and diphenyl oxide. The fluid is dyed clear to light yellow to aid in leak detection.
- The hot dowtherm fluid from the reactor is sent to a waste heat recovery boiler to generate steam
- The vapour stream is cooled using a integrated heat exchanger using the unreacted vapour stream generated from an absorber.
- The vapour stream is then sent to the heat integrated exchanger and is then sent back to the reactor and a fraction of that is purged to eliminate the accumulation of inerts such as Nitrogen and Argon.
- The product vapors are compressed and sent to a water absorber which absorbs ethylene oxide from the feed vapors. Eventually, the ethylene oxide rich water stream is sent to a stripper which desorbs the ethylene oxide + water as vapour and generates the regenerated water as bottom product. The regenerated water reaches   the absorber through a heat integrated exchanger.
- The ethylene oxide + water vapour mixture is compressed (to about 4 - 5 atms) and then sent to a stripper to generate light ends + H_2O as a top product and the bottom product is then sent to another fractionators to produce ethylene oxide as top product. The heavy ends are obtained as bottom product.

17.2.3 Technical questions

1. What is Dowtherm?

Ans: Dowtherm is an organic liquid that can attain to temperatures upto 300 ^{o}C. These are special fluids used instead of steam/water. In this example, the operating temperature is about 250 - 300 ^{o}C and therefore usage of Dowtherm fluid is perfect.

2. In what way compression is beneficial to the absorption?

Ans: It is a known fact that absorption is most favoured at low temperature and high pressure. Therefore, compression of the cooled product gases will be very beneficial to maximize the dissolution of ethylene oxide in the water. Of course, along with ethylene oxide other light ends and heavy ends also dissolve in water and we have no control over that.

3. Why again another compressor is used before the stripper?

Ans: The second compressor aids to enhance the boiling points of the mixtures. Thereby, water can be used as a cooling fluid in the distillation columns, as the boiling point of the products is enhanced by compression. In this regard, it should be noted that ethylene oxide has a boiling point of 10.7 ^{o}C which can be drastically enhanced by compression to $4 - 5$ atms.

4. Why ethylene and air are separately compressed?

Ans: This is due to the danger of generating an explosive mixture during compression step of the mixture.

5. What process modifications are possible for the flowsheet?
- Using a fluidized bed instead of packed bed reactor
- Using oxygen instead of air

6. Discuss the energy integration capacity of the process?

Ans: In this process, the heat integration drastically reduced process steam requirements. Steam is only required in the strippers and fractionators. This steam can be generated using waste heat recovery units using dowtherm fluid as the hot fluid to generate the steam. Thus in this process, it is observed that for 1 ton of ethylene oxide produced, only 0.1 ton of steam is required. This is all possible due to significant heat integration in the process.

17.3 Ethanolamines

17.3.1 Reactions

- Ethylene Oxide + Ammonia → Monoethanolamine
- Monoethanolamine + Ammonia → Diethanolamine
- DIethanolamine + Ammonia → Triethanolamine
- The above reactions are series reaction scheme
- Reaction is exothermic
- Ammonia is in aqueous phase and ethylene oxide is in vapour state. Therefore, the reaction will be gas-liquid reaction
- Ethylene oxide is the limiting reactant

17.3.2 Process technology (Figure 17.2)
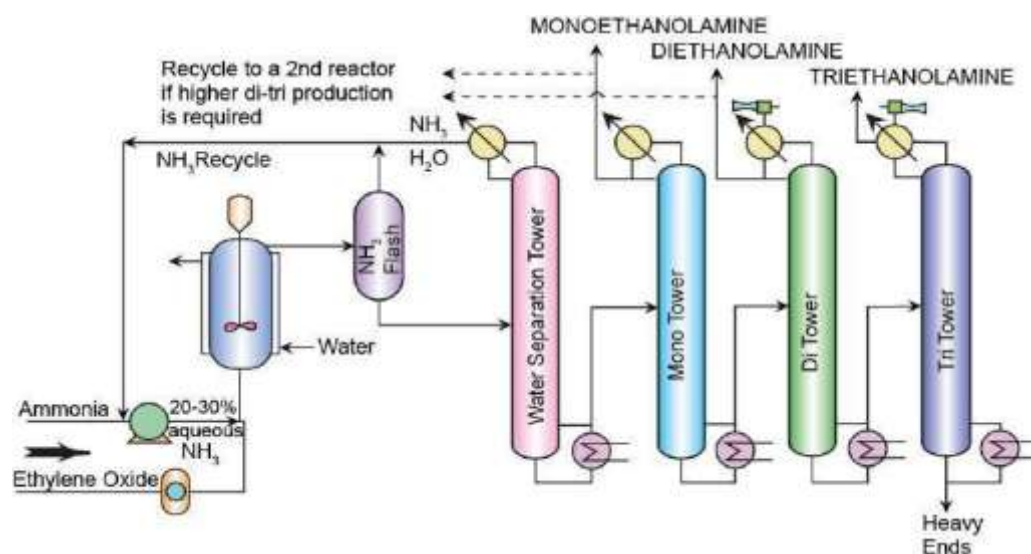
Figure 17.2 Flow sheet of production of ethanolamines

- Ammonia is mixed with ammonia recycle stream from the process and pumped to the CSTR where liquid phase ammonolysis takes place.
- Ethylene oxide is compressed and fed to the CSTR.
- The CSTR operating pressure will be such that the feed (and product) mixtures do not vaporize and good liquid phase reaction can occur.
- The reactor is cooled using water in the cooling jacket as the reactions are mildly exothermic
- The product stream is then sent to a flash unit that separates $NH_3 + H_2O$ as a vapour stream and water + ethanolamines as a liquid stream.
- The ammonia + water stream is recycled to mix with the fresh ammonia and enter the reactor.
- The bottom product from ammonia flash unit is sent to a water separation tower that again removes dissolved ammonia in the ethanolamine rich solution. Once again ammonia + water are generated and this stream is also recycled to mix with fresh ammonia feed.
- The bottom product consisting of crude mixture of ethanolamines and heavy ends.
- This mixture is fed to a monoethanolamine tower first to separate the monoethanol amine from the other two and heavy ends
- The bottom product from the first distillation tower then enters the second and third distillation towers which are operated under vacuum to produce diethanolamine and triethanolamine as top products. The bottom product from the last distillation tower is the heavy ends product.

17.3.3 Technical questions

1. **In what way operating the CSTR In liquid phase is beneficial?**

Ans: Liquids have higher mass transfer coefficients than solids. Therefore, if the reaction needs be facilitated with two components, if they are in liquid phases, then reactions could be faster. Therefore, pressure can play an important role in both altering the selectivity as well as conversion of the series reactions scheme.

2. **Why ammonia + water needs to be separated from the second tower i.e., water separation tower?**

Ans: Ammonia dissolves instantaneously in water to form ammonia solution. This chemical affinity of ammonia is very difficult to get it through. On the other hand, despite using flash unit, some ammonia will remain the water consisting of ethanolamines and heavy ends. Therefore, the second water separation tower is required to remove once again ammonia + water from the solution.

3. Why vacuum is used in the second and third distillation towers?

Ans: The diethanol and triethanolamines dissociate at high operating temperatures. Therefore, vacuum is used to reduce the operating temperature of the distillation columns (second and third).

4. What process modifications you can suggest for better operation?

Ans: When higher quantitites of di or triethanolamine is desired, then the monoethanolamine can be sent to another reactor in which ethylene oxide is added. It's not advisable to recycle it the CSTR shown in the process flow sheet as it can form amino-ethers but not diethanolamine.

5. Can solvents (extraction) be used instead of vacuum distillation for the separation of di and triethanolamines?

Ans: No, this is due to the reason that solvents tend to have similar solubility factors for both di and triethanolamines.

References:

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

Lecture 18: Isopropanol and Acetone from Propylene

18.1 Introduction

- In this lecture we study the process technology associated to the manufacture of isopropanol and acetone.
- Isoprpanol is manufactured from hydration of propylene
- Acetone is produced using the dehydrogenation route of isopropanol
- We first present the isopropanol process technology

18.2 Isopropanol manufacture

18.2.1 Reaction

- Sulfation: $CH_3CHCH_2 + H_2SO_4 \rightarrow (CH_3)_2CH(OSO_3H)$ (Isopropyl acid sulphate)
- Hydrolysis: Isopropyl sulphate + $H_2O \rightarrow$ Isopropanol + Sulfuric acid
- Thus sulphuric acid is regenerated in the process
- Side reaction: Disiopropyl sulphate + $H_2O \rightarrow$ Diisopropyl ether + Sulfuric acid
- Therefore, the primary reaction is a gas liquid reaction in which propylene is absorbed into a tray tower fed with sulphuric acid.
- Operating conditions: Room temperature but 20 – 25 atms pressure
- Reaction is highly exothermic

18.2.2 Process technology (Figure 18.1)
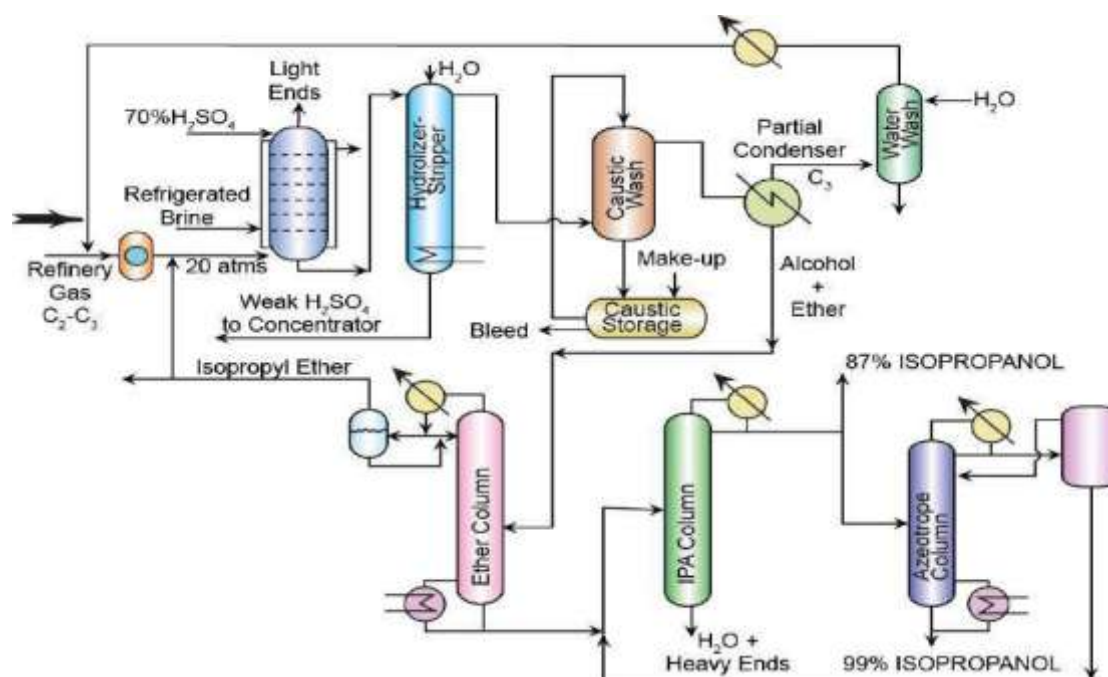
Figure 18.1 Flow sheet of Isopropanol manufacture

- Either pure propylene or a mixture of Propylene and other C_2, C_3 components can be fed to a reactor.
- The hydrocarbon feed is compressed and fed to the reactor at about $20 - 25$ atms pressure.
- Sulphuric acid of about 70% acid strength is fed in a countercurrent mode to the tray column where reactive absorption takes place. Here, sulfonation reaction takes place.
- The reaction is highly exothermic and therefore, refrigerated brine is used to control the temperature in the absorber. Jacketed arrangement will be preferred for the tray absorption column to circulate the refrigerated brine in the cooling jacket.
- After reaction, the unreacted light ends such as saturated components will leave the unit as the gas stream.
- The sulfonated product rich stream is then sent to a hydrolyzer cum stripper where isopropanol is produced and is vaporized due to existing stripper temperatures.
- The hydrolyzer is fed with water to facilitate the conversion of the sulfonate product.
- The isopropanol rich vapors then enter a caustic wash unit to remove the acidic impurities.
- The isopropanol rich vapors then enter a partial condenser which separates the unreacted propylene from the alcohol + ether mixture. Here, propylene is separated as the vapour and alcohol + ether is separated as the liquid stream.
- The separated propylene gas is once again subjected to water wash to remove soluble impurities (such as ethers and alcohols). Subsequently, pure propylene is sent to mix with the fresh feed stream. Before sending to the unit, the propylene is cooled to room temperature so as to have identification conditions as the fresh feed stock.
- The alcohol and ether enter a ether column that separates isopropyl ether which is returned to the reactor.
- The bottom product consisting of isopropyl alcohol and water is sent to a isopropyl alcohol column that produces water + heavy ends as the bottom product and 87 % isoprpanol-water azeotrope mixture as the top product.
- The azeotrope is sent to an azeotropic distillation column that uses isopropyl ether as a azeotropic agent to obtain 99 % isopropanol as the bottom product. The top product is a mixture of isopropyl ether and water. The top product is a low boiling azeotrope. This stream upon gravity settling will produce the isopropyl ether as the top product which is sent as a reflux stream to the azeotropic column. The bottom product is a mixture of isopropanol and water is recycled back to the isopropyl alcohol column along with the bottom product generated from the ether separating column.

18.2.3 Uses of Isopropanol :

There may be many uses of iso-propanol, industrial as well as common uses. It finds use in pharmaceutical applications because of the low toxicity of any residues. Isopropanol is also used as a chemical intermediate in some industrial processes. It is also used as a gasoline additive.

18.2.4 Technical questions

1. **Why refrigerated brine is used in the sulfonation reactor?**

Ans: The reaction temperature is room temperature (25 – 30 ^{o}C). Therefore, refrigerated fluid is used. Brine is used here, as refrigerated is antifreeze and can allow solution to reach lower temperatures without freezing problem.

2. **Why a partial condenser but not total condenser is used to separate C$_3$ from alcohol + ether?**

Ans: Apart from costs, the total condenser produces a single stream and this is of no use as propylene must be separated and sent as a gas back to the sulfonation reactor. All this is achieved in a single process unit by using partial condensation principle.

3. **Why is isopropyl ether circulated back to the sulfonation reactor?**

Ans: To suppress the side reaction and hence decomposition of sulfonation to less valued product.

4. **Present the working principle of an azeotropic distillation column?**

Ans: The azeotropic distillation column is fed with the azeotrope mixture and another component which forms a low boiling heterogenous azeotrope with the feed (azetropic mixture) components as one of the products and a purer compound as the other product. The low boiling azeotrope is then sent to a gravity settler that separates the heterogeneous phases into two products namely the azeotropic agent and an impure mixture of the original components. The impure mixture is actually fed to one of the distillation columns in the process flow sheet at a location that matches with the purity of the stream.

5. **What happens to the water in which acid gets dissolved in the hydrolyzer cum stripper column?**

Ans: Here, the stream is a weak acid stream that is fed to a multiple effect evaporator to concentrate the weak acid solution to a strong acid solution. The strong acid solution then can be used as one of the raw materials in the process.

6. **Can you do heat integration for the partial condenser with the sulfonation reactor?**

Ans: No, the reason is that sulfonation reaction is highly exotermic and heat needs to be quickly removed. This is not possible when vapors are used as the cooling stream as gas phase heat transfer coefficients are significantly lower than the liquid phase heat transfer coefficients.

7. **Can a partial condenser be used for the ether column?**

Ans: Yes, the reason is that there is no hard and fast rule that isopropyl ether be added in the liquid phase to the sulfonation reactor. In fact, it should be added as a vapour phase only and therefore, partial condenser should be used in place of total condenser to save costs as well as meet the process specifications.

18.3 Acetone manufacture from isopropanol

18.3.1 Reactions

- Dehydrogenation of Isopropanol
- Isopropanol $\rightarrow$ Acetone + H_2
- Reaction pressure: 3 – 4 atms
- Reaction temperature: 400 – 500 ^{o}C
- Copper catalyst on porous carrier is used
- Vapor phase reaction

18.3.2 Process Technology (Figure 18.2)
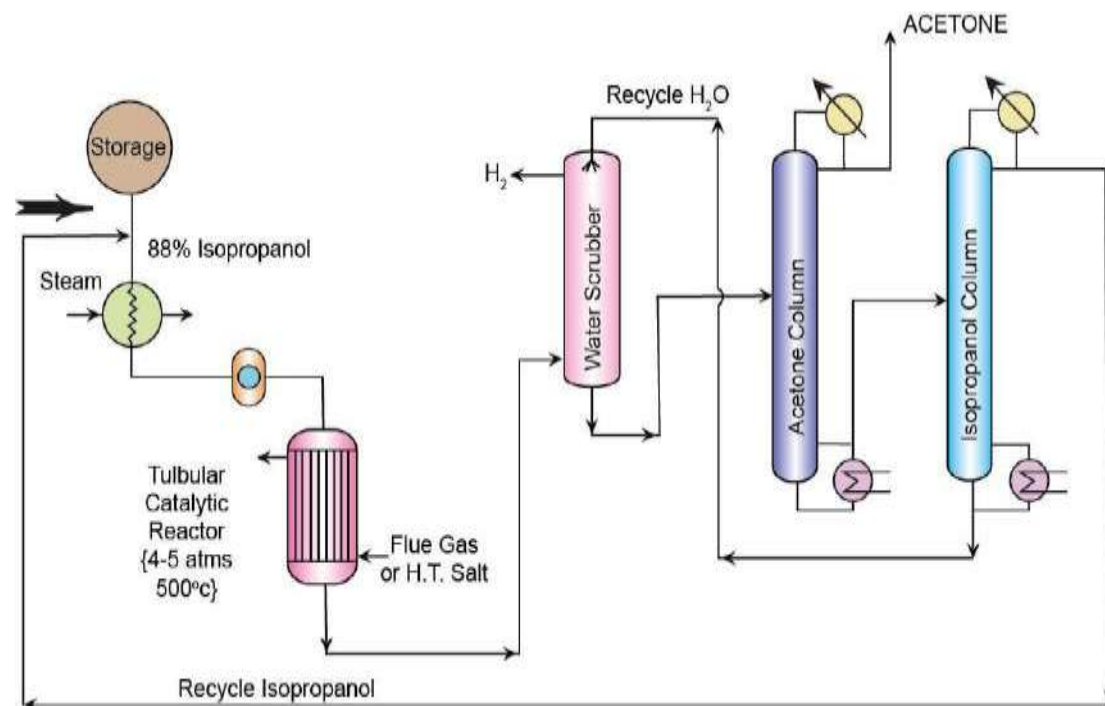
Figure 18.2 Flow sheet of acetone manufacture from isopropanol

- First, Isopropanol is heated using steam to vaporize the same
- Then, Isopropanol is compressed to desired reactor pressure i.e., 4 – 5 atms
- The compressed Isopropanol then enters a catalytic shell and tube reactor in the tube side. The tube is packed with the porous copper catalyst
- The reactor is operated at 400 – 500 ^{o}C using flue gas for heating. The flue gas is passed in the shell side of the shell and tube reactor.
- After reaction, the gases are condensed using cooling water condenser. The condensed isopropanol and acetone are sent for fractionation.
- The gases consisting of the remaining quantities of isopropanol and acetone are absorbed into water using a water scrubber.
- The acetone + isopropanol obtained from the condenser and water + isopropanol +acetone are sent to an acetone fractionator that separates acetone as the top product and isopropanol + water as bottom product.
- The bottom product isopropanol + water from the acetone fractionators is sent to a isoprpopanol column.
- This column produces water as the bottom product and isopropanol as the top product.
- The water is cooled using a water condenser and sent to the water scrubber as fresh water solvent.

18.3.3 Uses of Acetone :

Aceone is used as a polar, aprotic solvent in a variety of organic reactions. One important property for which it is used as laboratory solvent is because does not form an azeotrope with water.

Acetone is also used in various medical and cosmetic applications. It also forms an important component in food additives and food packaging.

18.3.4 Technical questions

1. Is pure isopropanol required as feedstock in the reactor?

Ans: This question is asked due to the fact that isopropanol production process involves the formation of an azeotrope with 87 % Isopropanol and 13 % water. Therefore, if the azeotrope itself can be used as feedstock, then one can save azeotropic column costs if an acetone plant is constructed next to the isopropanol.

Yes, isopropanol azeotrope can be used as a feed stock. In this case, the water will not react and will condense in the condenser after the reactor.

2. Can't we feed the product gases directly to the water absorber eliminating the condenser?

Ans: The condenser removes the condensable components from the product vapors. If condenser is not used, then the hot vapors move to the absorber and absorber load and degree of separation should be pretty high and hence higher cost. Therefore, it's better to use the water cooling condenser.

3. **Apply lechartlier principle and suggest what pressures be operated in the reactor. Eventually comment on the existing pressures?**

Ans: If we apply Lechartlier principle, dehydrogenation reaction is favoured by lower pressures. However, higher pressures are used in this case. If the pressure of the system does not play a critical role in the conversion, then higher pressures are favoured as they reduce the size of the reactor significantly for the throughput available. Also, higher pressures are favourable for absorption and reduce the water load in the absorption column.

4. **Why is water from the isopropanol fractionators cooled and sent to the water absorber unit?**

Ans: This is due to the fact that absorption is favoured at lower temperature and higher pressure.

5. **Why is isopropanol again sent to the compressor along with the feed?**

Ans: The operating pressures of the absorber, acetone fractionator and isopropanol fractionators reduce sequentially as the stream progresses to the right side. Therefore, the last column produces the product with about atmospheric pressure only. Therefore, to bring it back to 5 atm as in the reactor conditions, the stream has to be compressed along with the feed stream.

References:

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

Lecture 19: Cumene and Acrylonitrile from Propylene

19.1 Introduction

- In this lecture, we study the process technology associated to the production of cumene and acrylonitrile from propylene
- Both Cumene and Acrylonitrile are very important compounds that are required for the manufacture of other downstream petrochemicals
- We first present the process technology associated to the Cumene

19.2 Cumene

19.2.1 Reactions

- C6H6+
- The reaction is exothermic
- Side reaction:
- $C_6H_6 + C_3H_6 \longrightarrow nC_9H_{12}$
- Catalyst: H_3PO_4 impregnated catalyst on porous carrier
- Operating conditions: 25 atms pressure and 250 ^{o}C temperature.

19.2.2 Process technology (Figure 19.1)
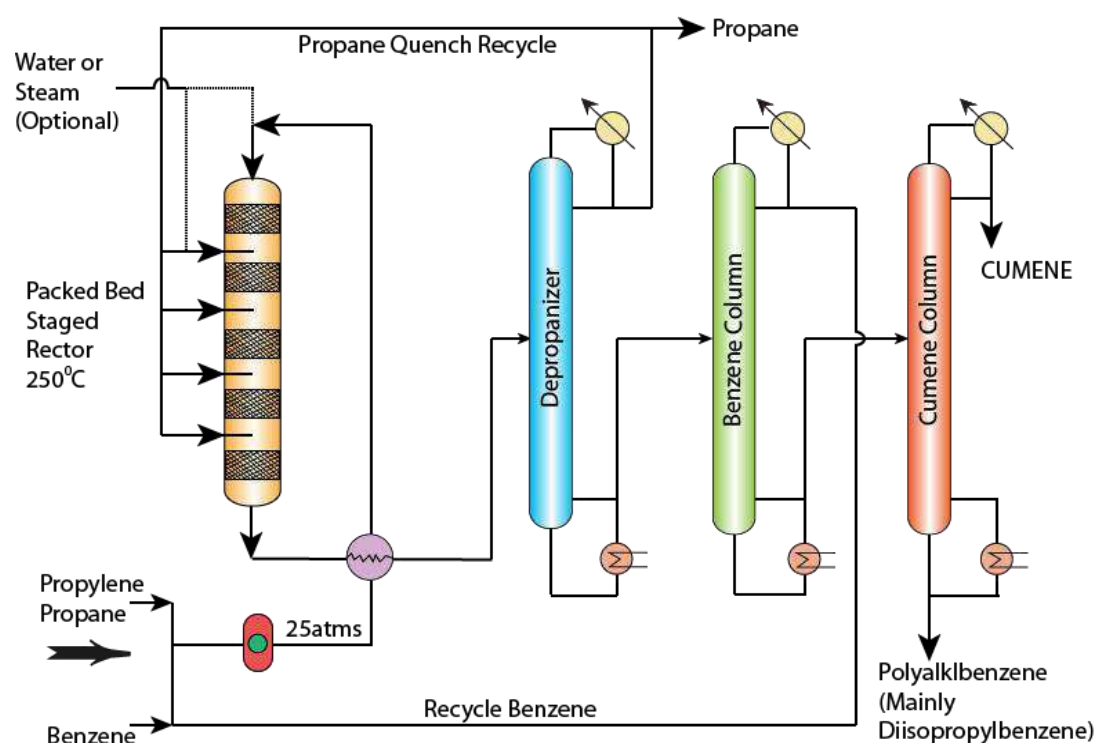
Figure 19.1 Flow sheet of Cumene production

- Propylene obtained from refinery processes as a mixture of propylene and propane
- The mixture along with benzene is compressed to 25 atms
- Eventually the mixture enters a heat integrated exchanger to heat the pre-heat the feed mixture.
- The feed mixture enters a packed bed reactor.
- The stream distribution in the packed bed reactor corresponds to cold shot arrangement i.e., cold propane from the distillation column in the process is added after every reactor with the product stream so that the temperature of the stream is controlled.
- Here, propylene is the limiting reactant and therefore, presumably all propylene undergoes conversion.
- Here, propane does not react but is a diluents or inert in the system. In that way it controls the reaction temperature.
- The reactor units are maintained at about $250^{o}C$
- The product vapors are cooled using the heat integrated exchanger
- The vapors then pass to a depropanizer which separates propane from the product mixture.
- The bottom product consisting of benzene, cumene and polyalkyl benzenes enters another distillation column which separates benzene from the mixture of cumene and polyalkyl benzene. The benzene stream is recycled to enter the compressor.
- The bottom product from the benzene column is sent to a cumene column which produces cumene as top product and poly alkyl benzene as bottom product.
- Therefore, the entire process technology is nothing but a simple reactor separator recycle arrangement.

19.2.3 Technical questions

1. **What alternative reactor arrangement is possible if pure propylene feed is used?**

Ans: When pure propylene is used, then there is no propane for quenching. Therefore, the packed bed reactor shall be provided a cooling jacket which can control the temperature of the reactor.

2. **Comment on the sequence of distillation columns separating propane, benzene and cumene in series?**

Ans: The distillation columns are so arranged so that lighter components are separated first followed by heavier components. Since no component is present which will decompose on long time heating, this arrangement is followed. If not, the component which can decompose upon long time heating will be separated first following by the lighter to heavier component sequence in the remaining components.

3. **In what way propane quenching plays a role in the reactions?**

Ans: Propane quenching reduces polymerization of cumene and formation of polyalkyl benzenes.

4. **How can one suppress polyalkylbenzene formation?**

Ans: By using high feed ratio of benzene to propylene and using propane as a diluent

5. **Is further heat integration not possible?**

Ans: A further heat integration can be carried out using hot vapors in the distillation column to be as hot streams in the reboilers of various distillation columns.

6. **In what way higher pressure in the product vapors from the reactor are beneficial for the deprpopanizer unit?**

Ans: The depropanizer unit requires condensation of propane vapors in the condenser. Propane's boiling point is less than 0^oC at 1 atm pressure. Therefore, higher pressures to the extent of 25 atms will enhance propane boiling point to about $25 - 30^o$C for which cooling water can be used as the cooling media in the condenser. If not, refrigerant needs to be used and the refrigerant will require a refrigerating unit along with the process. This is much much expensive than using cooling water as the cooling media.

19.3 Acrylonitrile

19.3.1 Reactions

- $C_3H_6 + NH_3 + O_2 \longrightarrow C_3H_3N + H_2O$
-
- The reaction is exothermic
- Stoichiometric ratio: $C_3H_6 : NH_3 : O_2 = 1:1:1.5$
- Operating conditions: $1.5 - 3$ atms pressure and $400 - 500^o$C
- By products: Acetonitrile and Hydrogen cyanide from side reactions
- Catalyst: Mo-Bi catalyst

19.3.2 Process Technology (Figure 19.2)
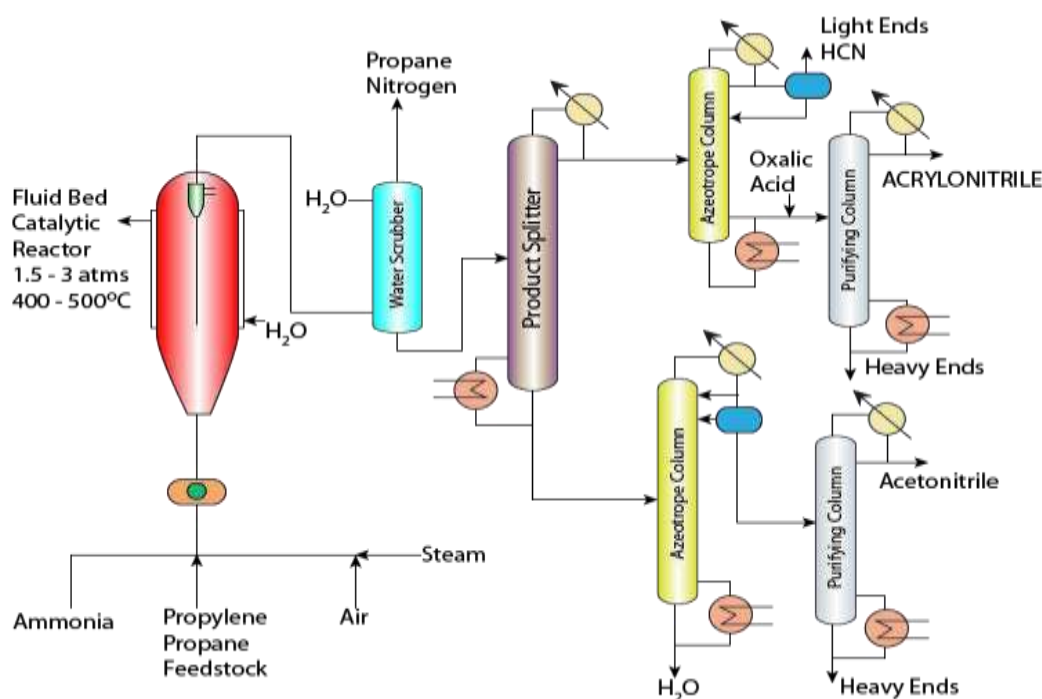
<p align="center">Figure 19.2 Flow sheet of Acrylonitrile production</p>

- Propylene + Propane, Air and Ammonia, Steamare compressed to required pressure and are sent to the fluidized catalytic reactor consisting of the Mo-Bi spherical catalyst. The reactor is maintained at $400 - 500^{o}C$.
- Cyclone separator is also kept in the fluidized bed reactor in which catalyst and product gases are separated after fludization. The contact time for fluidization is in the order of seconds.
- The product vapors then enter a water scrubber that does not absorb propane and nitrogen from the products. The products absorbed in the water include acrylonitrile, acetonitrile and other heavy ends.
- The very dilute acryolonitrile (about 3 %) solution in water is sent to a fractionator. The fractionators separates acrylonitrile + heavy ends + HCN + light ends as a top product stream and acetonitrile + water + heavy ends as a bottom product.
- The top product then enters an extractive distillation column with water as extractant. The azeotropic distillation column vapour is partially condensed to obtain a vapour, aqueous and organic layer. The vapour consists of Light ends and HCN and is let out. The organic layer consists of acrylonitrile and heavy ends is sent for further purification. The aqueous layer is sent as a reflux to the azeotropic column. In other words, addition of water enabled the formation of a heterogenousazeotropic mixture at the top.
- The bottom product from the azeotropic distillation column enters a product purification unit along with oxalic acid where acrylonitrile is further purified from heavy ends (+ oxalic acid) and is obtained as a 99.5 % pure product.

- In similarity to this, the bottom product from the product splitter enters an azeotropic column which produces water as a bottom product. The total condenser in this column generates both aqueous and organic layers. The organic layer is rich in acetonitrile and heavy ends where as the aqueous layer is sent back as a reflux to the azeotropic column.
- The bottom product from the acetonitrile azeotropic column enters a purification unit where distillation principle enables the separation of acetonitrile from the heavy ends.

19.3.3 Technical questions

1. **Why is oxalic acid added in the acrylonitrile purification column?**

Ans: One of the byproducts of the ammonoxidation of propylene are cyanohydrins.These organic compounds readily dissociate to form volatile compounds. These volatile compounds are severely polluting compounds. Therefore, to avoid this, oxalic acid is added to the purification column in order to form complex compounds with these cyanohydrins and these compounds eventually enter the heavy end products.

2. **A careful analysis of the process flowsheet shown indicates that while absorption is favoured at lower temperatures and higher pressures, exactly opposite conditions exist for the reactor outlet stream (at about 1 atm pressure and 400 – 500°C). What additional process modifications are suggested?**

Ans: Cooling the vapour product stream from 400°C to about 50°C in a series of heat exchangers. Since vapour is involved, extended area exchangers will be beneficial. Heat integration with the reboilers of any of the distillation columns is also beneficial.

Pressurizing the vapour pressure to higher pressure and allowing it to enter the scrubber at the same temperature. This is beneficial but compressor costs will be enormous.

Therefore, in the light of the process costs, cooling the vapour stream is beneficial than compression to favour good absorption.

3. **In certain processes for acrylonitrile production, cyanohydrins removal is desired. If so, what process modifications are suggested?**

Ans: Cyanohydrins are in the bottom product obtained in the product splitter. Therefore, the bottom product can be sent to a reactor where cyanohydrins can be converted to acrolein and these acroleins can be separated and sent back to the ammonoxidation reactor (fluidized beds). In that case, oxalic acids are not used and the heavy ends will not also get produced significantly and therefore process topology will be somewhat different from what is being shown here. For further details upon how the process flowsheet changes please refer to Chemical Engineering Design

(Book) by Sinnott where in Appendix these modifications have been explained thoroughly in the process description.

4. **Is a partial condenser required in the acetonitrile azeotropic column?**

Ans: No, the reason is that the bottom product from the product splitter consists of heavy ends, acetonitrile and water and does not consist of lighter ends and HCN. Therefore, a partial condenser is not required and a total condenser producing two separate liquid phase streams that separate upon gravity is required.

5. **A feed stock heater is not shown in the process. However, reactor operating conditions are indicate high temperature operation. How is the feed stock heated?**

Ans: The heat for achieving the feed to desired temperature is provided by superheated steam that is mixed along with the feedstock. Typical feed molar composition is propylene 7, ammonia 8, steam 20 and air 65. Additional heat for the reaction is obtained from the highly exothermic reaction in the fluidized bed catalytic reactor.

6. **What are the advantages of the fluidized catalytic reactor when compared to a packed bed reactor?**

Ans: It is well known that the heat and mass transfer coefficients of gases are predominantly lower than those of the liquids. Therefore, fluidization principle effectively enhances bulk phase mass and heat transfer coefficients of the gas solid catalytic reaction. In other words, due to fluidization, less contact time that is required in the process, higher conversions can be achieved.

References:

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

Lecture 20: Isoprene and Oxoprocessing

20.1 Introduction

- In this lecture, we discuss the process technology for isoprene and oxoprocessing.
- Isoprene is prepared using propylene and is an important commodity for polymerization reactions and products.
- Oxoprocessing involves reaction between olefins and synthesis gas at high pressure to yield aldehydes. The aldehydes can be subsequently subjected to hydrolysis to obtain short as well as long chain alcohols.
- We first present the process technology associated to isoprene manufacture

20.2 Isoprene

20.2.1 Reactions

- Isoprene is manufacture from propylene using three consecutive reactions. These are
  - o Dimerization of propylene to obtain 2-methyl-1-pentene

$$2.H_2C = CH - CH_3 \xrightarrow{\text{dimerization}} H_2C = C - CH_2 - CH_2 - CH_3$$

(propylene)   (2-methyl-1-pentene)

with CH_3 substituent on the C.
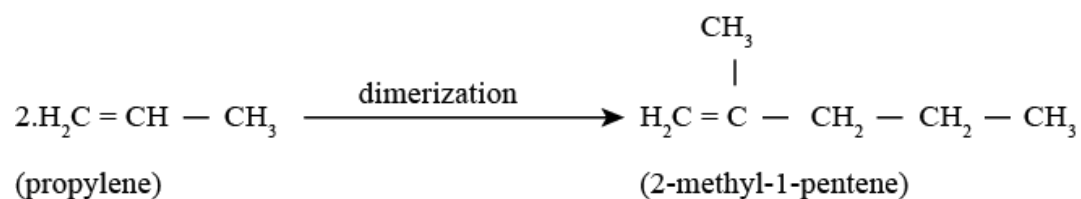
  - o Isomerization of 2-methyl-1-pentene to obtain 2-methyl-2-pentene

$$H_2C = C - CH_2 - CH_2 - CH_3 \xrightarrow{\text{isomerization}} H_3C - C = CH - CH_2 - CH_3$$

(2-methyl-1-pentene)   (2-methyl-2-pentene)

with CH_3 substituents.
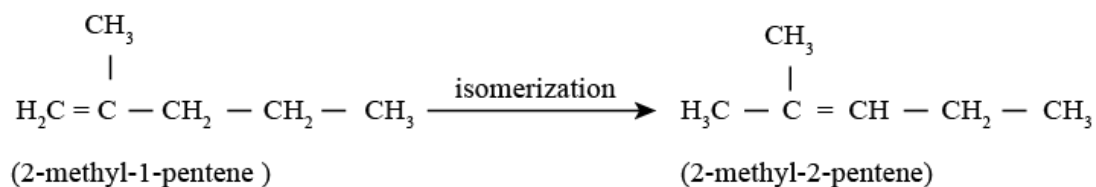
  - o Pyrolysis of 2-methyl-2-pentene to obtain isoprene along with methane as a side – product.

$$H_3C = C - CH - CH_2 - CH_3 \xrightarrow{\text{pyrolysis}} CH_2 - C = CH - CH_2 + CH_1$$

(2-methyl-2-pentene)   (isoprene)   (methane)

with CH_3 substituents.
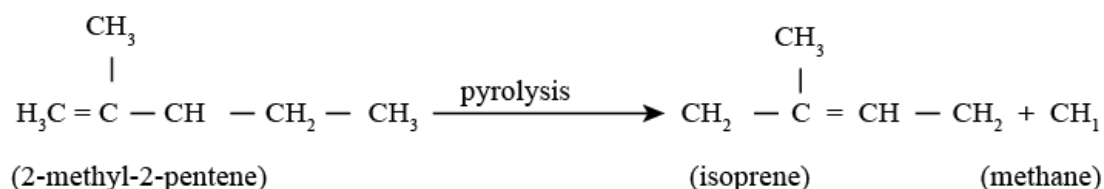
- Since three reactions are involved that have distinct operating conditions as well as catalyst requirements, the process involves a series of reactor-separator-recycle networks.
- We therefore, consider presenting all these cases separately so that the process can be well understood.

20.2.2 Dimerization reaction

o Catalyst is tripropyl aluminium
o A solvent carrier is used that enables the recovery of the catalyst from the product stream.
o Operating conditions are $150 – 200^o$C and 200 atms.

20.2.3 Isomerization reaction

o The reaction requires an acid catalyst on porous carrier
o Operating conditions are $150 – 300 \ ^o$C and normal pressure conditions

20.2.4 Pyrolysis reaction

o HBr catalyst is used
o Operating conditions are $650 – 800 \ ^o$C and normal pressure.

20.2.5 Process technology (Figure 20.1)
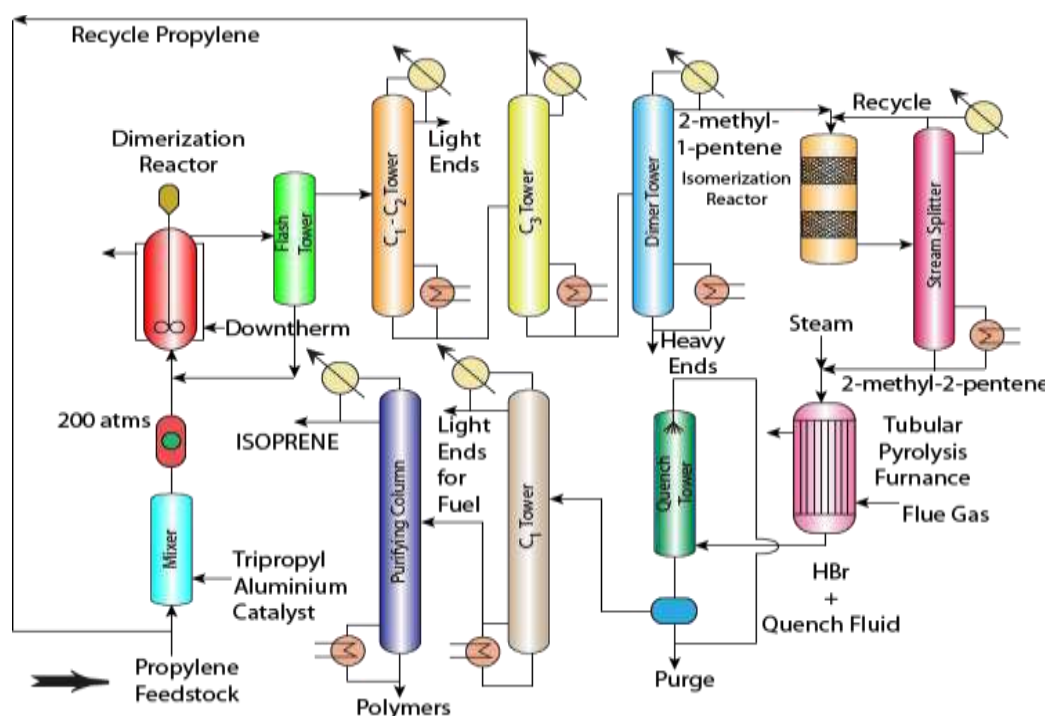
Figure 20.1 Flow sheet of isoprene production

- The process technology consists of three major blocks namely
  - o Dimerization-separator-recycle network (DSR)
  - o Isomerization-separator-recycle network (ISR)
  - o Pyrolysis-separator-recycle network (PSR)

20.2.6 DSR network

- o Propylene feed is mixed along with unreacted propylene (recovered in a distillation column in the DSR) to enter a mixer.
- o The mixer is fed with tripropyl aluminium catalyst (this catalyst is in liquid phase)
- o The mixture is compressed to about 200 atms. At these conditions, the mixture is in the liquid phase.
- o The liquid phase dimerization feed enters the dimerizatoin reactor
- o The dimerization reactor is a CSTR with dowtherm fluid circulated in the cooling jacket to remove the heat generated from the exothermic reaction
- o After the reaction, the liquid stream is subjected to flash operation. From the flash tower a vapour and liquid stream are produced. The liquid stream consists of the catalyst + solvent where as the vapour stream consists of the unreacted propylene, light ends and the product formed.
- o The liquid stream from the flash tower is recycled back to the dimerization CSTR.
- o The vapour stream enters a fractionation tower that produces light ends such as C_1-C_2 as the top product. The bottom product consists of propylene and dimerized product i.e., 2-methyl-1-pentene
- o This product is subjected to again fractionator in a separate tower to obtain 2-methyl-1-pentene as the bottom product and propylene as the top product. The top propylene product is then recycled back to mix with the fresh propylene feed stock and enter the mixer unit.

20.2.7 ISR network

- o 2-methyl-1-pentene enters an isomerisation reactor which consists of acid catalyst (on porous carrier).
- o The isomerisation reactor is a packed bed reactor operated at desired operating temperature.
- o After the reaction, the products are sent to a fractionators that separates unreacted 2-methyl-1-pentene from the isomerized product i.e., 2-methyl-2-pentene.

20.2.8 PSR network

- o 2-methyl-2-pentene enters a pyrolysis furnace.
- o Steam is also mixed with the organic vapors so as to quickly facilitate cracking in the pyrolysis furnace.
- o The furnace is a shell and tube arrangement with the reactants entering the tubes and the hot flue gases enter the shell.
- o HBr catalyst also enters the tubes of the pyrolysis furnace
- o After reaction, the product gases (HBr+product+reactant) are taken out and are quenched with a solvent in a quench tower. The quenching then produces a gas liquid mixture which is sent to a phase separator unit. The liquid stream from the phase separator stream consists of HBr+solvent and this is sent for quenching.
- o Fresh HBr can be generated from the HBr + solvent obtained from the phase separator
- o The gas fraction from the phase separator enters a C_1 tower that separates fuel gas and other light ends as a top product.
- o The bottom product from this tower consists of polymeric compounds and isoprene is fed to a purification tower to fractionate isoprene from the polymeric compounds

20.2.9 Technical questions

1. **What solvent can be used in the quenching process?**

Ans: HBr can be readily absorbed into water. Therefore, water can be used as a solvent in the quenching process. There is a patent available where it says that acetone can be used to recover HBr. More details can be obtained of this patent by furthering the search on the patent data base using the internet.

2. **In the process flow sheet given the HBr recovery is not shown. Do you think the flow sheet is correct. Suggest any modifications to the flow sheet?**

Ans: Yes, the flowsheet has an error in that sense. The flowsheet should give a section for HBr recovery where HBr is recovered in the quenched solvent and the fresh HBr gas is allowed to enter the pyrolysis furnace along with the steam. In such case, one has to put an additional HBr stripper which can strip HBr from the HBr + solvent stream that is fed to this unit and the HBr can be sent to the pyrolysis unit. The fresh solvent can be then sent to a cooler and sent to the quench tower and the existing recycle stream to the quenching tower will not be there. Instead, this stream will go to the stripper as a feed stream.

3. **Can we not do heat integration partially for the pyrolysis furnace with the vapour products?**

Ans: HBr is very corrosive and therefore, if we go for heat integration using the vapour product, then the shelf life of the pyrolysis furnace will be minimized. Therefore, better we don't go for heat integration in this way.

4. **Is a purge stream required in the process flowsheet shown for the quench fluid + HBr mixture?**

Ans: Yes, and this is not shown in the process flow sheet. Some impurities such as some light ends that might dissolve with the solvent will have to be purged, if not these can cause coking problems and can cause unwanted organics in the pyrolysis furnace reactor.

5. **What sort of regeneration would you recommend for the isomerisation catalyst?**

Ans: Heating the catalyst in oxygen or air to remove coke would be beneficial to regain the activity of the isomerisation catalytic bed.

6. **Suggest what changes will be there in the process flow sheet if pure propylene instead of a mixture of propylene, propane and C_1-C_2 components is used?**

Ans: The C_1-C_2 tower and C_3 towers can be replaced with a single tower after flash unit. This new unit will separate all light ends in trace amounts in a single tower with middle product being 2-methyl-1-pentene and heavy ends as bottom product. Therefore, a complex distillation unit arrangement would be at the maximum required replacing three distillation columns in series.

20.3 Oxo processing of olefins

20.3.1 Introduction

- In an oxo process, we react an olefin with synthesis gas to obtain aldehyde i.e.,
- Olefin + CO + H_2 $\rightarrow$ Aldehyde
- This reaction is called as hydroformylation
- **Dimerization (Option):** Alternatively, if desired, the aldehyde dimerization reaction can be also carried out. In that case, two molecules of aldehydes react to obtain a higher order aldehyde.
- In short, the oxo processing can be targeted to generate both short chain and long chain aldehydes.
- **Hydrogenation (Option):** When short and long chain aldehydes are subjected to hydrogenation then one can produce alcohol or an acid.
- **Oxygenation (Option):** When short and long chain aldehydes are subjected to reaction with oxygen or air, then acids can be formed.
- Thus the oxo processing of olefins can generate

- o Short and long chain aldehydes
- o Short and long chain alcohols
- o Short and long chain acids
- Therefore, gases can be converted into these useful products. Various applications of these compounds include plasticizers for polymerization reactions, solvents, detergent raw materials etc.
- The process will be demonstrated for propylene but can be suitably extended to other alkenes such as butylenes or ethylene.

20.3.2 Reactions and Operating conditions

- **Addition reaction**
    - o Catalyst: Cobalt naphthanate
    - o Operating conditions: Pressure of 100 – 400 atms and temperature of 100 – 200 ^{o}C
    - o The reaction is exothermic
    - o Reaction occurs on a packed bed reactor where the packed bed acts as a surface to deposit the catalyst i.e., Cobalt.
    - o In due course of reaction, the Cobalt enters the product stream and therefore needs to be recovered.
- **Dimerization reaction**
    - o Catalyst: Zinc salt
    - o Operating conditions: Higher pressure and moderate temperatures.
- **Hydrogenation reaction**
    - o Catalyst: Nickel
    - o Operating conditions: 100 atms and 150 ^{o}C

20.3.3 Process technology
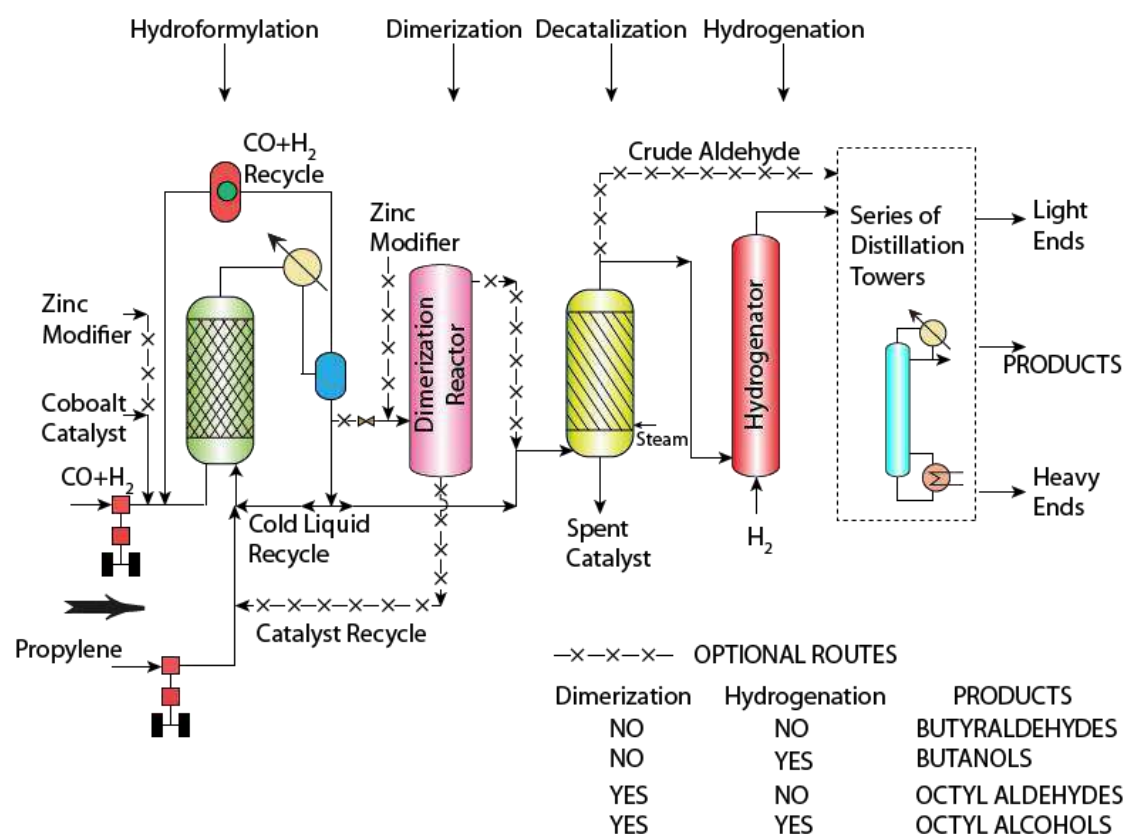
Figure 20.2 Flow sheet of Oxo processing of olefins

- To produce alcohols, the process consists of four basic steps namely hydroformylation, decatalization, hydrogenation and a separation network
- **Hydroformylation**
    o Propylene and synthesis gas are separately compressed and sent to the hydroformylation reactor along with the Cobalt catalyst (i.e., Cobalt napthanate).
    o The concentration of Cobalt Naphthenate is about 1 wt % Cobalt in the feed mixture.
    o During the reaction at the existing operating conditions some Cobalt gets deposited on the porous carrier.
    o Since the reaction is highly exothermic, there shall be cooling. To do so, cold liquid stream obtained after phase separation is recycled.
    o The product liquid from the reactor is sent to a partial condenser followed by phase separator. The phase separator separates the unreacted synthesis gas (by considering the propylene in the feed stock to be limiting) and the liquid product stream. The liquid product stream is partially recycled back to the reactor to serve as a diluent to control the temperatures in the packed bed reactor.
    o The liquid product stream consists of dissolved cobalt and hence it needs to be extracted back as the salt to enter the hydroformylation reactor.

- o Therefore, the product stream is partially sent to the Decatalization process so as to remove the catalyst from the stream
- **Decatalization**
    - o The liquid product from the phase separator is sent to a packed bed unit where it is mixed along with steam at 180°C at a pressure of 20 atms.
    - o At this condition, Cobalt salt in the hydrocarbon liquid gets transferred to the porous carrier as cobalt oxide.
    - o For reuse, the cobalt oxide on the porous carrier is treated with acid to generate the cobalt naphthanate and this will be sent back to the hydroformylation reactor.
    - o The vapors generated from decatalization unit consist of the aldehyde products
    - o These are sent to the hydrogenation unit next to convert aldehydes to alcohols
- **Hydrogenation**
    - o The aldehyde product vapors are fed to a nickel catalytic bed reactor
    - o Hydrogen is also fed to the reactor at about 150 ^{o}C and 100 atms.
    - o After reaction, butanols and other alcohols are sent to a separator network
- **Separator network**
    - o The separator network consists of several fractionators in series
    - o The fractionators in series produce light ends and heavy ends in addition to the desired product i.e., butanol

20.3.4 Technical questions

1. **The flow sheet presented corresponds to production of butanol from propylene. If higher order alcohols are desired, how does the flow sheet get modified?**

Ans: An additional unit process entitled "Dimerization" will be part of the flow sheet. In such case, the cold liquid stream from the phase separator enters the dimerization reactor to convert lower order aldehydes to higher order aldehydes.

2. **Suppose we wish to produce both short chain and long chain aldehydes and do not wish to produce alcohols then how does the process topology change?**

Ans: When both short and long chain aldehydes are required, then we have to allow the cold liquid from the phase separator to enter the dimerization reactor partially only. Then the dimerization reactor product as well as the phase separator stream enter the decatalization unit to achieve catalyst recovery.

3. Can the hydroformylation reactor be used as a dimerization reactor as well?

Ans: Yes, in this way, we can produce all desired products in a single reactor and we can avoid dimerization reactor. But the balance between cobalt and zinc catalysts will dictate the product composition palette.

4. Why high pressure is required in the hydroformylation reactor?

Ans: Higher pressures enable the formation of a complex between Cobalt and the hydrocarbons participating in the reaction. If higher pressure is not existent, the cobalt complex can decompose and this does not favour higher conversions.

5. Can the series of distillation columns in the separator network be replaced with a complex distillation column?

Ans: Yes, this is possible and this is recommended as the light end and heavy end products are not significant in make and the aldehyde products are the actual products that are desired. A complex distillation reduces the number of columns required, enables complex interaction between both vapour and liquid streams and facilitates drastic reduction in the cost.

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Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

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Lecture 21: Butadiene and Benzene Manufacture

21.1 Introduction

- In this lecture, we present the process technologies associated to Butadiene and Toluene.
- Butadiene manufacture is considered using n-Butane as the feed stock.
- Benzene process technology refers to the famous hydrodealkylation process that uses toluene as the feed stock.
- We first present the process technology associated to Butadiene.

21.2 Butadiene

21.2.1 Reactions

- Main reaction: n-Butane → Butadiene + Hydrogen.
- Side reaction: n-Butane→ n-Butylene + Hydrogen.
- Catalyst: Chromium oxide on alumina.
- Coke deposition is a very important issue. Therefore, catalyst regeneration needs to be carried out very frequently.
- Reaction is exothermic .
- Operating conditions: $650^{o}C$ and 120-150 mm Hg (low pressure).
- Feed stock: n-Butane with some isopentane from refinery processes.

21.2.2 Process Technology (Figure 21.1)
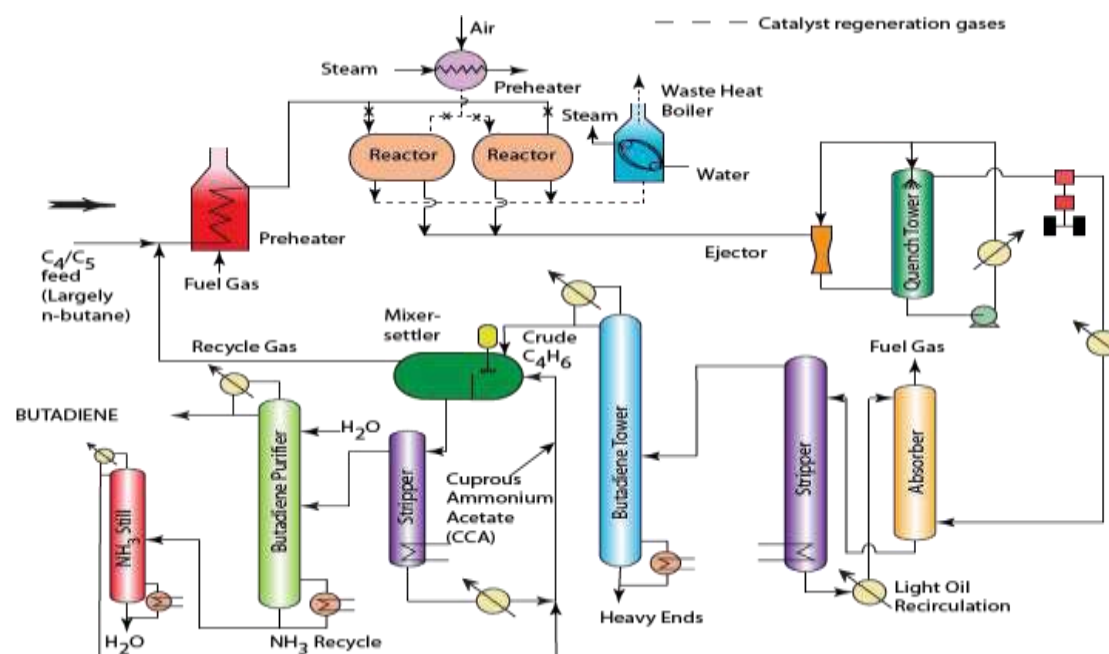
Figure 21.1 Flow sheet of Butadiene manufacture

- The process technology for Butadiene manufacture consists of a reactor-separator-recycle system.

- The separation network is extremely complex and involves quenching, absorption, distillation and extractive distillation process.
- First, the feed stock is pre-heated in a furnace along with unreacted gases that have been recovered in the process using the separator network.
- After pre-heating in a furnace to desired temperature, the gases enter the catalytic packed bed reactors loaded with the catalyst.
- After the specified residence time, the product is withdrawn and the feed to the unit is stopped. The product withdraw and stoppage of the feed flow to the reactor unit is carried out using valves.
- The coked catalyst is subjected to combustion using pre-heated air. Air pre-heating is done using steam in an extended area heat exchanger equipment. Therefore during regeneration, another set of valves operate to allow the pre-heated air in and enable the product withdrawal after the combustion.
- The pre-heated air not only removes the coke as CO_2 but increases the reactor temperature to 650 ^{o}C.
- The flue gases are sent to a waste heat recovery boiler so as to generate steam from water.
- The entire operation of a feed entry, product withdrawal, pre-heated air entry and combustion gases withdrawal from the packed bed reactor corresponds to one single cycle.
- Since the above operation is a batch operation, to make the operation continuous in accordance to the separation network, two reactors are used and these reactors are operated in cyclic fashion i.e., when the first reactor is subjected to reaction, the second reactor is subjected to catalyst regeneration and vice-versa.
- The hot reactor outlet gases are sent to a quenching operation where light gas oil is used to quench the gases using a recirculating quenching tower.
- After product gases from the quenching tower are compressed and cooled to enter an absorber
- In this absorber, naphtha is used as an absorbent to absorb all hydrocarbons except fuel gas.
- The absorbent + hydrocarbons enter a stripper that produces fresh naphtha and hydrocarbon mixture. The hydrocarbon mixture consists of unreacted feed stock and butadiene and some heavy ends.
- This mixture now enters a fractionator to separate the crude butadiene and heavy ends.
- The crude butadiene consists of butadiene and unreacted feed stock i.e., n-butane and isopentane. The separation of n-butane, other hydrocarbons with butadiene is one of the difficult separations and they cannot be separated using ordinary distillation. Therefore, a complicated route of separation is followed next that involves azeotropic distillation using ammonia.

- The crude butadiene is mixed with ammoniated cuprous ammonium acetate solution in a mixer settler. This solution is generated by absorbing ammonia into fresh cuprous ammonium acetate solution.
- The ammoniated cuprous ammonium acetate is sent to a mixer settler unit where the butadiene dissolves in the ammoniated solution. The gas from the mixer settler unit is recycled to mix with the feed stock and enter the pre-heater.
- The ammoniated cuprous ammonium acetate solution is thereby stripped to separate butadiene + ammonia from the ammonium acetate solution. The regenerated fresh solvent is allowed to absorb NH_3 and thereby enter the mixer-settler unit.
- The ammonia + butadiene mixture enters a fractionator fed with water. Here, water interacts with ammonia and generates the ammonium hydroxide product as the bottom product and butadiene is obtained as the top product.
- The ammonia solution is subjected to stripping to separate water and ammonia. The water is recycled back to the butadiene purifier and ammonia is allowed to get absorbed into the fresh cuprous ammonium acetate solution. This process is not followed in India . In India, it is manufactured from ethanol by catalytic cracking at 400-450 ^{o}C over metal oxide catalyst.

21.2.3 Technical questions

1. **Can the steam generated in the waste heat recovery boiler be sufficient to pre-heat the air if a principle of steam reuse is adopted?**

Ans: From the basic principle of thermodynamics, somewhere heat needs to be added to the system. If we presume that the feed pre-heater heats the feed to 650°C (the desired temperature of the reactor) and the catalyst is regeneration energizes the catalyst by 100°C (from 550 to 650°C), the flue gas should be able to generate some steam. However, it can be speculated that the steam generated will not be enough to meet the total air pre-heater requirements. Therefore, some make up steam will be always required.

2. **Why is ammonia allowed to get absorbed into cuprous ammonium acetate?**

Ans: Ammonia absorption into cuprous ammonium acetate facilitates maximum absorption of butadiene. This is because ammonia in many cases enhanced absorption factors by allowing chemical interaction between molecules which is better than just physical absorption.

3. **Why is the fluid recirculated in the quench tower?**

Ans: We are targeting gas quenching using a liquid in this process. Quenching a liquid with liquid is instantaneous but quenching a gas with a liquid needs considerable amount of time, and hold up time is very important. Therefore, fluid internal recirculation is required in the vapour quenching tower.

4. Why a cooler is used in the quenching tower?

Ans: The quenching operation increases the temperature of the fluid that is used for quenching. And we can see that the fluid is always circulated. Therefore, the purpose of quenching is to just cool the gas and don't absorb any of the components into itself. Therefore, to do so, the fluid shall be cooled in between.

5. Why compressor and cooler are at all required after quenching process?

Ans: The unit following quench tower is absorption. Absorption is favoured at higher pressure and lower temperature. Therefore both compressor and cooler are required to achieve these conditions of favourable absorption.

6. Why cooler is followed after compression but not vice versa?

Ans: In general, compression enables enhancement in the temperatures of the gas/vapour. This is because we don't usually follow adiabatic compression but we follow polytropic compression in reality. And polytropic compression will enable heating the gas/vapour. Therefore, cooling is used after compressor but not vice-versa. If cooler is used before compressor then the gas entering absorber will be at a higher temperature and this is not favourable for absorption.

7. Explain in a more elaborate way what happens in the Butadiene purification fractionators?

Ans: The butadiene purification fractionator is fed with ammonia + Butadiene stream in which somehow ammonia should be recovered. Therefore, this unit is part of the azeotropic distillation that separates butadiene + ammonia as one of the products and eventually butadiene and ammonia are separated using water, as water absorbs ammonia instantaneously to form ammonium hydroxide. Eventually, it is also easy to strip the ammonia gas from aqueous ammonia solution.

8. Why we cannot separate butadiene-butane mixture using ordinary fractionation?

Ans: Their boiling points are very close and distillation requires large differences between boiling points of the components to be separated.

21.3 Benzene production using hydrodealkylation route

21.3.1 Reactions

- Toluene does not have much market value.
- Therefore, Toluene is reacted with H_2 to produce Benzene and Methane
- Main reaction: Toluene + H_2→ Benzene + Methane
- Reactor operating conditions: 600 – 650 ^{o}C and 35 – 40 atms
- Catalyst: Chromia on porous carrier.
- Other reactions: Alkyl aromatics + H_2→ Benzene + Alkanes

21.3.2 Side reactions

- ○ Toluene →Diphenyl + H_2
- ○ Toluene + Benzene → Methyl diphenyl
- ○ Toluene + H_2→ Alkanes (Cracking reaction)

21.3.3 Process Technology (Figure 21.2)
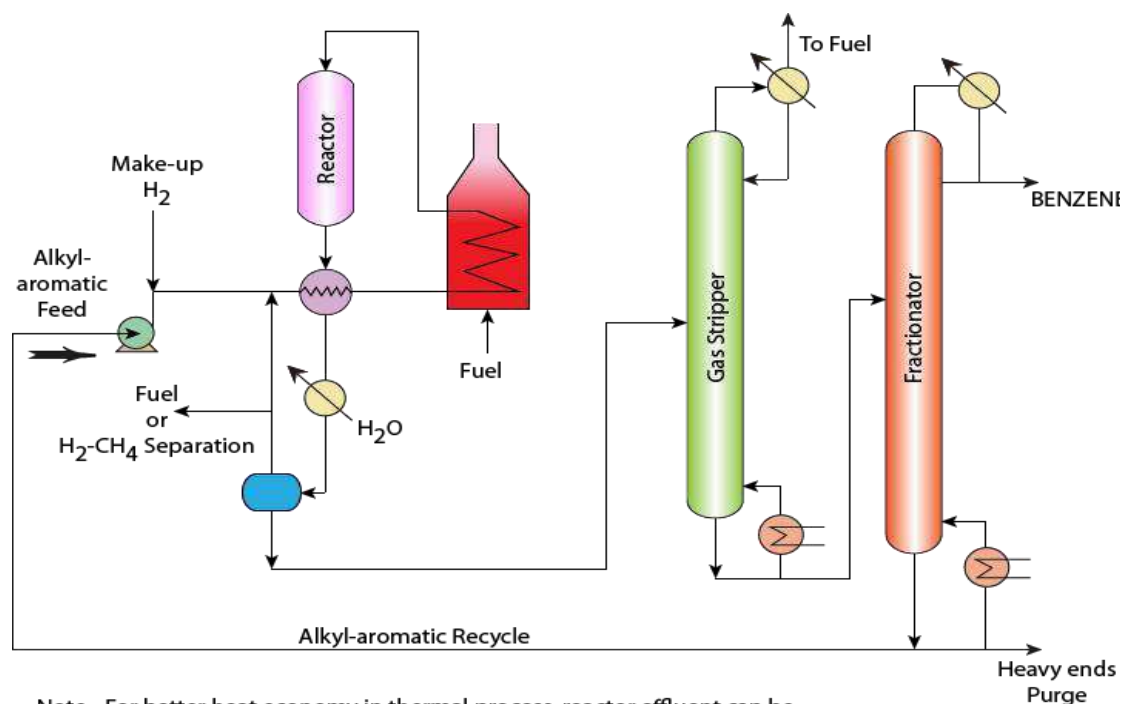
Note - For better heat economy in thermal process, reactor effluent can be used for stripper and fractionator reboiler heat supply.

Figure 21.2 Flow sheet of Benzene production using hydrodealkylation route

- The process corresponds to a simple reactor-separator-recycle system facilitated with heat integration.
- Alkyl-aromatics (Toluenes and other higher order alkyl aromatics) along with makeup H_2 and recycle stream consisting of unreacted toluene is allowed to enter a feed pre-heater.
- The feed pre-heater increases the temperature of the reactants at the desired pressure.
- After the reaction, the reactor products are cooled using heat integration concept by exchanging heat with the cold feed stream. Further cooling of the stream is carried out using a water based cooler.
- The stream enters a phase separation unit where the fuel gas components such as H_2 and CH_4 are removed as vapour stream. The liquid stream consists of H_2, CH_4, Light ends, Benzene, Toluene, Diphenyl and other higher order aromatics.
- The vapour stream is partially purged and to a large extent recycled as the stream has good amount of H_2. The gas phase purge stream is for controlling the concentration of methane in the reactor.

- The liquid stream enters a gas stripper which removes the light ends as a gaseous product stream from the top tray. The bottom product is then sent to a fractionator.
- The fractionator separates benzene from all heavy ends. The heavy end product consisting of unreacted toluene, diphenyl etc. is largely sent back to the reactor by allowing mixing with the fresh feed.
- A purge stream is facilitated to purge components such as diphenyl in order to not allow their build up in the reactor.

21.3.4 Technical questions

1. **Despite removing H_2 and CH_4 from the phase separator, why again we remove them from the gas stripper unit?**

Ans: This is due to the basic problem in the difficulty of sharp equilibrium factors which do not exist for these components. The equilibrium separation factors in a phase separator unit where the governing pressure and temperature dictate the distribution of components in the liquid and gas stream. Mostly methane and H_2 are removed as vapour stream in the unit. But still at the pertaining pressure and temperature of the phase separator, some lower order alkanes stay back in the liquid stream. Therefore, gas stripping is carried out to remove these.

2. **Comment upon fuel efficiency in the process and possibilities to enhance it?**

Ans: The process should indicate maximum fuel efficiency. This can be achieved by

a) Heat integration of feed and product streams to the reactor
b) Re use of fuel gas streams as a fuel in the pre-heating furnace.

If these two options are followed, then the process has maximum fuel efficiency and can be regarded to be very energy efficient.

3. **Do you suggest to put one more distillation column for the heavy end compounds. If so why?**

Ans: Yes, putting one more distillation column will separate toluene + diphenyl from other heavy end compounds. While diphenyl acts towards favouring forward reaction, the other heavy end compounds could tend to produce more coke during the reaction. Therefore, one more distillation unit to separate toluene+diphenyl from the heavy end compounds is recommendable.

4. Do you suggest any other alternative to eliminate the water cooler and even enhance the energy efficiency of the process?

Ans: Yes, it is possible, but existing temperatures of the gas stripper bottom sections need to be carefully analyzed. This is also due to the fact that phase separator operates at 450 psig and 100°F. Therefore, heat integration with gas stripper or fractionator reboilers can be beneficial and this way the process can be made even more energy efficient.

5. What is the basic problem of H_2 in the reactor?

Ans: Hydrogen causes embrittlement due to severe adsorption on the metal surface at higher pressures. Therefore, chrome steel is used to avoid these embrittlement problems as material of construction for the reactor.

6. Why is methane purged using the gas purge stream from the phase separator?

Ans: The reaction kinetics dictate the maximum concentration of methane in the gas stream entering the reactor. Therefore, to achieve maximum conversion, methane is purged.

References:

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Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

Lecture 22: Phenol from Cumene and Toluene

22.1 Introduction

- Phenol is one of the most important petrochemicals. Ranging from solvents to polymers, phenol is required for several petrochemical processes as an important raw material.
- Phenol can be produced from many sources such as
    o Cumene
    o Toluene
    o Benzene
- Depending upon these raw materials, various chemical transformations and underlying physical principles apply.
- In this lecture, we discuss upon the process technology associated to Phenol production from Cumene and Toluene

22.2 Phenol production from Cumene

22.2.1 Reactions

- **Peroxidation:** Cumene + Air → CumeneHydroperoxide
- **Hydrolysis:** CumeneHydroperoxide + H_2SO_4→ Phenol + Acetone

22.2.2 For Peroxidation

    o Aqueous emulsion is prepared using emulsification agents
    o Operating conditions: Normal T & P
    o Emusification agent: NaOH (Alkali)

22.2.3 For Hydrolysis

    o 10 – 25 % H_2SO_4 (Aqueous) is used
    o Operating conditions: $55 – 65^oC$ and atmospheric pressure conditions

22.2.4 Process Technology (Figure 22.1)
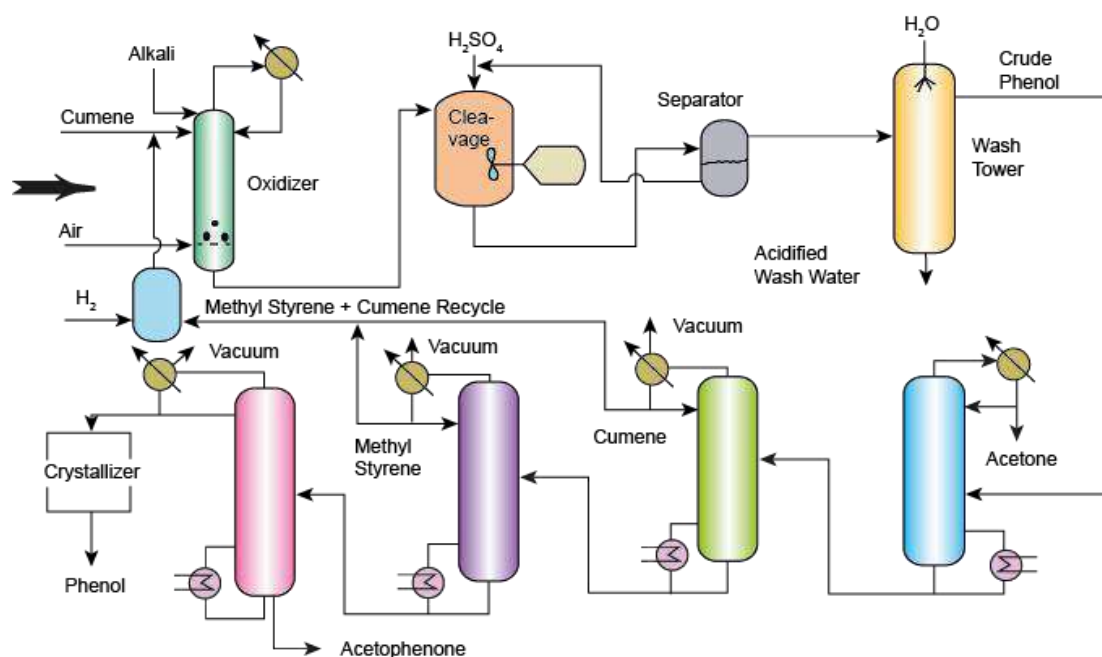
Figure 22.1 Flow sheet of Phenol production from Cumene

- Fresh cumene is mixed with hydrogenated unreacted cumene, cumene + alpha methyl styrene (recycle streams) .
- The pre-purification step involves converting unsaturates such as alpha methyl styrene and others to saturates. This is done by using nickel catalyst at $100\,^{o}C$ and feeding hydrogen to the pre-purification reactor. The product from this unit then mixes with the fresh cumene.
- The fresh cumene and processed cumene and alpha methyl styrene are fed to the oxidation reactor. The oxidation reactor refers to a gas liquid reaction between air (Oxygen) and the cumene.
- An emulsion of cumene is prepared in the oxidation reactor by adding alkali to it.
- pH is maintained in the range of 8.5 – 10.5 to suit good emulsification conditions.
- After reaction, vent gases are condensed and recycled back and the product is sent to a cleavage unit.
- The cleavage unit consists of a stirrer and is fed with fresh and recycled H_2SO_4 aqueous solution to enable the hydrolysis of cumenehydroperoxide.
- The product streams from the cleavage unit enter a settler (phase separator) which upon gravity settling yields two streams namely the acid rich aqueous stream and the phenol rich organic stream.
- The aqueous stream consists of the sulphuric acid and is sent back to the cleavage unit as a recycle stream.
- The organic stream consists of cumene (unreacted), phenol (product), acetone (side product), alpha methyl styrene (side product) and acetophenone (side product).

- The organic stream from the gravity settler unit then enters a scrubber fed with water. In this operation, water extracts the remaining acids in the organic stream and produces crude phenol stream. Water leaving the unit consists of acidified wash water.
- The crude phenol then enters a distillation unit that separates acetone from the other components.
- The bottom product from this distillation column enters a vacuum distillation column that produces cumene as a top product.
- The bottom product from the distillation column enters another vacuum distillation unit to produce alpha methyl styrene.
- The bottom product of this distillation column enters the final vacuum distillation unit to produce phenol as top product and acetophenone as the bottom product.

22.2.5 Technical questions

1. Why unsaturates are saturated before entering the oxidization reactor?

Ans: Unsaturated compounds will produce compounds other than cumenehydroperoxide. Since cumenehydroperoxide will only convert to phenol but not others, the product quality will drastically reduce if unsaturates are available in the feed stock.

2. What is the basic advantage of emulsification?

Ans: A gas liquid reaction requires maximum interfacial area to enhance reaction rates. Usually gas is sparged through liquid. But in this case, the liquid itself is emulsified so that the interfacial area can be even further enhanced.

3. Are there any safety issues related to the oxidation reactor?

Ans: Yes, cumenehydroperoxide is explosive after a certain minimum concentration. Therefore, all designs shall ensure that this component should not get accumulated beyond a specified concentration in any section of the units.

4. Why are the vent gases recycled back?

Ans: The vent gases in addition to N_2, unreacted O_2 will consist of hydrocarbons as the hydrocarbons could escape to the vapour phase due to their low boiling points even at room temperature. Therefore, these hydrocarbons including cumene are recycled back by using a condenser at the top.

5. **Suggest a technology for processing acidified wash water from environmental perspective?**

Ans: The acidified wash water can be neutralized using NaOH to obtain NaCl in these waters. Eventually, the NaCl rich solution can be concentrated using multiple effect evaporators to reduce the huge water problems. Near zero discharge is difficult for such cases.

6. **Why is alpha methyl styrene also recycled back to the reactor via hydrogenator?**

Ans: Alpha methyl styrene can be hydrogenated to convert to cumene. This is because alpha methyl styrene consists of a double bond in the alkyl group attached to the benzene ring. Therefore, by hydrogenation we convert unsaturated compound to cumene and this way it is recycled back to the reactor.

7. **Why there is sulphuric acid even after gravity settling in the organic phase?**

Ans: This is a basic problem of equilibrium separation factors for the sulphuric acid, as the acid has propensity to remain maximum in the aqueous phase but also to a little extent in the organic phase.

8. **Why vacuum distillation is required for all three distillation columns?**

Ans: To the best of the instructors knowledge, all organic compounds form azeotropes with others at atmospheric pressure when fractionated. Therefore, to bypass the formation of azeotrope, the pressure of the system is reduced which enhanced the relative volatility and eliminates the formation of the azeotrope. Further justification of this is available in the following azeotrope data bank:

a) Phenol-acetophenone forms an azeotrope with 7.8 wt % of phenol at 202 $^{\circ}$C and 1 atm pressure.
b) Alpha methyl styrene-phenol forms an azeotrope with 93 % of alpha methyl styrene at 162 $^{\circ}$C and 1 atm.

When vacuum distillation is considered, relative volatility of the mixture is improved and this improvement bypasses the azeotrope formation. Hence, purer products can be obtained.

9. **Don't you think water will also enter crude phenol?**

Ans: Yes, water also enters crude phenol as solvent loss in the wash tower will provide some water into the crude phenol stream. But its concentration is not significant when compared to the concentration of the organics.

22.3 Phenol from Toluene Oxidation

22.3.1 Reactions

Oxidation to Benzoic acid

- o Toluene + Oxygen → Benzoic acid + Water
- o Catalyst: Cobalt Naphthenate
- o Operating conditions: 150 °C and 3 atms
- o Exothermic reaction

Oxidation of Benzoic acid to phenol

- o Benzoic acid + Oxygen → Phenol + CO_2
- o Catalyst: Cupric Benzoate
- o Operating conditions: 220 °C and 1.3 – 1.7 atms
- o This reaction is also exothermic

22.3.2 Process technology (Figure 22.2)
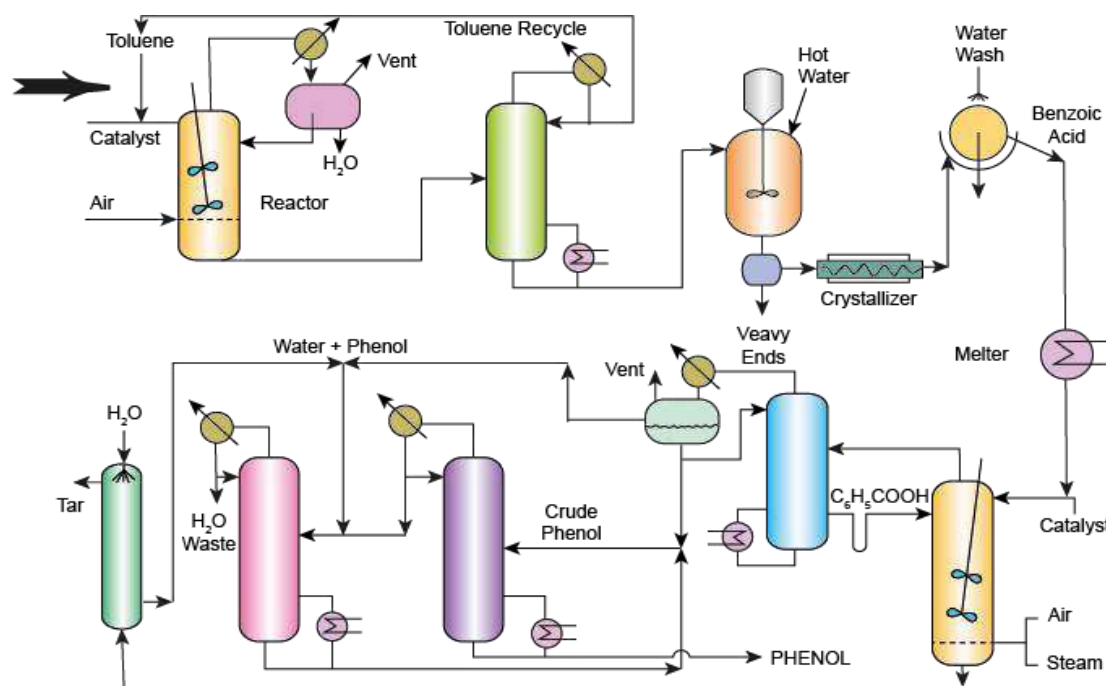
Figure 22.2 Flow sheet of Phenol manufacture from Toluene Oxidation

- Fresh and recycled toluene first enter the oxidation reactor
- The oxidation reactor is a gas-liquid reactor in which air is sparged through a column of liquid (toluene)
- To reduce side reactions, toluene is used as a limiting reactant
- The catalyst is fed to the reactor along with the toluene stream
- After reaction, several products are formed including undesired impurities such as benzaldehyde, benzyl alcohol, benzyl benzoate, CO and CO_2
- The reactor is facilitated with vent after cooling and partial condensation of the air mixed hydrocarbon vapour stream.

- The liquid product from the reactor then enters a distillation column which separates toluene from the other organics
- The organics then enters a hot water wash unit where hot water extracts benzoic acid. All other impurities don't dissolve in water and leave the wash unit as heavy ends
- The benzoic acid rich hot water stream is sent to a crystallizer where benzoic acid crystals are formed.
- The benzoic acid crystals are once again washed with water to obtain benzoic acid crystals
- The benzoic acid crystals are then melted and fed to the second oxidation reactor
- The second oxidation reactor is fed with air and cupric benzoate catalyst. Steam is also added to the reactor so as to enhance the temperature of the reactants quickly.
- Once again gas liquid reaction is facilitated. Cooling is facilitated by using a jacket or cooling tubes.
- From the reactor two phases are obtained namely vapour and liquid
- The vapour and liquid both consist of phenol and therefore, both are subjected to series of separation steps to extract phenol and enrich the same.
- The vapour enters a fractionating tower which separates the unreacted benzoic acid from other compounds. The top product is obtained after partial condensation followed by phase separation. The phase separator produces three streams namely the vent stream (that consists of N_2, CO and CO_2), the aqueous water + phenol stream and the organic crude phenol stream. The crude phenol stream is partially sent as a reflux to the fractionators and withdrawn as a product as well.
- The bottom product from the second oxidation reactor consists of organic compounds and is sent to water wash. After water wash, heavy compounds such as tar are removed and phenol is dissolved in water. This water + phenol mixture is mixed with the water + phenol mixture obtained from the fractionators separating benzoic acid.
- The crude phenol is fed to a fractionator to obtain purified phenol as bottom product and phenol + water mixture as a top product. The top product here is an azeotrope.
- The phenol + water coming from three different sources is allowed to enter a distillation column that generates water waste as a top product and a crude phenol stream as a bottom product.

22.3.3 Technical questions

1. **Why are benzoic acid crystals again subjected to water wash?**

Ans: The benzoic acid crystals could have some water soluble impurities despite having water wash. This is because of the fact that in real life, infinite separation factors don't exist and components do get distributed in both phases. Therefore, an additional water wash facilitates the removal of these impurities.

2. **Why phenol enters both bottom and top product?**

Ans: The trick in the operation of the second oxidation reactor is to maintain temperature and pressure such that benzoic acid leaves the unit as vapour. This way, benzoic acid can be easily fractionated and sent back to the reactor. However, this has a limit as well i.e., phenol gets evenly distributed between the vapour and liquid phases.

3. **Is there any opportunity for energy integration in the process?**

Ans: Yes, the vapours from the reactor can be heat integrated with the reboilers in the toluene column or any other reboilers in the other two columns.

4. **What exactly happens in the column that is fed with phenol + water mixture, given the fact that phenol forms an azeotrope with water?**

Ans: At atmospheric pressure, phenol forms an azeotrope with water at about 9.4 wt % phenol and 90.6 wt % water. Therefore, crude phenol column shall produce a water rich stream at the top which is the azeotrope and the pure phenol product as the bottom product. From the VLE data (not shown here), it is also apparent that from about 10 wt % phenol to about 90 % phenol, the relative volatility value is pretty low and after 90 % phenol in the feed solution, the relative volatility increases significantly.

Therefore, it makes sense now to understand that crude phenol fed to the first tower splits into azeotrope at the top (with 9.4 wt % phenol) and a purer phenol product at the bottom. Eventually, the phenol + water stream entering the second unit along with the azeotrope composition is improved substantially in its composition to move away from the azeotropic composition (with more phenol in water) and hence, it should again tend to produce a purer phenol product and a waste water product at the top. The waste water product could be again an azeotrope of a different class.

Again, if we alter the pressures of these columns, the VLE data (not shown here) will reduce the phenol composition in the wastewater stream and that's what would be probably considered to extract maximum phenol using the distillation technology.

Alternatively, extractive distillation process can be used in which toluene can be used as a solvent to alter the relative volatility. Probably, this process

is more common presently in the industry than the process outlined in this lecture.

References:

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

Lecture 23: Phenol from Benzene

23.1 Introduction

Phenol can be manufactured from Benzene using several ways

- o Benzene hydrochlorination to form Benzyl chloride followed by hydrolysis of benzyl chloride to form phenol.
- o Benzene chlorination to form benzyl chloride which is transformed to sodium benzoate and eventually to phenol using NaOH and HCl
- o Benzene sulfonate process: In this process, benzene is convered to benzene sulfonate using sulphuric acid and eventually through neutralization, fusion and acidification, the benzene sulfonate is gradually transformed to phenol.
- o In this lecture, we restrict our discussion to the manufacture of phenol from
  - Benzene hydrochlorination route
  - Benzene from chlorobenzene route

23.2 Phenol using Hydro chlorination route

23.2.1 Reactions

First reaction

- o Benzene + HCl + Oxygen $\rightarrow$ Benzyl chloride + Water
- o Catalyst: $FeCl_3$ + $CuCl_2$
- o Operating conditions: $240^{o}C$ and atmospheric pressure

Second reaction

- o Benzyl chloride + water $\rightarrow$ Phenol + HCl
- o Catalyst: SiO_2
- o Here, HCl is regenerated and will be recycled.
- o Operating conditions: $350^{o}C$ and atmospheric pressure

23.2.2 Process Technology (Figure 23.1)
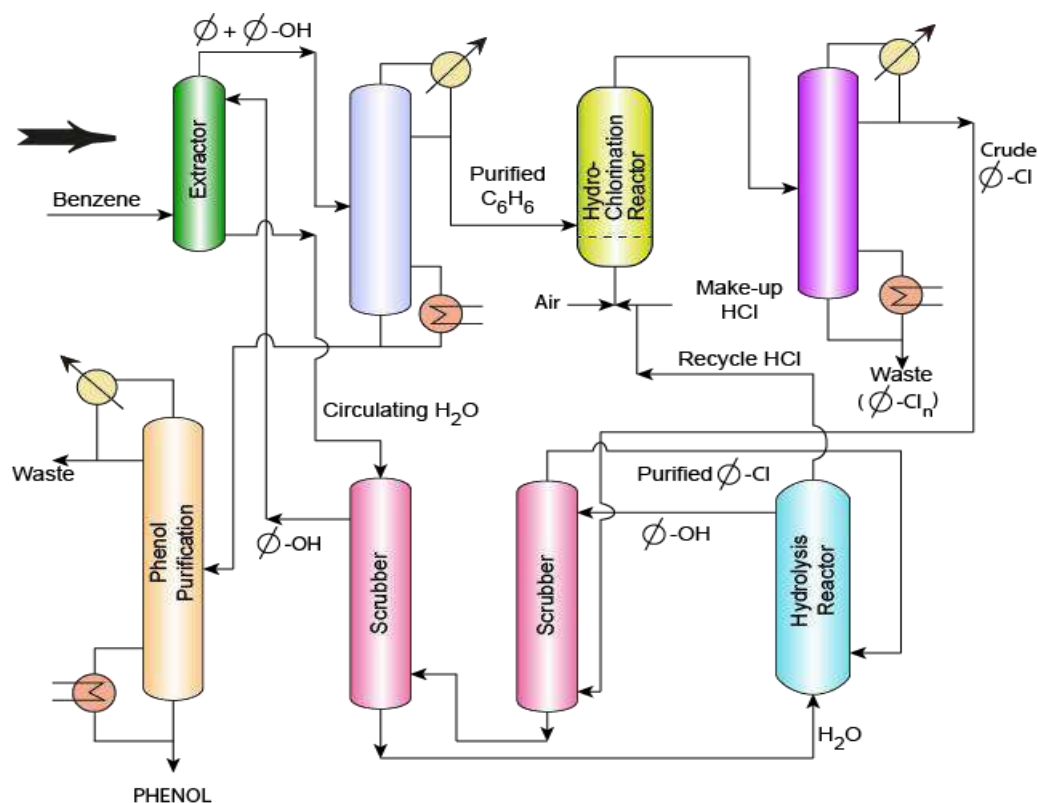
Figure 23.1 Flow sheet of manufacture of phenol using hydro chlorination route

- In this process, Benzene is used to extract phenol from phenol +water mixture. This unit is termed as an extraction unit (liquid liquid extraction principle). Therefore, this unit takes up fresh benzene and phenol + water mixture and produces two streams namely water stream (bottom product) and benzene + phenol stream (top product). The water stream is fed to a scrubber unit (i.e., Unit B that will be described later).
- Then onwards, the organic mixture is fed to a distillation column that produces purer benzene as the top product. The bottom product is phenol with other impurities.
- The bottom phenol rich product is sent to the phenol fractionator to obtain waste product as top product and pure phenol as bottom product.
- The purer benzene then enters the hydrochlorination reactor in which a mixture of HCl and O_2 is fed at 220 ^{o}C. Under these conditions, Benzene will be also in vapour state.
- Therefore, the reactor is a gas solid reactor.
- The conversions are pretty low and not more than 20 % of the benzene is converted to benzyl chloride.
- Eventually, the products are sent to two fractionators that separate unreacted benzene, crude benzyl chloride and poly benzyl chlorides as various products. The unreacted benzene is sent back to the hydrochlorination reactor as a recycle stream.

- The crude benzyl chloride then enters an absorber unit A where phenol is used to purify the benzyl chloride from other organic compounds (such as benzene and polybenzyl chlorides).
- The purified benzyl chloride stream then enters the hydrolysis reactor in which water is passed along with benzyl chloride over the silica catalyst. The reactor itself is a furnace with catalyst loaded in the tubes and hot fuel gases are circulated in the shell to obtain the desired higher temperature.
- Under these conditions, both reactants are in vapour state (with the benzyl chloride boiling point of $179^{o}C$) and therefore, the reaction is also a gas solid reaction.
- After hydrolysis reaction, the product vapors are sent to a partial condenser that separates the HCl from the organic phase.
- The HCl is recycled to the hydrochlorination reactor.
- The phenol rich product stream is sent as a solvent for the scrubber (unit A) that purifies crude benzyl chloride to purer benzyl chloride. The bottom product from the scrubber (i.e., unit A) enters another scrubber (unit B) that receives water from the extractor.
- The unit B enables washing of the phenol to remove any water soluble impurities. The water from the unit B enters the hydrolysis reactor.

23.2.3 Technical questions

1. **Discuss the merits of the process from waste minimization perspective?**

In this flow sheet, the raw material itself is used as a solvent to extract the product. Also, one of the reactants (water) is used as another absorbent. The usage of raw materials and intermediates in the process as absorbents itself is very attractive from waste minimization perspective as waste water streams are not produced significantly. Also, the solvent used is benzene itself which reduces the complexity of using another solvent and subsequent safety related issues.

2. **Comment upon the corrosion issues of the processes?**

HCl is very corrosive and therefore, enough precaution shall be taken towards the plant and process design.

3. **What impurities are removed in the unit B scrubber using water?**

Benzyl chloride has limited solubility with water. Therefore, it is expected that benzyl chloride is dissolved to some extent in the unit B scrubber where benzyl chloride as an impurity in minor amounts can be removed from phenol.

4. **Why do you think make up HCl is required?**

Some HCl gets reacted to form poly benzyl chlorides. Some HCl gets lost as a vapour in various operations. Therefore, some make up HCl is definitely required in the process though, HCl is largely regenerated.

5. Compared to other Benzene based phenol production processes, what advantage this process has towards phenol production?

In this process, very little quantities of other raw materials are required. These are HCl. Air is inexpensive and is freely available. Therefore, the plant can be build easily as many other auxillary processes are not required provided benzene is available in large quantities in the vicinity. However, one basic drawback is that the fixed costs of units will be high in this case as HCl is involved.

23.3 Phenol from Chlorobenzene route

23.4 Reactions

- There are three reactions to convert benzene to phenol using chlorination route

23.4.1 Chlorination

- o Benzene + $Cl_2 \rightarrow$ monochloro benzene
- o Operating temperature: 85 ^{o}C
- o Catalyst: Fe or $FeCl_3$ catalyst

23.4.2 Causticization

- o Benzyl chloride + NaOH $\rightarrow$ sodium benzoate
- o NaOH is in aqueous media
- o Operating conditions: 425 ^{o}C and 350 atms
- o Exothermic reaction

23.4.3 Hydrolysis

- o Sodium benzoate + HCl (aq) $\rightarrow$ Phenol + NaCl (aq)
- o Operating conditions: Nothing specific

23.4.4 Process Technology (Figure 23.2)
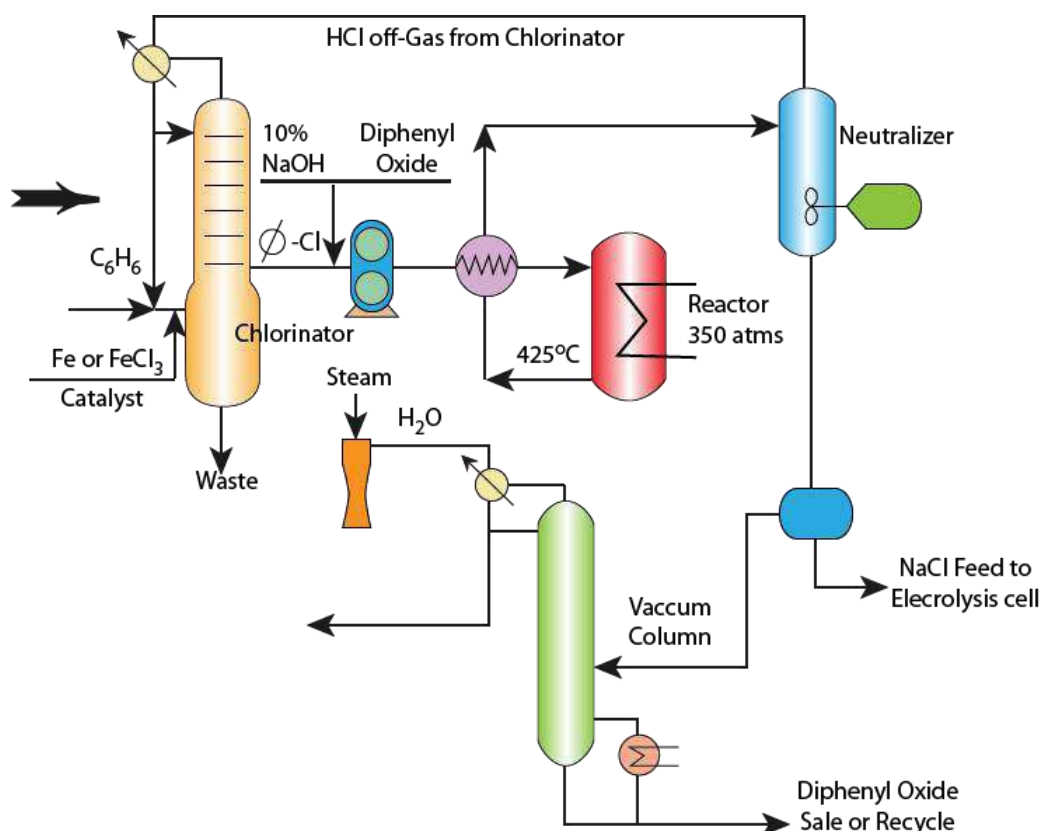
Figure 23.2 Flow sheet of manufacture of phenol from chlorobenzene route

- Benzene is first dried. Dry benzene and FeCl₃ catalyst enters the chlorination reactor
- After the solid-gas-liquid reaction, the products are further heated up to enter a fractionator
- The fractionator separates benzene as a top product and monochloro benzene as the bottom product. The top product also consists of HCl off gas that is obtained as the vapour stream from the partial condenser.
- The benzene is further cooled and sent back to the reactor and also as a reflux to the fractionator.
- The bottom product monochloro benzene is mixed with 10 % NaOH solution and diphenyl oxide to enter a high pressure pump followed with heat integrated heat exchanger that pre-heats the feed to higher temperature.
- The feed then enters the causticization reactor which has cooling water tubes to control the temperature.
- The product stream is cooled using heat integrated exchanger and then enters a neutralizer that is fed with the HCl obtained from the fractionator partial condenser.
- After neutralization, the product phenol is separated from the aqueous phase using gravity settling principle.

- The organic layer rich in phenol is sent to a vacuum column to separate the phenol from diphenyl oxide (bottom product). The bottom product is partially recycled to enter the cauticization reactor.

23.4.5 Technical questions

1. **Why is diphenyl oxide added to the causticization reactor?**

Ans: To suppress the formation of more diphenyl oxide at the causticization reactor.

2. **How can you regenerate Cl_2 for this process?**

Ans: Brine when subjected to electrolysis will produce Cl_2 and NaOH. Therefore, electrolytic process will be beneficial to produce Cl_2 and us e it to the requirements as well as produce excess NaOH and sell it too. This way, the process becomes more commercially attractive.

3. **Can the chlorinator and the fractionators be integrated into a single unit where the bottom section is a reactor and the top section is a fractionator?**

Ans: Yes, this is possible, as after chlorination the products are in vapour state and they can enter the trays above the reactor section of a single column. The heavier product in this case is the monochlorobenzene from fractionation perspective and this is the product as well. Therefore, integrating both reactor and separator in a single unit can reduce the costs significantly.

References:

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

Lecture 24: Styrene and Phthalic Anhydride Production

24.1 Introduction

- In this lecture we present the process technology for the production of styrene and pthalic anhydride
- Styrene is produced from benzene via the ethylbenzene route followed by dehydrogenation
- Pthalic anhydride is produced from Napthalene and o-Xylene
- We first present the process technology associated to styrene production

24.2 Styrene

24.2.1 Reactions

Alkylation of Benzene

- o Benzene + ethylene $\rightarrow$ Ethyl benzene
- o Catalyst: $AlCl_3$ granules
- o C_2H_5Cl provides hydrogen and chlorine free radicals
- o Operating conditions: 95^oC and 1 atm pressure
- o Reaction is exothermic

Dehydrogenation of ethylbenzene

- o Ethylbenzene $\rightarrow$ Styrene + Hydrogen
- o Reaction is endothermic
- o Catalyst: SnO or FeO
- o Operating conditions: 800^oC

24.2.2 Process technology (Figure 24.1)
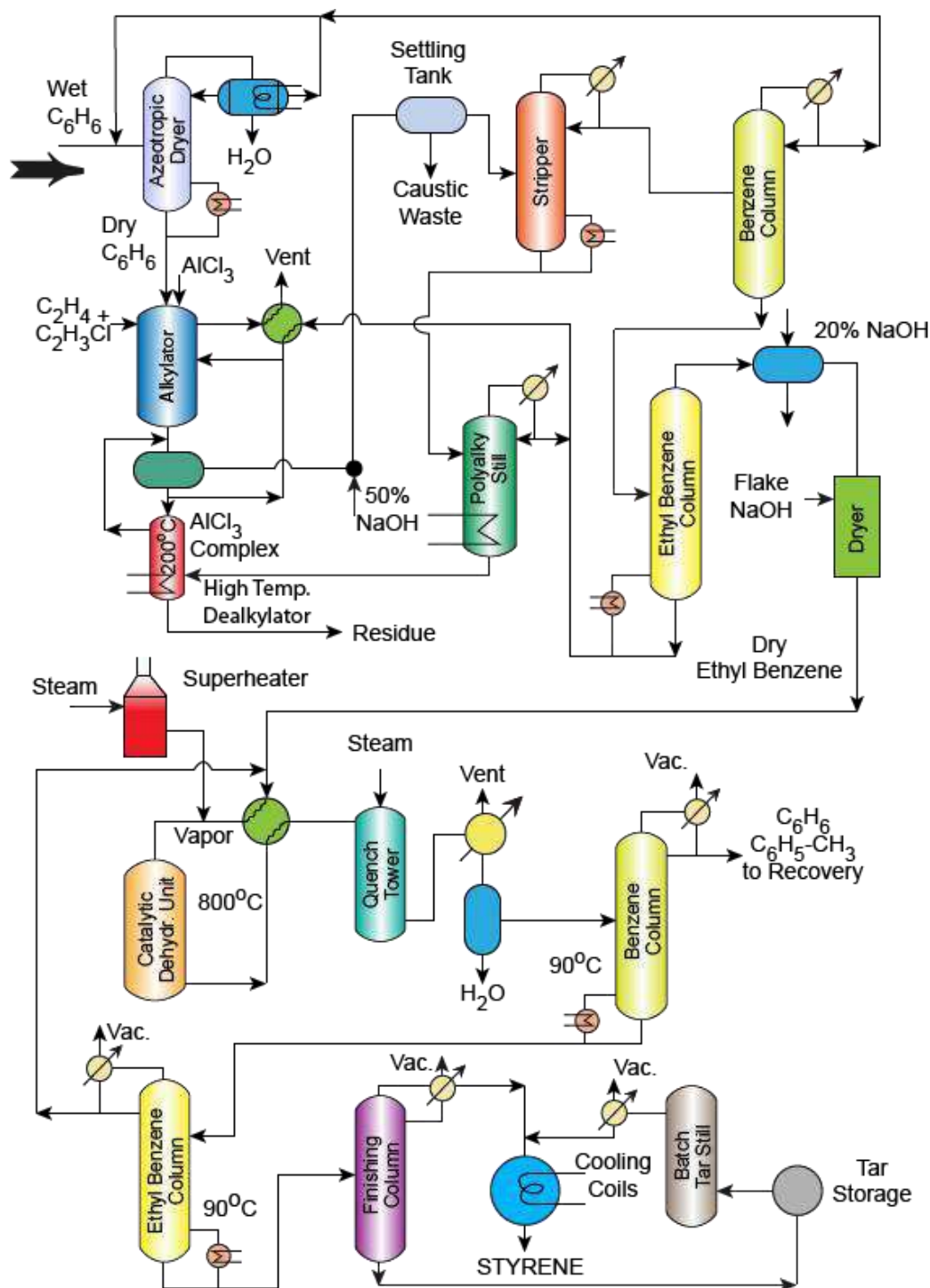
Figure 24.1 Flow sheet of manufacture of styrene

- The process consists of two separate reactor-separator-recycle networks in which one corresponds to the ethylbenzene flow sheet and the other corresponds to styrene flowsheet.
- We first present the flowsheet for ethylbenzene production
- Benzene (wet) is sent first to an azeotropic distillation unit that separates water and produces dry Benzene. Dry Benzene is required so as to avoid

unnecessary reactions in the alkylation reactor as well as damage to the catalyst as alumina can get formed.

- Dry Benzene + Ethylene + Ethyl chloride + AlCl$_3$ enter the alkylator catalyst
- The reactor could be a jacketed tower where water is used as a cooling fluid in the jacket to control the reactor temperature.
- The reactor produces two products namely uncondensible gases and the liquid product in which AlCl$_3$ complex is available. This complex needs to be regenerated and sent back to the alkylator.
- The alkylator product is sent to a cooler which upon cooling to 40°C separates the aluminium chloride complex stream from the product stream. The other stream from the cooler is the ethylbenzene rich product stream.
- The aluminium chloride stream is partially recycled to the alkylator so as to maintain the required catalyst requirements. The other portion of the AlCl$_3$ complex is sent to a dealkylator unit in which the feed is heated to 200 ^{o}C. By doing so, the polyethylbenzenes formed in the alkylator are converted to benzene and ethylbenzene (cracking reaction).
- The benzene and ethylbenzene are returned to the cooler.
- The delkylator produces a residue product consisting of tar + AlCl$_3$ mixture.
- From this mixture, AlCl$_3$ is recovered using water extraction as AlCl$_3$ is soluble in water. From there AlCl$_3$ is recovered from the water and returned back to the alkylation reactor.
- The product stream from the cooler consisting of ethylbenzene is mixed with 50 % NaOH to remove acidic impurities. Eventually, after settling waste is eliminated.
- The purified ethylbenzene then enters a stripper that separates ethylbenzene + benzene from the polyalkylbenzenes. The polyalkylbenzenes are sent to a polyalkyl still that separates the benzene + ethylbenzenes from the polyalkylbenzenes (bottom product). The polyalkyl still is operated under vacuum. The polyalkylbenzenes are fed to the dealkylator and the benzene + ethylbenzene rich stream is sent to a heat integrated exchanger that extracts heat from the vent gases and then eventually enters the alkylation reactor.
- The top product from the stripper is ethylbenzene + benzene and it enters a benzene column that separates wet benzene from crude ethylbenzene. The wet benzene is recycled to the azeotropic dryer where it is mixed with fresh wet benzene to enter the azeotropic dryer.
- The crude ethylbenzene is further purified in a fractionator where the bottom product (with benzene) is mixed with the top product of the polyalkyl still. Thereby, the stream enters the heat integrated exchanger.
- The ethylbenzene is further subjected to caustic wash and finally it is sent to a dryer to produce dry ethylbenzene.
- We now move to the dehydrogenation flow sheet.
- The ethylbenzene (dry) is heated with superheated steam to enter the catalytic dehydrogenator. Excess steam is used in this process. The feed pre-heating is

carried out using the product vapour stream. The reaction is gas phase catalytic reaction.

- The vapour stream after cooling with the feed stream in a heat integrated exchanger is fed to a quench tower using steam quenching.
- After quenching, partial condensation of the quenched vapors produces three streams one being the vapour vent, the other being water and the third being the organic phase rich with styrene.
- The styrene rich stream is sent first to a benzene column to recover the benzene + toluene and this is sent to a benzene-toluene distillation column to recover benzene. The benzene is sent to the azeotropic distillation unit as a raw-material.
- The bottom product from the benzene column enters an ethylbenzene column which separates ethylbenzene from the styrene stream. The ethylbenzene stream is mixed with the dry ethylbenzene to enter the catalytic dehydrogenator.
- The bottom product from the ethylbenzene column is the styrene enriched stream and this is sent to the finishing column where styrene is further purified from unwanted impurities such as tar. The tar is further batch distilled to recover styrene from the tar. The styrene finishing column also produces styrene product. Both styrene products from batch still and styrene finishing column are mixed and cooled to store as styrene product.
- All three columns namely benzene, ethylbenzene and finishing columns are operated under vacuum.

24.2.3 Uses :

Styrene is mainly used for making plastic toys and model kits. Moreover, housing for machines as well as refrigerator doors and air conditioner cases are made of styrene.

24.2.4 Technical questions

1. **Explain how azeotropic distillation unit functions to convert wet benzene to dry benzene?**

Ans: Wet benzene upon heating produces a heterogenous azeotrope at the top and dry benzene at the bottom. Therefore, the unit upon condensation of the top vapors produces two streams namely water and benzene rich wet stream which is recycled back as the reflux stream.

2. **Why is the benzene + ethylbenzene stream returned back to the cooler but not the alkylation reactor?**

Ans: The alkylation reactor should be fed with very important chemicals only. It is possible that the temperatures prevailing in the dealkylator could enable the loss of polyalkylbenzenes to the vapour. Therefore, there is no point in feeding this stream to the alkylator. Instead the stream is sent to the

cooler so that any polyalkylbenzenes could be condensed back and sent to the dealkylator again.

3. Why the AlCl₃ complex is partially returned to the reactor?

Ans: To maintain the required catalyst conditions. If not, then $AlCl_3$ fresh has to be provided to the reactor as $AlCl_3$ forms a complex with the hydrocarbons and would leave the alkylator along with the product streams.

4. Why do polyalkylbenzenes enter the ethylbenzene rich product?

Ans: This is the basic problem of the equilibrium separation factors of polyalkylbenzenes between the $AlCl_3$ complex rich product and the ethylbenzene rich product. Since sharp distribution of these compounds is not possible, polyalkylbenzenes get distributed between both these organic phases.

5. Why there are ethylbenzene + benzenes still available in the bottom product of the stripper?

Ans: The answer is same as that of question 3 i.e., the phase equilibrium limitations enable the availability of both benzene + ethylbenzene in the polyalkylbenzene stream.

6. Why the benzene is wet from the benzene column?

Ans: This is because caustic wash operation enabled the contact with water and some water will enter the organic phase due to phase equilibrium of water with the organic phase. This water therefore enters the benzene stream from the benzene column.

7. Why caustic wash followed by drying is carried out is carried out for the ethylbenzene stream?

Ans: Caustic wash removes any undesired impurities where as dryer removes the water. Both water and acid are important compouds which if not eliminated contribute significantly to side reactions during the heating process with superheated steam. Therefore, totally dry and acid free conditions are targeted for ethylbenzene.

8. Why vacuum is used in the polyalkyl still unit?
a) To enhance relative volatility of components that can be easily removed
b) To reduce dissociation of polyalkyl components in the column

9. Why steam quenching but not water quenching is adopted?

Ans: Water quenching can give rise to additional reactions. Steam quenching does not allow condensation and hence is safe in that sense not to trigger any unwanted reactions of the styrene and ethylbenzene.

10. What gases are removed in the vent following quenching tower?

Ans: Gases such as hydrocarbons that are resultant of undesired cracking are removed as non-condensibles in the partial condenser. These are vented out.

11. Why tar consist of styrene?

Ans: Styrene being organic compound has affinity to get dissolved in the tar. Therefore, the batch still is used to extract styrene from the tar.

12. Why vacuum is used for the separation of benzene, toluene, ethylbenzene and styrene?

Ans: All these compounds are closely boiling systems. By going for vacuum distillation, we are able to enhance the relative volatility of the components and hence better separation. The increasing order of higher vacuum levels is applied for these three columns in series i.e., benzene column, ethylbenzene column and finishing column.

24.3 Pthalic Anhydride

24.3.1 Reactions

- Basic raw material is Naphthalene or o-xylene
- Naphthalene $+ O_2 \rightarrow$ Pthalic anhydride $+ H_2O + CO_2$
- O-Xylene $+ O_2 \rightarrow$ Pthalic anhydride $+$ Water
- Side reaction products: Maliec anhydride, Complete combustion products: CO_2 and water
- Catalyst: Vanadium pentoxide
- Operating conditions: 340 - 385 ^{o}C
- Reaction is highly exothermic

24.3.2 Process technology (Figure 24.2)
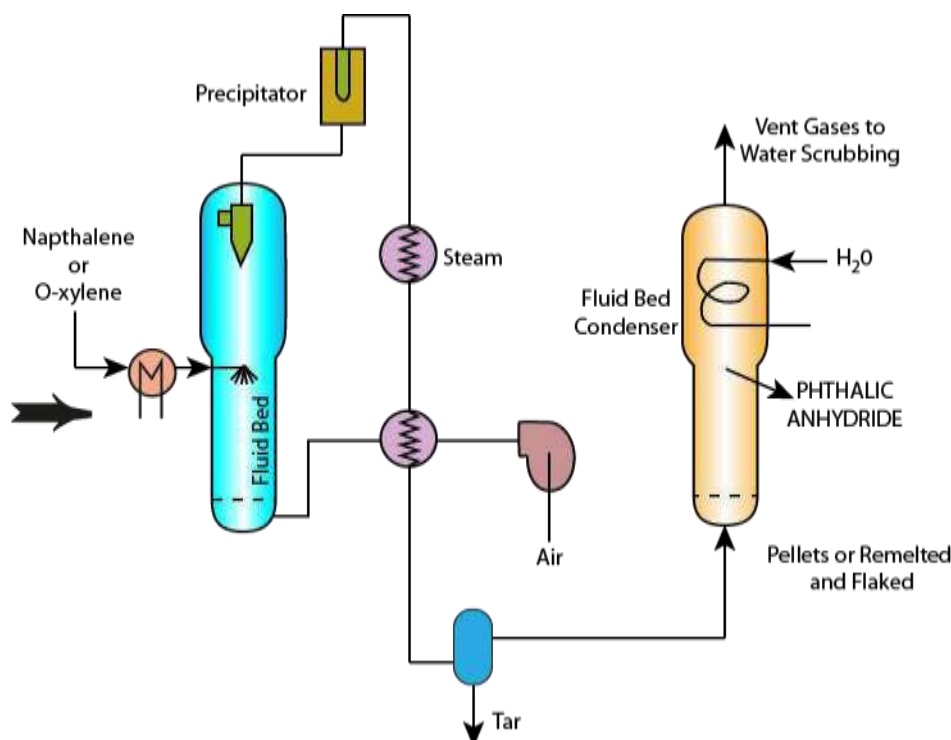
Figure 24.2 Flow sheet of manufacture of phthalic anhydride

- In this lecture, we present the usage of both multitubular reactor or fluidized bed reactor for the production of pthalic anhydride.
- While multitubular reactor is demonstrated for o-xylene, the fluidized bed reactor is demonstrated for naphthalene
- Ortho xylene to Pthalic anhydride (Fixed bed reactor)
  - o Air is filtered and compressed to enter a air pre-heater
  - o O-xylene is also separately vaporized to generate the o-xylene vapour
  - o The o-xylene and compressed air enter a multitubular reactor. The reactor design is essentially a shell and tube set up where the catalyst is held in the tubes.
  - o Salt solution is circulated to cool the reactor in the shell side. The salt solution that gets heated up is sent to a waste heat recovery boiler to generate process steam.
- Napthalene to Pthalic anhydride (Fludized bed reactor)
  - o Napthalene and air are allowed to enter the fluidized bed. Napthalene in molten form is sprayed on to the fluidized bed of catalyst in air.
  - o The operating temperature is about 600 ^{o}C in this case.
  - o Eventually, the vapors (+ catalyst dust) enter a cyclone unit to separate the catalyst particles and the vapors from the cyclone separator.
  - o The fluidized bed is supplemented with cooling tubes in which salt solution is circulated to eventually obtain steam from the waste heat recovery boiler.

- o The fluidiized bed reactor does not provide higher yields of maleic acid
- Separation network (common for both fluidized bed reactor and packed bed reactor technologies)
  - o The reactor effluent (vapour) is sent to a steam generator where the vapors are cooled to condense the pthalic anhydride and the boiler feed water is converted to steam. Here, pthalic anhydride is just cooled to a temperature slightly above its dew point.
  - o After cooling the pthalic anhydride, the condensed pthalic anhydride is sent to switch condensers that enable the generation of crude product. The switch condensers enable the generation of pthalic anhydride solid product.
  - o The condensers generate maleic anhydride and fumaric acid as the non-condensibles from the switch condensers.
  - o The crude product is subsequently melted, distilled and sent to a crystallization process or pellization process to obtain high purity product.

24.3.3 Uses :

Phthalic anhydride is used as a versatile intermediate in organic chemical reactions, mainly because it is bifunctional and is cheaply available. It may also be used in the manufacture of phathalate plasticizers like DOP, DEP etc.

24.3.4 Technical questions

1. **Why is the fluidized bed operated at a higher temperature?**

Ans: The advantage of fluidized bed reactor is to achieve maximum mass transfer and if this principle is better exploited then it is also possible to alter the selectivity of the process. Therefore, fluidization bed is operated at 600°C so that no maleic anhydride is produced and a higher yield of pthalic anhydride is obtained.

2. **Is it justified to use spray of the feed in the case of fluidized bed reactor where as packed bed reactor received the vaporized feed stream?**

Ans: Well, since fludization involves better mass and heat transfer effects when compared to packed bed reactor and since fludized bed reactor is operating at a far higher temperature than the packed bed reactor, it is easy for us to understand that the sprayed feed (i.e., naphthalene) will vaporize instantaneously and will undergo the desired reaction. Also, it is worthy to note that for better facilitating these variations, the gas hour space velocity and air to feed ratio of the fluidized reactor is chosen totally different from those existing in the packed bed reactor.

3. How do switch condensers assist in generating the crude pthalic anhydride solid product?

Ans: The switch condensers operate like an on and off switch involving the crystallization of pthalic anhydride and once these crystals are formed they are allowed for partially melting the same (by offing the condensation process) and this way, the flakes melt from the condenser tubes to obtain as a crude pthalic anhydride.

When the crystallization is on, it implies that cooling fluid is circulated and when crystallization is off, then hot fluid is circulated. These are circulated in an on and off mode and hence we got the name as switch condensers.

4. Why are the switch condensers not called as switch crystallizers but switch condensers?

Ans: Here, the vapors are received above the dew point of the pthalic anhydride and they are subjected to cooling. Since phthalic anhydride is sublime (solid generating vapour), the crystallization process is called as switch condensation.

5. In the flowsheet shown, the non-condensible gases such as CO_2 are not shown to be vented out. Where do you think they will be vented out and why?

Ans: CO_2 is vented out along with non-condensible gases from the switch condensers. Other than this, there is no other place to remove the same as the product gases are sent to these units only. In case of packed bed reactor technology, the vent also consists of maleic anhydride and fumaric acid which are absorbed in a scrubber using water as a solvent.

References:

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

Lecture 25: Manufacture of Maleic Anhydride and DDT

25.1 Introduction

- In this last lecture for the petrochemicals module, we demonstrate the process technology for Maleic anhydride and DDT.
- Maleic anhydride is manufacture from benzene by butane oxidation
- DDT is a pesticide and is manufactured from benzene, chlorine and ethanol using sulphuric acid as a catalyst.
- We next present the process technology for maleic anhydride. Along with this compound, fumaric acid is also produced as another product.

25.2 Maleic anhydride &Fumaric acid

25.2.1 Reactions

- Benzene + O_2 (Air) $\rightarrow$ Maleic anhydride + H_2O + CO_2
- Reaction is exothermic
- Operating temperature is 400 – 500 ^{o}C
- Catalyst is V_2O_5
- For fumaric acid, the reaction is Maleic acid $\rightarrow$ Fumaric acid.
- Fumaric acid is an isomer of Maleic acid.
- HCl is used as a catalyst for the isomerisation reactor at normal pressure and temperature.

25.2.2 Process technology(Figure 25.1)
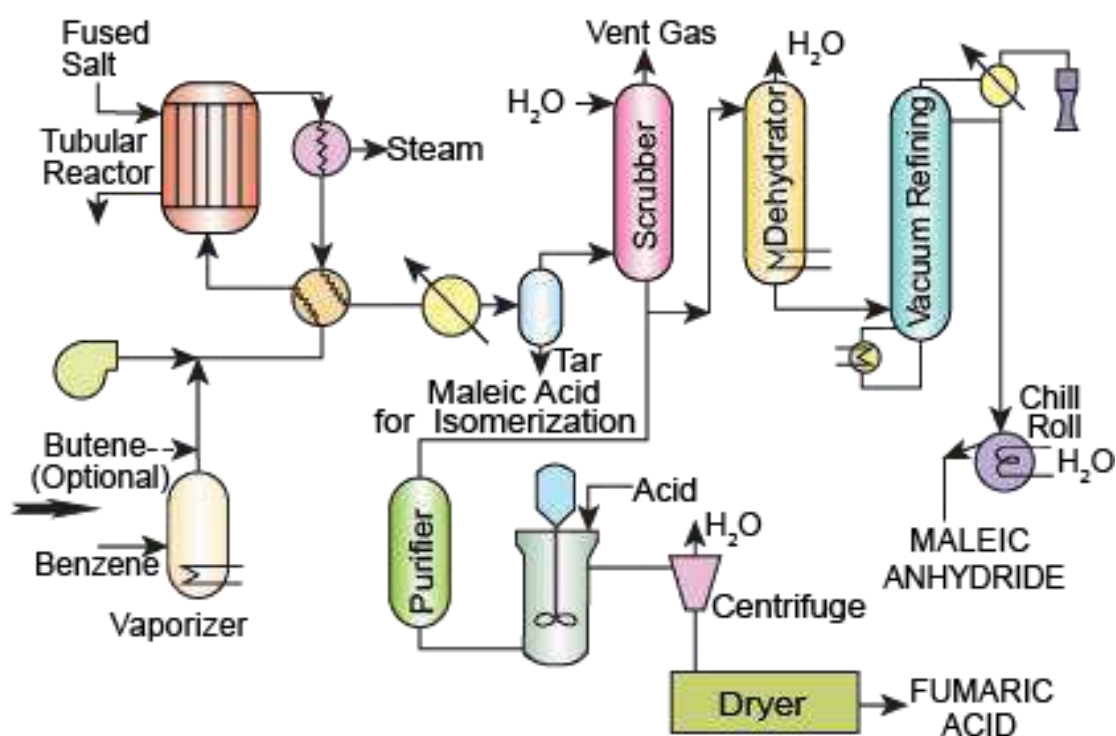
- The process technology is similar to phthalic anhydride production.
- Benzene or butane is first vaporized in excess air.
- Then the mixture enters the catalytic tubular reactor (with shell arrangement). The catalytic reactor is circulated with salt solution so as to absorb the heat generated using the reaction.
- The reactor products enter a waste steam recovery boiler where the boiler water is converted to steam.
- The product vapors eventually enter an integrated heat exchanger to exchange heat with the pre-heated feed stream.
- Eventually, the vapors are condensed followed with gravity settling to remove tar as a product in the gravity settling. The vapors then enter a water scrubber to obtain 40 % maleic acid solution. The leaving gases consist mainly of CO_2.
- The maleic acid from the absorber is partially sent to a dehydrator that removes water using azeotropic distillation principle. The purified maleic anhydride product is further sent to vacuum distillation to obtain the maleic anhydride product.
- The dilute maleic acid solution is partially sent to an isomerisation unit where HCl is used as the isomerisation catalyst.
- After reaction, the product is sent to a centrifuge that separates water from the fumaric acid.
- Eventually, fumaric acid is sent to a drier to obtain dry fumaric acid.

25.2.3 Uses :

Maleic anhydride can be used as a highly reactive and versatile raw material. It can be used in the manufacture of alkyd resins, which in turn are used for making paints and coatings. It can also be used in making agricultural chemicals like herbicides, pesticides and plant growth regulators.

25.2.4 Technical questions

1. **Whyisbenzene separately vaporized in excess air ?**

Ans. To avoid the formation of explosive compositions, benzene is separately vaporized and then mixed with air. The lower flammability limit of benzene-air mixture is 1.35 % and the upper flammability limit of benzene is 6.35 %. Therefore, with such low levels of flammability limits, heating the benzene in hot process air can keep the process safe. Directly generating benzene vapors and mixing it with air is more dangerous.

2. **Explain in brief how azeotropic distillation of maleic acid is carried out to generate maleic anhydride.**

Ans. The aqueous maleic acid is fed to the azeotropic distillation column which is fed with an azeotropic agent such as xylene. The water is removed along with xylene as overhead vapors as a minimum boiling heterogenousazeotrope as the top product and the bottom product is the

maleic anhydride. The heterogeneous azeotrope can be easily separated from the xylene with gravity settling principle and the recovered xylene is fed back to the distillation column as the reflux stream.

3. **Explain why waste steam recovery boiler is kept before heat integrated exchanger from the vapour products perspective**

Ans. The reaction is highly exothermic and heating the feed to a high temperature is not desired. Had it been so, the waste steam recovery boiler would be kept after the heat integrated exchanger. This way, we generate good quality process steam from waste heat recovery boiler.

4. **Explain how the usage of centrifuge is justified from process technology perspective**

Ans. From physical property data, the solubility of maleic acid and fumaric acids are 68 g/100 ml water and 0.63 g/100 ml water respectively. This indicates that while maleic acid is soluble in water, fumaric acid is not. Therefore, after isomerisation reaction, the fumaric acid solids rich solution is sent to a centrifuge so as to separate the solids from the water. This clearly indicates how physical properties play an important role in choosing the separation process.

5. **Can the process steam generated from the waste heat recovery boiler be also used for reboiler requirements in the azeotropic distillation unit, benzene vaporizer, vacuum distillation unit etc**. ?

Ans. Yes, this way we reduce the total utility requirements in the process. In fact the exact steam requirements (fresh) cannot be estimated unless we have a good idea of the total energy balances for the system.

6. **Why is vacuum distillation required for maleic anhydride refining ?**

Ans. Maleic anhydride tends to polymerize upon aging and heating. Therefore, heating the maleic anhydride in vacuum conditions reduces the boiling point. Also, maleic anhydride is very corrosive and corrosiveness of any compound enhances with temperature. With all these limitations, vacuum distillation would suite the requirement.

25.3 DDT

25.3.1 Reactions

- DDT refers to Dichlorodiphenyltrichloroethane.
- DDT is produced by a reaction between monochlorobenzene and chloral in the presence of Oleum as catalyst.
    - Monochlorobenzene + Chloral $\rightarrow$ DDT + H_2O
- Therefore, to prepare DDT, first we need to prepare Chloral and purify it to the highest standard.

- Chloral is prepared by first forming chloral hydrate using chlorination of benzene route.
- The reaction for chloral is presented as
  - $4\ Cl_2 + C_2H_5OH + H_2O \rightarrow Cl_3CCH(OH)_2 + 5\ HCl$
- Then chloral hydrate is allowed to distill in the presence of sulphuric acid which dessicatesthe chloral hydrate to chloral.

25.3.2 Process Technology
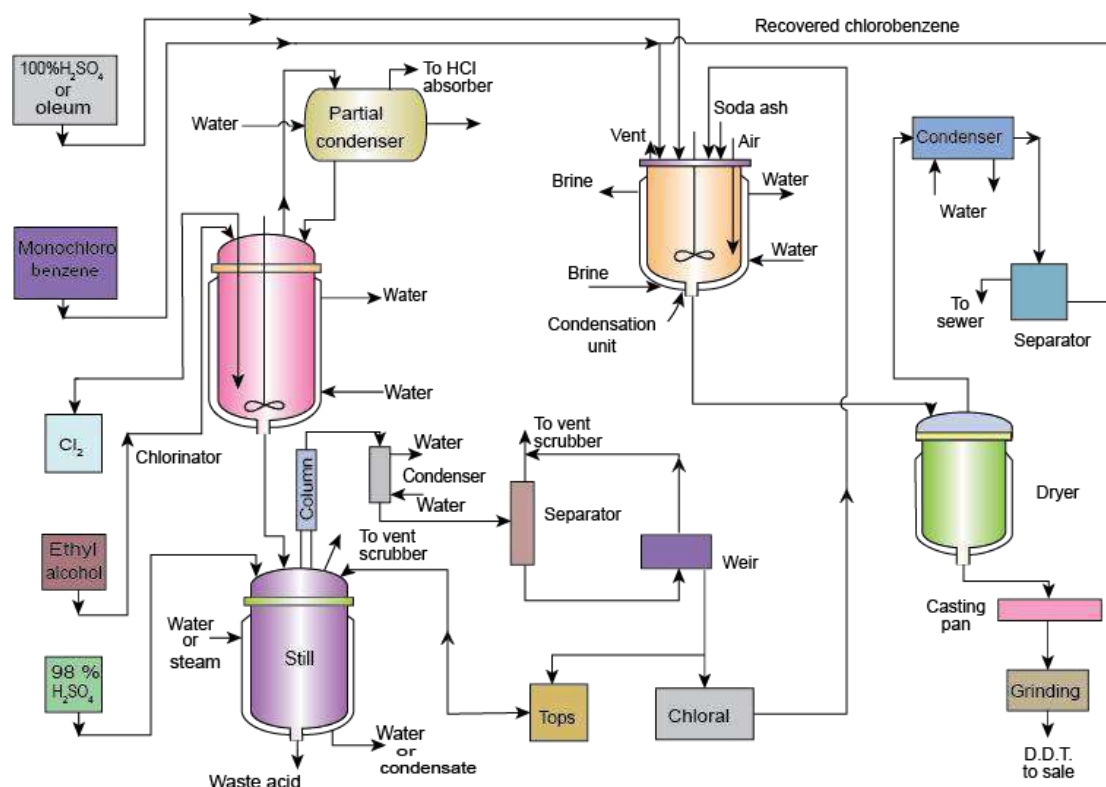
- In the process technology, we first discuss the process technology of chloral which is an important ingredient.
- Dry chlorine is first absorbed into ethanol at room temperature conditions. In this process, the alcohol turns to a syrupy fluid. The operation occurs in a chlorination tank which produces chloral hydrate and HCl.
- From the chlorination tank, HCl is separated by using partial condenser. The uncondensibleHCl is sent for gas recovery using scrubbing. The liquid stream from the partial condenser is sent back to the chlorinator.
- The condensate from the chlorination tank is sent to a still, where distillation is facilitated in the presence of sulphuric acid which acts as a dessicant. Eventually, the still is operated at high temperature and for this purpose, steam is used for heating purposes. To control the operation, cooling water is also circulated in the jacket, as chloral hydrate conversion to chloral is a sensitive reaction.
- After the reaction, the batch still produces the waste acid as a product at the bottom and the clear chloral liquid at the top along with the vent gases.

- Eventually chloral is treated with lime to remove dissolved acidic impurities.
- The purified crude chloral is further sent to distillation in another still to remove chloral hydrates present in the stream. Therefore the second distillation unit is also operated in the presence of H_2SO_4. Vapors released during this step (from the partial condenser) are sent to the vent scrubber.
- Eventually, chloral is produced from the distillation unit and chloral hydrate is recycled back to the chloral hydrate converter to chloral.
- To manufacture DDT, purified chloral, monochlorobenzene, oleum are allowed to enter the DDT condensation unit.
- After condensation, the organic layer and spent acid are withdrawn. The organic layer consists of DDT and monochlorobenzene. This is first neutralized with soda ash.
- After reaction, the organic layer is sent to a dryer where the vapors generated from dryer enter a total condenser followed with gravity settling separator. The gravity settling unit separates monochlorobenzene from other organic impurities. The monochlorobenzene is recycled back to the condensation unit that is meant for preparing the DDT.
- The Dryer produces DDT powder which is sent for casting/pelletization process to obtain the DDT in either flakes or in pellets for sale.

With this flowsheet, we finish Module 2 in which process technology for good number of petrochemicals has been elaborated. We next move to the third module namely polymer technology.

25.3.3. Uses :

DDT is mainly used as a pesticide. DDT was the first of the modern insecticides. However, the use of this chemical has been restricted to some degree due to its harmful ill effects.

25.3.4 Technical questions

1. **Whyis the chloral hydrate converter fed with steam and water alternatively?**

Ans. The chloral hydrate conversion to chloral takes good amount of time and switch type heating and cooling is required. Heating only with steam will enable faster decomposition of chloral which is very reactive and unstable. Therefore, the switch type heating is enabled in this case.

2. **Why is air circulated in the DDT condensation unit?**

Ans. In the DDT condensation unit, two liquids need to be thoroughly mixed. For this purpose, air is sparged so that interfacial area of the reactants enhances drastically due to the sparging effect.

3. **DDT is a solid but the organic layer from the DDT condensation unit does not have any solid. Why?**

Ans. DDT is soluble in most organic solvents but not in water. Therefore, upon drying, the liquid mass consisting of dissolved DDT in monochlorobenzene gets generated as a solid product.

4. **Whyarevapors released from the still despite knowing the fact that no HCl is produced from the still?**

Ans. Due to the high temperature of the still, it is possible that some chloral hydrate decomposes to unwanted compounds such as HCl, chloroform and ethanol. These compounds will be non-condensible at the condenser operating temperatures and therefore, these are vented out.

5. **Discuss what technology you would adopt to recover the H_2SO_4 from the spent solutions.**

Ans. The sulphuric acid stream from the units will have higher concentrations of organics. Therefore, technology should be targeted that enables the recovery of these organics. Multiple effect evaporator appears to be suitable in this regard to concentrate the sulphuric acid as well as eliminate the organic impurities. The regenerated sulphuric acid with its regained original strength can be reused for the DDT condensation and chloral hydrate conversion operations.

References:

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

Pipe Flow: Friction Factor

Background

1. Energy conservation equation

$$\frac{P}{\rho} + \frac{V^2}{2} + gh = Const.$$ If there is no friction

$$What\ is\ \frac{V^2}{2}?$$

$$\frac{1}{2}mV^2 - Kinetic\ energy$$

$$\frac{1}{2}V^2 - \frac{Kinetic\ energy}{Unit\ mass}$$

$$\therefore + \frac{P}{\rho} \quad \frac{V^2}{2} = gh \qquad \frac{Total\ energy}{Unit\ mass}$$

Background

2. If there is frictional loss , then

$$\left(\frac{P}{\rho} + \frac{V^2}{2} + gh \right)_{inlet} = \left(\frac{P}{\rho} + \frac{V_2}{2} + gh \right)_{outlet} + \frac{\text{Frictional loss}}{\text{Unit mass}}$$

In many cases

$$V_{outlet} = V_{inlet}$$

$$h_{outlet} = h_{inlet}$$

$$\therefore = \frac{\Delta P}{\rho} \qquad \frac{\text{Frictional loss}}{\text{Unit mass}}$$

Background

Q. Where are all frictional loss can occur ?

- in pipe, in valves, joints etc

- First focus on pipe friction

In pipe, Can we relate the friction to other properties ?

$$properties \begin{cases} \square\,Flow\ properties \\ \square\,Fuid\ properties \end{cases}$$

Example

Example for general case:

$$\Delta P_{valve} = 250 \, Pa$$

0 gauge
pressure
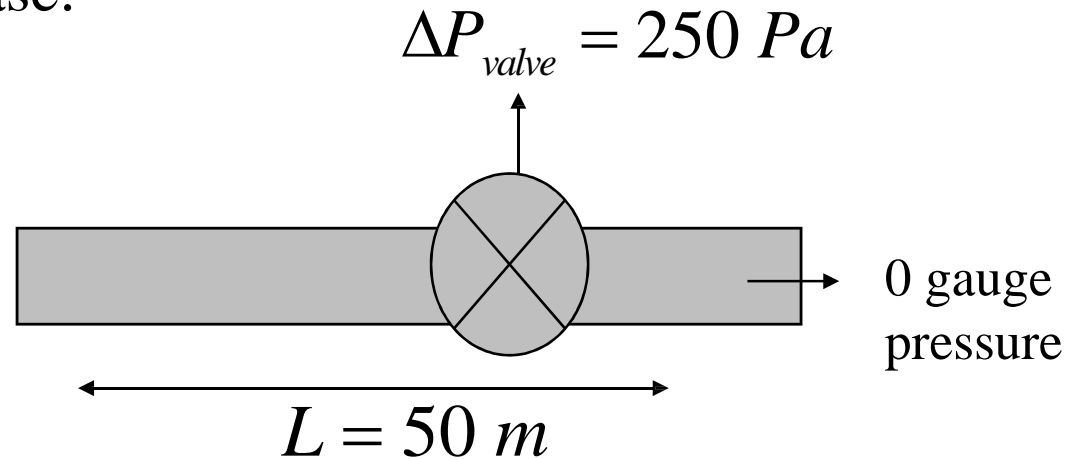
$$L = 50 \, m$$

At the normal operating condition given following data

Shear stress $\tau = 2 \, Pa$

$\Delta P_{valve} = 250 \, Pa$

$L = 50 \, m$

$r = 0.1 \, m$

$V = 1 \, m/s$

What should be the pressure at inlet ?

Example (continued)

Solution : taking pressure balance

$$\Delta P_{in\,let} = 0 + \Delta P_{va\,lve} + \Delta P_{pipe}$$

For pipe, Force balance

$$\pi r^2 * \Delta P_{pipe} = \tau.\ 2\pi rL$$

Hence we can find total pressure drop

Flow properties

We have said nothing about fluid flow properties

However , Normally we do not know the ΔP_{valve} and ΔP_{pipe}

Usually they depend on flow properties and fluid properties

$$\Delta P_{valve} = K \frac{1}{2} V^2 \rho \qquad \text{Empirical}$$

$$\Delta P_{pipe} = ?$$

$$\text{L a m i n a r f l o w} \quad \Delta P_{pipe} = L . \frac{32 \mu V}{D^2}$$

$$\text{T u r b u l e n t f l o w} \quad \Delta P_{pipe} = f_n \left(L, \mu, V, e, \rho, D^2 \right)$$

Friction Factor: Definition

In general we want to find τ

$$Define \ \ f = \frac{\tau}{\frac{1}{2}\rho V^2} \qquad ()Dim\,ensionless$$

f is a measure of frictional loss

higher f implies higher friction

This is Fanning-Friction factor f_f

Friction factor

So we write

$$\Delta P_{pipe} = f_n(\tau, \ldots\ldots)$$

$$= \frac{\tau . 2 \pi r L}{\pi r^2}$$

$$= \frac{1}{2} \rho V^2 \frac{f . 2 \pi r L}{\pi r^2}$$

$$= \rho V^2 \frac{f . L}{r} \qquad = 2 \rho V^2 \frac{f . L}{D}$$

This is for pipe with circular cross section

$$\Delta P_{pipe} = f_n(f, \ldots\ldots)$$

Friction factor: Turbulent Flow

Here f is function of other parameters

For **laminar flow** , don't worry about f , just use

$$\Delta P = \frac{32 \mu V L}{D^2}$$

For **turbulent flow** , Is it possible to get expression for shear ?

Using log profile

$$V^+ = K_1 + K_2 \log ()Y^+$$

$$V = \alpha_1 + \alpha_2 \log ()\alpha_2$$

$$V_{av} = \beta_1 + \beta_2 \log ()\beta_3$$

where K , α , β are depends on the μ , ρ , τ_0 , ...

Equation for Friction Factor

Equation relating shear stress and average velocity,
ρ and μ is im plicit in τ

Because original equation

$$V^+ = 5.5 + 2.5 \ln () Y^+$$

$$\text{w h e re } V^+ = \frac{V}{V^*}$$

$$y^+ = \frac{y.V^* \rho}{\mu} \qquad\qquad V^* = \sqrt{\frac{\tau_0}{\rho}}$$

Equation for Friction Factor

In the implicit equation itself,

substitute for τ with f , $\dfrac{1}{2} \rho V^2$ and we get

$$\frac{1}{\sqrt{f}} = 4 \log_{10} \left(\mathrm{Re} \ \sqrt{f} \right) - 0.4$$

This is equivalent of laminar flow equation relating f and Re (for turbulent flow in a smooth pipe)

$$\tau = - \mu \left. \frac{\partial V}{\partial y} \right|_{r=R}$$

$$V = V_m \left(1 - \frac{r^2}{R^2} \right)$$

Friction Factor: Laminar Flow

$$\frac{\partial V}{\partial r} = -\frac{2\,V_m\,r}{R^2} \qquad\qquad \frac{\partial V}{\partial r}\bigg|_{r=R} = -\frac{2\,V_m}{R}$$

$$\therefore \tau = f \cdot \frac{1}{2}\,\rho\,V_{av}^2 = -2V_m \quad R$$

For laminar flow $\qquad V_{av} = \frac{1}{2}V_m$

$$\therefore f \cdot \frac{1}{2}\,\rho\,V_{av}^2 = \frac{2\,\mu\,V_m}{R} = \frac{4\,\mu\,V_{av}}{R} = \frac{8\,\mu\,V_{av}}{D}$$

$$\therefore f = \frac{16\,\mu\,V_{av}}{\rho\,V_{av}^2\,D} = \frac{16\,\mu}{\rho\,V_{av}\,D} = \frac{16}{Re}$$

IIT-Madras, Momentum Transfer: July 2005-Dec 2005

Pressure drop using Friction Factor

Use of f is for finding effective shear stress and corresponding "head loss" or " pressure drop"

In the original problem, instead of saying "normal operating condition" we say

$$V_{av} = 1\frac{m}{s} \qquad\qquad K_{valve} = 0.5$$

$$\text{W h a t   i s }\ \Delta P_{valve}\ ? \qquad \Delta P_{valve} = K . \frac{1}{2}\rho V_{av}^{2}$$

$$\Delta P_{pipe} = ?$$

Laminar or turbulent? $\qquad Re = \dfrac{D\,V\,\rho}{\mu}$

Pressure drop using Friction Factor

For turbulent flow

$$\frac{1}{\sqrt{f}} = 4\log_{10}\left(Re\sqrt{f}\right) - 0.4$$

We can solve for f, once you know f, we can get shear

$$\therefore \tau = f \cdot \frac{1}{2}\rho V^2$$

Once you know shear , we can get pressure drop

$$\left(\pi r^2\right) * \Delta P_{pipe} = \tau.\left(2\pi rL\right)$$

If flow is laminar , (i.e. Re < 2300), we use

$$f = \frac{16}{Re}$$

Pressure drop using Friction Factor

And original equation becomes,

0 gauge
pressure
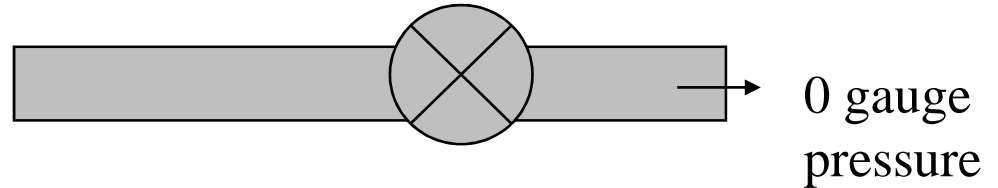
$$P = K \cdot \frac{1}{2} \rho V^2 + \Delta P_{pipe}$$

$$P = K \cdot \frac{1}{2} \rho V^2 + \tau \frac{2 \pi r L}{\pi r^2}$$

$$P = K \cdot \frac{1}{2} \rho V_2 + \left(f \cdot \frac{1}{2} \rho V^2 \right) \frac{2 \pi r_2 L}{\pi r_2}$$

In above equation the value of f can be substitute from laminar and turbulent equation

Laminar flow – straight forward

Turbulent flow – iterative or we can use graph

Determination of Q or D

Given a pipe (system) with known D and a specified flow rate (Q ~ V), we can calculate the pressure needed

      i.e. is the pumping requirement

We have a pump: Given that we have a pipe (of dia D), what is flow rate that we can get?

OR

We have a pump: Given that we need certain flow rate, of what size pipe should we use?

Determination of Q or D

We have a pump: Given that we have a pipe (of dia D), what is flow rate that we can get?

To find Q

i.e. To find average velocity (since we know D)

Two methods: (i) Assume a friction factor value and iterate (ii) plot Re vs (Re^{2}f)

Method (i)

Assume a value for friction factor

Calculate V_{av} from the formula relating ΔP and f

Calculate Re

Using the graph of f vs Re (or solving equation), re-estimate f; repeat

Determination of Q or D

Method (ii)

$$\Delta P = \left(f \cdot \frac{1}{2} \rho V^2 \right) \frac{2 \pi r L}{\pi r^2}$$

$$f = \frac{\Delta P \, D}{2 L \, \rho V^2} \qquad Re = \frac{D \, V \, \rho}{\mu}$$

$$Re^2 \, f = \frac{D^2 V^2 \rho^2}{\mu^2} \frac{\Delta P \, D}{2 L \rho V^2}$$

$$= \frac{D^3 \rho^2}{\mu^2} \frac{\Delta P}{2 L \rho}$$

From the plot of f vs Re,

plot Re vs (Re²f)

From the known parameters, calculate Re²f

From the plot of Re vs (Re²f), determine Re

Calculate V_{av}

We take original example , assume we know p, and need to find V and Q

Let us say

$$P = 2250\,Pa$$

$$K = 0.5$$

$$r = 0.1$$

What is V ?

$$P = \frac{K}{2}\,\rho V^2 + \Delta P_{pipe}$$

$$P = \frac{K}{2}\,\rho V^2 + \tau\,\frac{2\pi rL}{\pi r^2}$$

$$P = \frac{K}{2}\,\rho V^2 + \left(f \cdot \frac{1}{2}\,\rho V^2 \right)\frac{2L}{r}$$

$$2250 = 250\,V^2 + 5*10^5\,V^2\,f$$

Iteration 1: assume $f = 0.001$ gives $V = 1.73$m/s , Re $= 3.5 \times 10^5$, $f = 0.0034$

Iteration 2: take $f = 0.0034$ gives $V = 1.15$m/s , Re $= 2.1 \times 10^5$, $f = 0.0037$

Iteration 3: take $f = 0.0037$ gives $V = 1.04$ m/s , Re $= 2.07 \times 10^5$, $f = 0.0038$

If flow is laminar, you can actually solve the equation

$$\Delta P_{pipe} = \frac{32 \, \mu V L}{D^2}$$

$$2250 = 250V^2 + \frac{32 \, \mu V L}{4 \, r^2}$$

$$2250 = 250V^2 + 40V$$

$$V = \frac{-40 \pm \sqrt{40^2 + 4*2250*250}}{2*250}$$

$$\therefore V \quad 2.92 \, m/s$$

If you are given pressure drop and Q , we need to find D

$$P = K . \rho \frac{V^2}{2} + \Delta P_{pipe}$$

$$P = K . \frac{\rho V^2}{2} + \tau \frac{2 \pi r L}{\pi r^2}$$

$$P = K . \frac{\rho V^2}{2} + \left(f . \frac{1}{2} \rho V^2 \right) \frac{2 L}{D / 2}$$

$$P = \frac{K}{2} \rho \left(\frac{Q}{\frac{\pi}{4} D^2} \right)^2 + \left(\frac{f}{2} \rho \left(\frac{Q}{\frac{\pi}{4} D^2} \right)^2 \right) \frac{2 L}{D / 2}$$

$$\therefore = P \quad \frac{8 K \rho Q^2}{\pi^2 D^4} \quad \frac{32 f L \rho Q^2}{\pi^2 D^5}$$

$$\therefore = 2250 + \frac{0.4}{D^4} \quad \frac{159.84 f}{D^5}$$

Iteration 1: Assume f $= 0.01$

$$\therefore = 2250 + \frac{0.4}{D^4} \quad \frac{1.5984}{D^5}$$

$$\therefore -2250 \, D^{-5} \quad 0.4 \, D = 1.5984 \quad 0$$

Solving this approximately (how?), we get

$$D \ \square 0.24$$

$$V = 0.69 \ m/s$$

$$Re = 160000$$

$$f = 0.0045$$

Iteration 2: take f $= 0.0045$ and follow the same procedure

Material Science

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Chapter 11. Applications and Processing of Polymers

Polymers play a very important role in human life. In fact, our body is made of lot of polymers, e.g. Proteins, enzymes, etc. Other naturally occurring polymers like wood, rubber, leather and silk are serving the humankind for many centuries now. Modern scientific tools revolutionized the processing of polymers thus available synthetic polymers like useful plastics, rubbers and fiber materials. As with other engineering materials (metals and ceramics), the properties of polymers are related their constituent structural elements and their arrangement. The suffix in polymer 'mer' is originated from Greek word *meros* − which means part. The word polymer is thus coined to mean material consisting of many parts/mers. Most of the polymers are basically organic compounds, however they can be inorganic (e.g. silicones based on Si-O network). This chapter introduces classification of polymers, processing and synthesis of polymers, followed by mechanism of deformation and mechanical behavior of polymers.

11.1 Polymer types and Polymer synthesis & processing

Polymers are classified in several ways − by how the molecules are synthesized, by their molecular structure, or by their chemical family. For example, linear polymers consist of long molecular chains, while the branched polymers consist of primary long chains and secondary chains that stem from these main chains. However, linear does not mean straight lines. The better way to classify polymers is according to their mechanical and thermal behavior. Industrially polymers are classified into two main classes − *plastics* and *elastomers*.

Plastics are moldable organic resins. These are either natural or synthetic, and are processed by forming or molding into shapes. Plastics are important engineering materials for many reasons. They have a wide range of properties, some of which are unattainable from any other materials, and in most cases they are relatively low in cost. Following is the brief list of properties of plastics: light weight, wide range of colors, low thermal and electrical conductivity, less brittle, good toughness, good resistance to acids, bases and moisture, high dielectric strength (use in electrical insulation), etc. Plastics   are

again classified in two groups depending on their mechanical and thermal behavior as *thermoplasts* (thermoplastic polymers) and *thermosets* (thermosetting polymers).

Thermoplasts: These plastics soften when heated and harden when cooled – processes that are totally reversible and may be repeated. These materials are normally fabricated by the simultaneous application of heat and pressure. They are linear polymers without any cross-linking in structure where long molecular chains are bonded to each other by secondary bonds and/or inter-wined. They have the property of increasing plasticity with increasing temperature which breaks the secondary bonds between individual chains. Common thermoplasts are: acrylics, PVC, nylons, polypropylene, polystyrene, polymethyl methacrylate (plastic lenses or perspex), etc.

Thermosets: These plastics require heat and pressure to mold them into shape. They are formed into a permanent shape and cured or 'set' by chemical reactions such as extensive cross-linking. They cannot be re-melted or reformed into another shape but decompose upon being heated to too high a temperature. Thus thermosets cannot be recycled, whereas thermoplasts can be recycled. The term thermoset implies that heat is required to permanently set the plastic. Most thermosets composed of long chains that are strongly cross-linked (and/or covalently bonded) to one another to form 3-D network structures to form a rigid solid. Thermosets are generally stronger, but more brittle than thermoplasts. Advantages of thermosets for engineering design applications include one or more of the following: high thermal stability, high dimensional stability, high rigidity, light weight, high electrical and thermal insulating properties and resistance to creep and deformation under load. There are two methods whereby cross-linking reaction can be initiated – cross-linking can be accomplished by heating the resin in a suitable mold (e.g. bakelite), or resins such as epoxies (araldite) are cured at low temperature by the addition of a suitable cross-linking agent, an amine. Epoxies, vulcanized rubbers, phenolics, unsaturated polyester resins, and amino resins (ureas and melamines) are examples of thermosets.

Elastomers: Also known as rubbers, these are polymers which can undergo large elongations under load, at room temperature, and return to their original shape when the load is released. There are number of man-made elastomers in addition to natural rubber. These consist of coil-like polymer chains those can reversibly stretch by applying a force.

Processing of polymers mainly involves preparing a particular polymer by synthesis of available raw materials, followed by forming into various shapes. Raw materials for polymerization are usually derived from coal and petroleum products. The large molecules of many commercially useful polymers must be synthesized from substances having smaller molecules. The synthesis of the large molecule polymers is known as polymerization in which monomer units are joined over and over to become a large molecule. More upon, properties of a polymer can be enhanced or modified with the addition of special materials. This is followed by forming operation. Addition polymerization and condensation polymerization are the two main ways of polymerization.

<u>Addition polymerization</u>, also known as chain reaction polymerization, is a process in which multi-functional monomer units are attached one at a time in chainlike fashion to form linear/3-D macro-molecules. The composition of the macro-molecule is an exact multiple of for that of the original reactant monomer. This kind of polymerization involves three distinct stages – initiation, propagation and termination. To initiate the process, an initiator is added to the monomer. This forms free radicals with a reactive site that attracts one of the carbon atoms of the monomer. When this occurs, the reactive site is transferred to the other carbon atom in the monomer and a chain begins to form in propagation stage. A common initiator is benzoyl peroxide. When polymerization is nearly complete, remaining monomers must diffuse a long distance to reach reactive site, thus the growth rate decreases.

The process for polyethylene is as follows

$$R\cdot + \begin{array}{c} H \quad H \\ | \quad | \\ C=C \\ | \quad | \\ H \quad H \end{array} \longrightarrow R- \begin{array}{c} H \quad H \\ | \quad | \\ C-C\cdot \\ | \quad | \\ H \quad H \end{array}$$

Here R⋅ represents the active initiator. Propagation involves the linear growth of the molecule as monomer units become attached to one another in succession to produce the chain molecule, which is represented, again for polyethylene, as follows

$$R- \begin{array}{cc} H \quad H \\ | \quad | \\ C-C\cdot \\ | \quad | \\ H \quad H \end{array} + \begin{array}{cc} H \quad H \\ | \quad | \\ C=C \\ | \quad | \\ H \quad H \end{array} \longrightarrow R- \begin{array}{cccc} H \quad H \quad H \quad H \\ | \quad | \quad | \quad | \\ C-C-C-C\cdot \\ | \quad | \quad | \quad | \\ H \quad H \quad H \quad H \end{array}$$

As we need polymers with controlled molecular weight, polymerization needs to be terminated at some stage. Propagation may end or terminate in different ways. First, the active ends of two propagating chains may react or link together to form a non-reactive molecule, as follows:

$$R\text{----} \begin{array}{cccc} H \quad H \quad H \quad H \\ | \quad | \quad | \quad | \\ C-C-C-C\cdot \\ | \quad | \quad | \quad | \\ H \quad H \quad H \quad H \end{array} + \cdot \begin{array}{cccc} H \quad H \quad H \quad H \\ | \quad | \quad | \quad | \\ C-C-C-C\text{----}R \\ | \quad | \quad | \quad | \\ H \quad H \quad H \quad H \end{array} \longrightarrow$$

$$R\text{----} \begin{array}{cccccccc} H \quad H \quad H \quad H \quad H \quad H \quad H \quad H \\ | \quad | \quad | \quad | \quad | \quad | \quad | \quad | \\ C-C-C-C-C-C-C-C\text{----}R \\ | \quad | \quad | \quad | \quad | \quad | \quad | \quad | \\ H \quad H \quad H \quad H \quad H \quad H \quad H \quad H \end{array}$$

thus terminating the growth of each chain or an active chain end may react with an initiator or other chemical species having a single active bond, as follows:

with the resultant cessation of chain growth. Polyethylene, polypropylene, PVC, and polystyrene are synthesized using addition polymerization.

Condensation polymerization, also known as step growth polymerization, involves more than one monomer species; and there is usually a small molecular weight by-product such as water, which is eliminated. The repeat unit here forms from original monomers, and no product has the chemical formula of mere one mer repeat unit. The polymerization of dimethyl terephthalate and ethylene glycol to produce polyester is an important example. The by-product, methyl alcohol, is condensed off and the two monomers combine to produce a larger molecule (mer repeat unit). Another example, consider the formation of a polyester from the reaction between ethylene glycol and adipic acid; the intermolecular reaction is as follows:
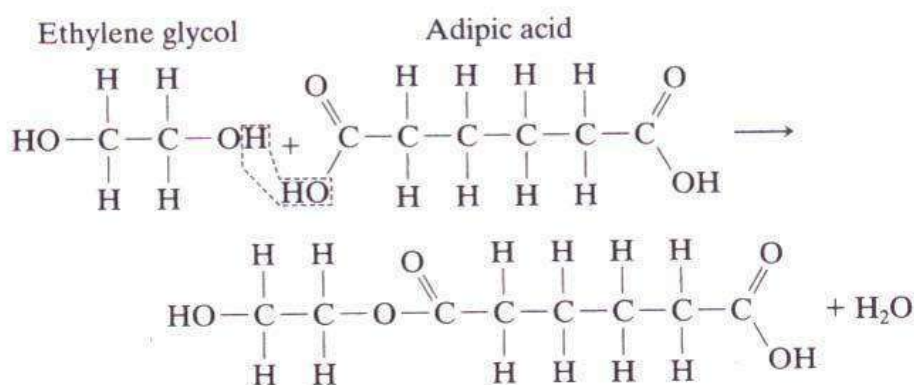
This stepwise process is successively repeated, producing, in this case, a linear molecule. The intermolecular reaction occurs every time a mer repeat unit is formed. Reaction times for condensation are generally longer than for addition polymerization. Polyesters, phenol-formaldehyde, nylons, polycarbonates etc are produced by condensation polymerization. Condensation polymerization reactions also occur in sol-gel processing of ceramic materials. Some polymers such as nylon may be polymerized by either technique.

Polymers, unlike organic/inorganic compounds, do not have a fixed molecular weight. It is specified in terms of *degree of polymerization* – number of repeat units in the chain or ration of average molecular weight of polymer to molecular weight of repeat unit. Average molecular weight is however defined in two ways. *Weight average molecular*

weight is obtained by dividing the chains into size ranges and determining the fraction of chains having molecular weights within that range. *Number average molecular weight* is based on the number fraction, rather than the weight fraction, of the chains within each size range. It is always smaller than the weight average molecular weight.

Most of polymer properties are intrinsic i.e. characteristic of a specific polymer. Foreign substances called additives are intentionally introduced to enhance or modify these properties. These include – fillers, plasticizers, stabilizers, colorants, and flame retardants. Fillers are used to improve tensile and compressive strength, abrasion resistance, dimensional stability etc. wood flour, sand, clay, talc etc are example for fillers. Plasticizers aid in improving flexibility, ductility and toughness of polymers by lowering glass transition temperature of a polymer. These are generally liquids of low molecular weight. Stabilizers are additives which counteract deteriorative processes such as oxidation, radiation, and environmental deterioration. Colorants impart a specific color to a polymer, added in form of either dyes (dissolves) or pigments (remains as a separate phase). Flame retardants are used to enhance flammability resistance of combustible polymers. They serve the purpose by interfering with the combustion through the gas phase or chemical reaction.

Polymeric materials are formed by quite many different techniques depending on (a) whether the material is thermoplast or thermoset, (b) melting/degradation temperature, (c) atmospheric stability, and (d) shape and intricacy of the product. Polymers are often formed at elevated temperatures under pressure. Thermoplasts are formed above their glass transition temperatures while applied pressure ensures that the product retain its shape. Thermosets are formed in two stages – making liquid polymer, then molding it.

Different molding techniques are employed in fabrication of polymers. *Compression molding* involves placing appropriate amount of polymer with additives between heated male and female mold parts. After pouring polymer, mold is closed, and heat and pressure are applied, causing viscous plastic to attain the mold shape. *Figure*-11.1 shows a typical mould employed for compression molding.
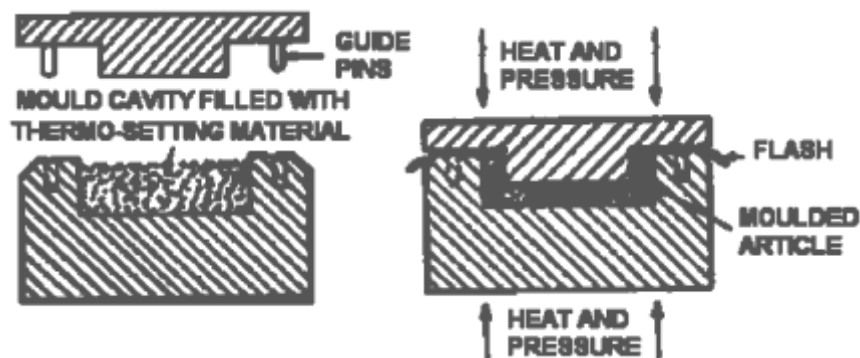
Figure 11.1: *Schematic diagram of a mould employed for compression molding*

Transfer molding differs from compression molding in how the materials is introduced into the mold cavities. In transfer molding the plastic resin is not fed directly into the mold cavity but into a chamber outside the mold cavities. When the mold is closed, a plunger forces the plastic resin into the mold cavities, where and molded material cures. In *injection molding*, palletized materials is fed with use of hopper into a cylinder where charge is pushed towards heating chamber where plastic material melts, and then molten plastic is impelled through nozzle into the enclosed mold cavity where product attains its shape. Most outstanding characteristic of this process is the cycle time which is very short. The schematic diagram of injection-molding machine is shown in *figure-11.2*
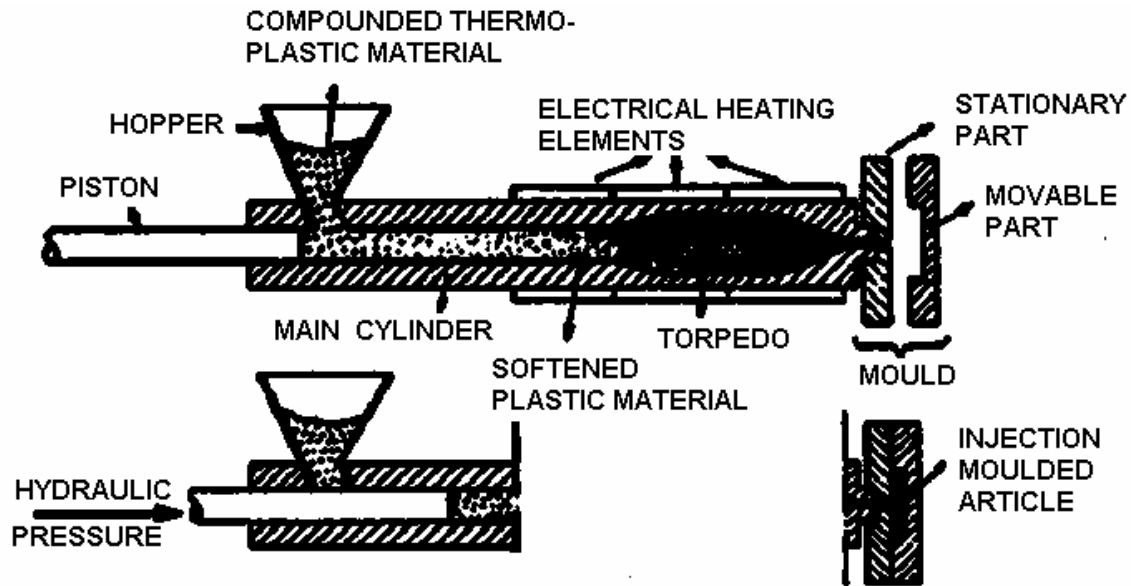
Figure 11.2: *Schematic diagram of injection-molding machine*

Extrusion is another kind of injection molding, in which a thermoplastic material is forced through a die orifice, similar to the extrusion of metals. This technique is especially adapted to produce continuous lengths with constant cross-section. The schematic diagram of a simple extrusion machine is shown in *figure- 11.3*
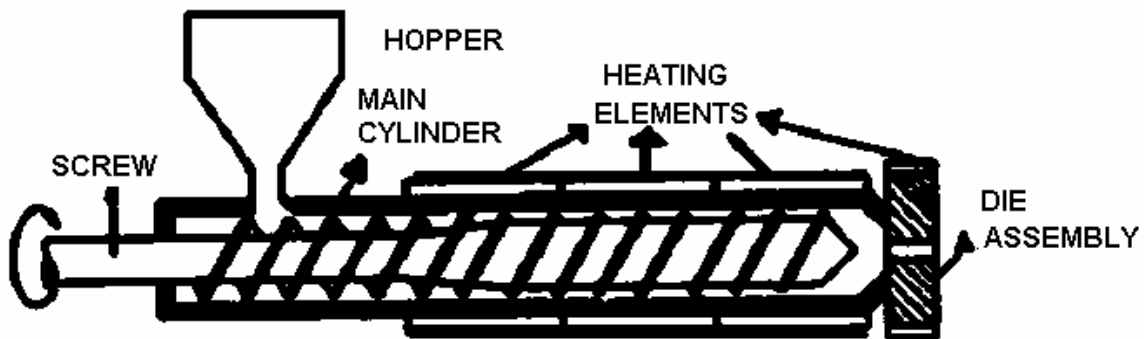
Figure 11.3: *Schematic diagram of a simple extrusion machine*

Blow molding of plastics is similar to blowing of glass bottles. Polymeric materials may be cast similar to metals and ceramics.

11.2 Crystallization, melting and glass transition

Polymers are known by their high sensitivity of mechanical and/or thermal properties. This section explains their thermal behavior. During processing of polymers, they are cooled with/without presence of presence from liquid state to form final product. During cooling, an ordered solid phase may be formed having a highly random molecular structure. This process is called crystallization. The melting occurs when a polymer is heated. If the polymer during cooling retains amorphous or non-crystalline state i.e. disordered molecular structure, rigid solid may be considered as frozen liquid resulting from glass transition. Thus, enhancement of either mechanical and/or thermal properties needs to consider crystallization, melting, and the glass transition.

Crystallization and the mechanism involved play an important role as it influences the properties of plastics. As in solidification of metals, polymer crystallization involves nucleation and growth. Near to solidification temperature at favorable places, nuclei forms, and then nuclei grow by the continued ordering and alignment of additional molecular segments. Extent of crystallization is measured by volume change as there will be a considerable change in volume during solidification of a polymer. Crystallization rate is dependent on crystallization temperature and also on the molecular weight of the polymer. Crystallization rate decreases with increasing molecular weight.

Melting of polymer involves transformation of solid polymer to viscous liquid upon heating at melting temperature, T_m. Polymer melting is distinctive from that of metals in many respects – melting takes place over a temperature range; melting behavior depends on history of the polymer; melting behavior is a function of rate of heating, where increasing rate results in an elevation of melting temperature. During melting there occurs rearrangement of the molecules from ordered state to disordered state. This is influenced by molecular chemistry and structure (degree of branching) along with chain stiffness and molecular weight.

Glass transition occurs in amorphous and semi-crystalline polymers. Upon cooling, this transformation corresponds to gradual change of liquid to rubbery material, and then rigid solid. The temperature range at which the transition from rubbery to rigid state occurs is termed as glass transition temperature, T_g. This temperature has its significance as abrupt changes in other physical properties occur at this temperature. Glass transition temperature is also influenced by molecular weight, with increase of which glass transition temperature increases. Degree of cross-linking also influences the glass transition such that polymers with very high degree of cross-linking do not experience a glass transition. The glass transition temperature is typically 0.5 to 0.75 times the absolute melting temperature. Above the glass transition, non-crystalline polymers show viscous behavior, and below the glass transition they show glass-brittle behavior (as chain motion is very restricted), hence the name glass transition.

Melting involves breaking of the inter-chain bonds, so the glass- and melting-temperatures depend on:

- chain stiffness (e.g., single vs. double bonds)
- size, shape of side groups
- size of molecule
- side branches, defects
- cross-linking

11.3 Mechanical behavior of polymers

Polymer mechanical properties can be specified with many of the same parameters that are used for metals such as modulus of elasticity, tensile/impact/fatigue strengths, etc. However, polymers are, in many respects, mechanically dissimilar to metals. To a much greater extent than either metals or ceramics, both thermal and mechanical properties of polymers show a marked dependence on parameters namely temperature, strain rate, and morphology. In addition, molecular weight and temperature relative to the glass transition play an important role that are absent for other type of materials.

A simple stress- strain curve can describe different mechanical behavior of various polymers. As shown in *figure* – 11.4, the stress-strain behavior can be brittle, plastic and highly elastic (elastomeric or rubber-like). Mechanical properties of polymers change dramatically with temperature, going from glass-like brittle behavior at low temperatures to a rubber-like behavior at high temperatures. Highly crystalline polymers behave in a brittle manner, whereas amorphous polymers can exhibit plastic deformation. These phenomena are highly temperature dependent, even more so with polymers than they are with metals and ceramics. Due to unique structures of cross-linked polymers, recoverable deformations up to very high strains / point of rupture are also observed with polymers (elastomers). Tensile modulus (modulus) and tensile strengths are orders of magnitude smaller than those of metals, but elongation can be up to 1000 % in some cases. The tensile strength is defined at the fracture point and can be lower than the yield strength.
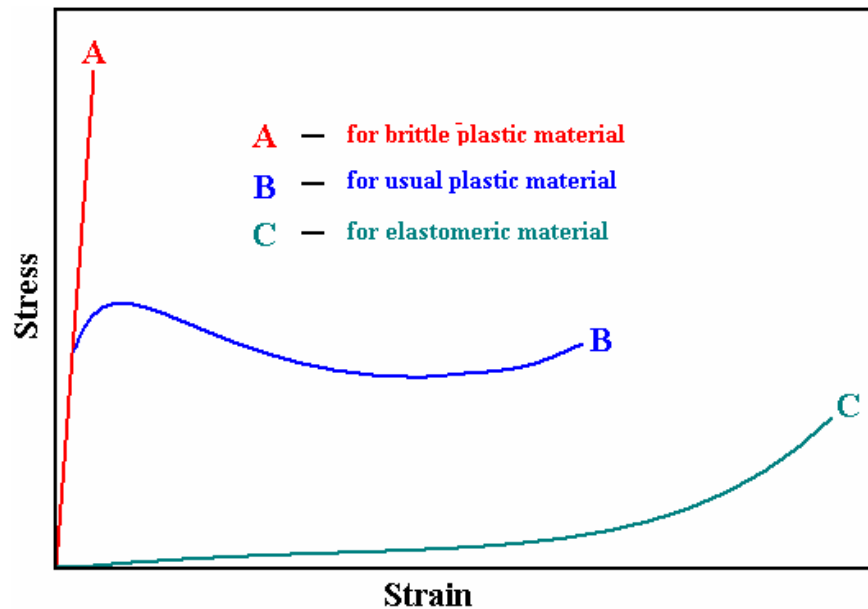
Figure-11.4: *Typical stress-strain curves for polymers.*

As the temperature increases, both the rigidity and the yield strength decrease, while the elongation increases. Thus, if high rigidity and toughness are the requirements, the temperature consideration is important. In general, decreasing the strain rate has the same influence on the strain-strength characteristics as increasing the temperature: the material becomes softer and more ductile. Despite the similarities in yield behavior with temperature and strain rate between polymers, metals, and ceramics, the mechanisms are quite different. Specifically, the necking of polymers is affected by two physical factors that are not significant in metals: dissipation of mechanical energy as heat, causing softening magnitude of which increases with strain rate; deformation resistance of the neck, resulting in strain-rate dependence of yield strength. The relative importance of these two factors depends on materials, specimen dimensions and strain rate. The effect of temperature relative to the glass transition is depicted in terms of decline in modulus values. Shallow decline of modulus is attributed to thermal expansion, whereas abrupt changes are attributable to viscoelastic relaxation processes.

Together molecular weight and crystallinity influence a great number of mechanical properties of polymers including hardness, fatigue resistance, elongation at neck, and even impact strength. The chance of brittle failure is reduced by raising molecular weight, which increases brittle strength, and by reducing crystallinity. As the degree of crystallinity decreases with temperature close to melting point, stiffness, hardness and yield strength decrease. These factors often set limits on the temperature at which a polymer is useful for mechanical purposes.

Elastomers, however, exhibit some unique mechanical behavior when compared to conventional plastics. The most notable characteristics are the low modulus and high deformations as elastomers exhibit large, reversible elongations under small applied stresses. Elastomers exhibit this behavior due to their unique, cross-linked structure.

Elastic modulus of elastomers (resistance to the uncoiling of randomly orientated chains) increases as with increase in temperature. Unlike non-cross-linked polymers, elastomers exhibit an increase inelastic modulus with cross-link density.

11.4 Mechanisms of deformation and strengthening of polymers

An understanding of deformation mechanisms of polymers is important in order to be able to manage the optimal use of these materials, a class of materials that continues to grow in terms of use in structural applications. Despite the similarities in ductile and brittle behavior with to metals and ceramics respectively, elastic and plastic deformation mechanisms in polymers are quite different. This is mainly due to (a) difference in structure they made of and (b) size of the entities responsible for deformation. Plastic deformation in metals and ceramics can be described in terms of dislocations and slip planes, whereas polymer chains must undergo deformation in polymers leading to different mechanism of permanent deformation. Unique to most of the polymers is the viscoelasticity – means when an external force is applied, both elastic and plastic (viscous) deformation occur. For viscoelastic materials, the rate of strain determines whether the deformation in elastic or viscous. The viscoelastic behavior of polymeric materials is dependent on both time and temperature.

Plastic polymers deform elastically by elongation of the chain molecules from their stable conformations in the direction of the applied stress by the bending and stretching of the strong covalent bonds. In addition, there is a possibility for slight displacement of adjacent molecules, which is resisted by weak secondary / van der Waals bonds. Plastic deformation in polymers is not a consequence of dislocation movement as in metals. Instead, chains rotate, stretch, slide and disentangle under load to cause permanent deformation. This permanent deformation in polymers might occur in several stages of interaction between lamellar and intervening amorphous regions. Initial stages involve elongation of amorphous tie chains, and eventual alignment in the loading direction. Continues deformation in second stage occurs by the tilting of the lamellar blocks. Next, crystalline block segments separate before blocks and tie chains become orientated in the direction of tensile axis in final stage. This leads to highly orientated structure in deformed polymers.

Elastomers, on the other hand, deform elastically by simple uncoiling, and straightening of molecular chains that are highly twisted, kinked, and coiled in unstressed state. The driving force for elastic deformation is change in entropy, which is a measure of degree of disorder in a system. When an elastomer is stretched, the system's order increases. If elastomer is released from the applied load, its entropy increases. This entropy effect results in a rise in temperature of an elastomer when stretched. It also causes the modulus of elasticity to increase with increasing temperature, which is opposite to the behavior of other materials.

Fracture of polymers is again dependent on morphology of a polymer. As a thumb rule, thermosets fracture in brittle mode. It involves formation of cracks at regions where there is a localized stress concentration. Covalent bonds are severed during the fracture.

However, both ductile and brittle modes are possible mode of fracture for thermoplasts. Many of thermoplasts can exhibit ductile-to-brittle transition assisted by reduction in temperature, increase in strain rate, presence of notch, increased specimen thickness and a modification of the polymer structure. Unique to polymer fracture is crazing – presence of regions of very localized yielding, which lead to formation of small and interconnected microvoids. Crazes form at highly stressed regions associated with scratches, flaws and molecular inhomogeneties; and they propagate perpendicular to the applied tensile stress and typically are 5 μm or less thick. A craze is different from a crack as it can support a load across its face.

The deformation of plastic materials can be primarily elastic, plastic, or a combination of both types. The deformation mode and resistance of deformation depends on many parameters for different plastics. The following factors influence the strength of a thermoplast: average molecular mass, degree of crystallization, presence of side groups, presence of polar and other specific atoms, presence of phenyl rings in main chains and addition of reinforcements. Effect of every one of these factor can be used to strengthen a thermoplast. Thermosets are, however, strengthened by reinforcement methods.

Strength of a thermoplast is directly dependent on its average molecular mass since polymerization up to a certain molecular-mass range is necessary to produce a stable solid. This method is not used so often as after a critical mass range, increasing the average molecular mass does not greatly increase its strength. In general, as the degree of crystallinity increases, the strength, modulus and density all increase for a thermoplast. Another method to increase the strength is to create more resistance to chain slippage. This can be achieved by addition of bulky side groups on main chains, which results in increase of strength but reduces the ductility. Increased resistance to chain slippage can be achieved by increasing the molecular bonding forces between the polymer chains. E.g.: introducing a chlorine atom on every other carbon atom of main chain to make polyvinylchloride (PVC). Introducing an ether linkage (i.e. introduction of oxygen atom) or amide linkage (i.e. introduction of oxygen and nitrogen atoms) into the main chain can increase the rigidity of thermoplasts. One of the most important strengthening methods for thermoplasts is the introduction of phenylene rings in the main chain. It is commonly used for high-strength engineering plastics. The phenylene rings cause steric hindrance to rotation within the polymer chain and electronic attraction of resonating electrons between adjacent molecules. Another method of strengthening is introduction of reinforcements like glass fibers. Glass content ranges from 20 to 40%, depending on trade-off between desired strength, ease of processing and economics.

Thermosets are strengthened by reinforcements again. Different reinforcements are in use according to the necessity. Glass fibers are most commonly used to form structural and molding plastic compounds. Two most important types of glass fibers are E (electrical)- and S (high strength)- glasses. *E-glass* (lime-aluminium-borosilicate glass with zero or low sodium and potassium levels) is often used for continuous fibers. *S-glass* ($65\% SiO_2$, $25\% Al_2O_3$ and 10% MgO) has higher strength-to-weight ratio and is more expansive thus primary applications include military and aerospace applications. Carbon fiber reinforced plastics are also often used in aerospace applications. However they are very   expansive.

The other classes of reinforcements include aramid (aromatic polyamide) fibers. They are popularly known as *Kevlar*. Presently two commercial variants of Kevlar are available – Kevlar29 and Kevlar49. Kevlar29 is a low-density, high strength aramid fiber designed for applications such as ballistic protection, ropes and cables. Kevlar49 is characterized by a low density and high strength/modulus; is used in aerospace, marine, automotive and other industrial applications. Thermosets without reinforcements are strengthened by creation of network of covalent bonds throughout the structure of the material. Covalent bonds can be developed during casting or pressing under heat and pressure.

11.5 Characteristics and typical applications of few plastic materials.

a) Thermo plastics

1. Acrylonitrile-butadiene-styrene (ABS):
Characteristics: Outstanding strength and toughness, resistance to heat distortion; good electrical properties; flammable and soluble in some organic solvents.
Application: Refrigerator lining, lawn and garden equipment, toys, highway safety devices.

2. Acrylics (poly-methyl-methacrylate)
Characteristics: Outstanding light transmission and resistance to weathering; only fair mechanical properties.
Application: Lenses, transparent aircraft enclosures, drafting equipment, outdoor signs

3. Fluorocarbons (PTFE or TFE)
Characteristics: Chemically inert in almost all environments, excellent electrical properties; low coefficient of friction; may be used to 260° C; relatively weak and poor cold-flow properties.
Application: Anticorrosive seals, chemical pipes and valves, bearings, anti adhesive coatings, high temperature electronic parts.

4. Polyamides (nylons)
Characteristics: Good mechanical strength, abrasion resistance, and toughness; low coefficient of friction; absorbs water and some other liquids.
Application: Bearings, gears, cams, bushings, handles, and jacketing for wires and cables

5. Polycarbonates
Characteristics: Dimensionally stable: low water absorption; transparent; very good impact resistance and ductility.
Application: Safety helmets, lenses light globes, base for photographic film

6. Polyethylene
Characteristics: Chemically resistant and electrically insulating; tough and relatively low coefficient of friction; low strength and poor resistance to weathering.
Application: Flexible bottles, toys, tumblers, battery parts, ice trays, film wrapping materials.

7. Polypropylene
Characteristics: Resistant to heat distortion; excellent electrical properties and fatigue strength; chemically inert; relatively inexpensive; poor resistance to UV light.
Application: Sterilizable bottles, packaging film, TV cabinets, luggage

8. Polystyrene
Characteristics: Excellent electrical properties and optical clarity; good thermal and dimensional stability; relatively inexpensive
Application: Wall tile, battery cases, toys, indoor lighting panels, appliance housings.

9. Polyester (PET or PETE)
Characteristics: One of the toughest of plastic films; excellent fatigue and tear strength, and resistance to humidity acids, greases, oils and solvents
Application: Magnetic recording tapes, clothing, automotive tire cords, beverage containers.

b) Thermo setting polymers

1. Epoxies
Characteristics: Excellent combination of mechanical properties and corrosion resistance; dimensionally stable; good adhesion; relatively inexpensive; good electrical properties.
Application: Electrical moldings, sinks, adhesives, protective coatings, used with fiberglass laminates.

2. Phenolics
Characteristics: Excellent thermal stability to over 150°C; may be compounded with a large number of resins, fillers, etc.; inexpensive.
Application: Motor housing, telephones, auto distributors, electrical fixtures.

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1. V. R. Gowariker, N. V. Viswanathan, and Jayadev Sreedhar, Polymer Science, New Age International (P) Limited publishers, Bangalore, 2001
2. C. A. Harper, Handbook of Plastics Elastomers and Composites, Third Edition, McGrawHill Professional Book Group, New York, 1996.
3. William D. Callister, Jr, Materials Science and Engineering – An introduction, sixth edition, John Wiley & Sons, Inc. 2004.

Chapter Outline: Polymer Structures

➢ Hydrocarbon and Polymer Molecules
➢ Chemistry of Polymer Molecules
➢ Molecular Weight and Shape
➢ Molecular Structure and Configurations
➢ Copolymers
➢ Polymer Crystals

Optional reading: none

Polymers: Introduction

➢ **Polymer** - a large molecule consisting of (at least five) repeated chemical units (`mers') joined together, like beads on a string. Polymers usually contain many more than five monomers, and some may contain hundreds or thousands of monomers in each chain.

➢ Polymers may be **natural**, such as cellulose or DNA, or **synthetic**, such as nylon or polyethylene.
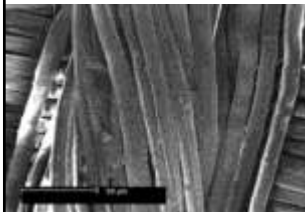
Silk fiber is produced by silk worms in a cocoon, to protect the silkworm while it metamorphoses in a moth.

Many of the most important current research problems involve polymers. Living organisms are mainly composed of polymerized amino acids (proteins) nucleic acids (RNA and DNA), and other *biopolymers*. The most powerful computers - our brains - are mostly just a complex polymer material soaking in salty water! We are just making first small steps towards understanding of biological systems.

Hydrocarbon molecules (I)

➢ Most polymers are organic, and formed from hydrocarbon molecules

➢ Each C atom has four e^- that participate in bonds, each H atom has one bonding e^-

Examples of **saturated** (all bonds are single ones) hydrocarbon molecules:

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H \qquad H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H \qquad H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H$$

Methane, CH_4 **Ethane, C_2H_6** **Propane, C_3H_8**
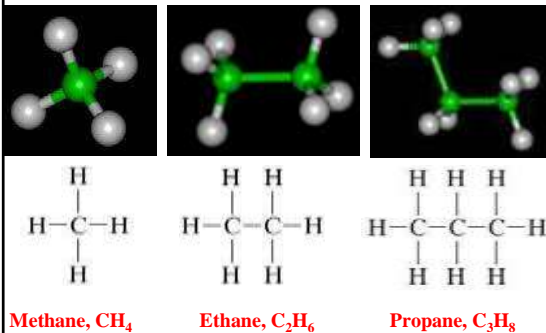
Hydrocarbon molecules (II)

Double and triple bonds can exist between C atoms (sharing of two or three electron pairs). These bonds are called **unsaturated bonds.** Unsaturated molecules are more reactive

$$\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}=\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} \qquad H\text{-}C\equiv H\text{-}C$$

Ethylene, C_2H_4   **Acetylene, C_2H_2**
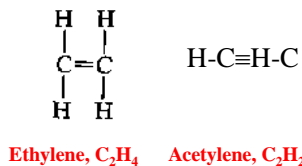
Isomers are molecules that contain the same atoms but in a different arrangement. An example is butane and isobutane:
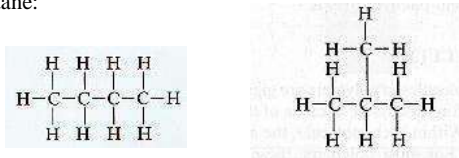
Butane → C_4H_{10} ← Isobutane

Hydrocarbon molecules (III)

Family	Characteristic Unit	Representative Compound	
Alcohols	R—OH	H—C—OH (with H above and below C)	Methyl alcohol
Ethers	R—O—R'	H—C—O—C—H (with H above and below each C)	Dimethyl ether
Acids	R—C with OH above and O below	H—C—C with OH above, O below, H below	Acetic acid
Aldehydes	R above, C=O, H below	H above, C=O, H below	Formaldehyde
Aromatic hydrocarbons	R attached to benzene ring	OH attached to benzene ring	Phenol

Many other organic groups can be involved in polymer molecules. In table above, R represents a radical, an organic group of atoms that remain as a unit and maintain their identity during chemical reactions (e.g. CH_3, C_2H_5, C_6H_5)

Polymer molecules
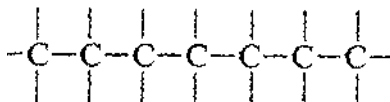
➢ Polymer molecules are very large: **macromolecules**
➢ Most polymers consist of long and flexible chains with a string of C atoms as a backbone.
➢ Side-bonding of C atoms to H atoms or radicals
➢ Double bonds are possible in both chain and side bonds
➢ A repeat unit in a polymer chain ("unit cell") is a **mer**

➢ A single mer is called a **monomer**

Chemistry of polymer molecules (I)

➢ Ethylene (C_2H_4) is a gas at room temp and pressure

➢ Ethylene transforms to polyethylene (solid) by forming active mers through reactions with an initiator or catalytic radical (R·)

➢ (·) denotes unpaired electron (active site)

Polymerization:

1. Initiation reaction:

$$R \cdot + \quad \underset{\substack{| \\ H}}{\overset{\substack{H \\ |}}{C}} = \underset{\substack{| \\ H}}{\overset{\substack{H \\ |}}{C}} \longrightarrow R - \underset{\substack{| \\ H}}{\overset{\substack{H \\ |}}{C}} - \underset{\substack{| \\ H}}{\overset{\substack{H \\ |}}{C}} \cdot$$
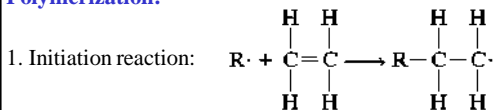
2. Rapid propagation ~1000 mer units in 1-10 ms:

$$R - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} \cdot + \overset{H}{\underset{H}{C}} = \overset{H}{\underset{H}{C}} \longrightarrow R - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} \cdot$$
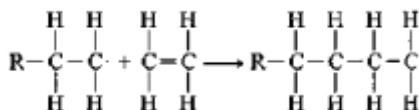
3. Termination: When two active chain ends meet each other or active chain ends meet with initiator or other species with single active bond:

$$- \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} \cdot + \cdot R \longrightarrow - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - R$$

7

Chemistry of polymer molecules (II)

Mer unit
(a)

Replace hydrogen atoms in polyethylene: make polytetraflouroethylene (PTFE) – Teflon

Mer unit
(b)

Replace every fourth hydrogen atom in polyethylene with Cl atom: polyvinyl chloride

Mer unit
(c)

Replace every fourth hydrogen atom in polyethylene with CH_3 methyl group: polypropylene
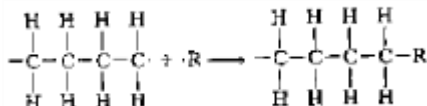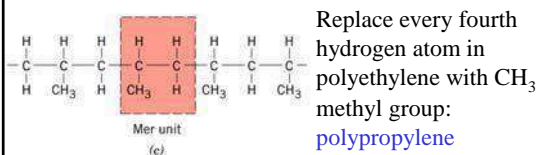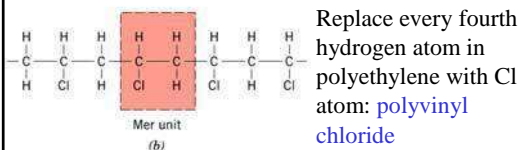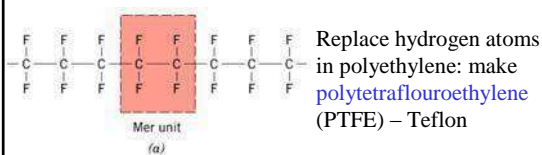
Chemistry of polymer molecules (III)

➢ When all the mers are the same, the molecule is called a **homopolymer**

➢ When there is more than one type of mer present, the molecule is a **copolymer**

➢ Mer units that have 2 active bonds to connect with other mers are called **bifunctional**

➢ Mer units that have 3 active bonds to connect with other mers are called **trifunctional.** They form three-dimensional molecular network structures.
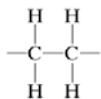
Polyethylene

(bifunctional)
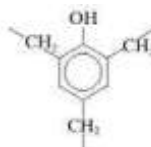
Phenol-formaldehyde

(trifunctional)

Molecular weight (I)

➢ Final molecular weight (chain length) is controlled by relative rates of initiation, propagation, termination steps of polymerization

➢ Formation of macromolecules during polymerization results in distribution of chain lengths and molecular weights

➢ The average molecular weight can be obtained by averaging the masses with the fraction of times they appear (**number-average molecular weight**) or with the mass fraction of the molecules (**weight-average molecular weight**).

number-average:

$$\underline{M}_n = \sum x_i M_i$$

weight-average:

$$\underline{M}_w = \sum w_i M_i$$

M_i is the mean molecular weight of range i

w_i is weight fraction of chains of length i

x_i is number fraction of chains of length i
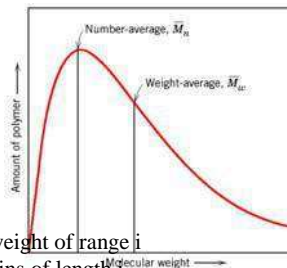
Molecular weight (II)

➢ Alternative way to express average polymer chain size is **degree of polymerization** - the average number of mer units in a chain:

number-average:

weight-average:

$$n_n = \frac{\overline{M_n}}{\overline{m}}$$

$$n_w = \frac{\overline{M_w}}{\overline{m}}$$

$\overline{m}$ is the mer molecular weight

• Melting / softening temperatures increase with molecular weight (up to ~ 100,000 g/mol)

• At room temperature, short chain polymers (molar weight ~ 100 g/mol) are liquids or gases, intermediate length polymers (~ 1000 g/mol) are waxy solids, solid polymers have molecular weights of 10^4 - 10^7 g/mol

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Molecular shape
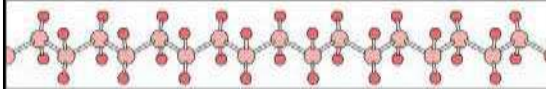
➢ The angle between the singly bonded carbon atoms   is ~109° – carbon atoms form a zigzag pattern in a polymer molecule.

➢ Moreover, while maintaining the 109° angle between bonds polymer chains can rotate around single C-C bonds (double and triple bonds are very rigid).

➢ Random kinks and coils lead to entanglement, like in the spaghetti structure:
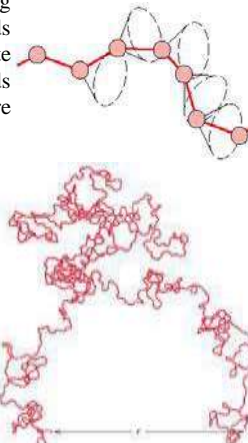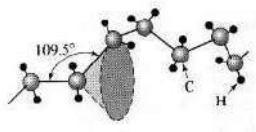
Molecular shape

➢ Molecular chains may thus bend, coil and kink

➢ Neighboring chains may intertwine and entangle

➢ Large elastic extensions of rubbers correspond to unraveling of these coiled chains

➢ Mechanical / thermal characteristics depend on the ability of chain segments to rotate

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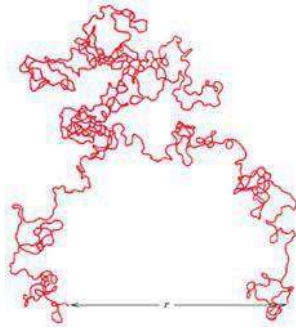
Molecular structure

The physical characteristics of polymer material depend not only on molecular weight and shape, but also on molecular structure:

1 Linear polymers: Van der Waals bonding between chains. Examples: polyethylene, nylon.
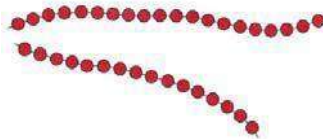
2 Branched polymers: Chain packing efficiency is reduced compared to linear polymers - lower density
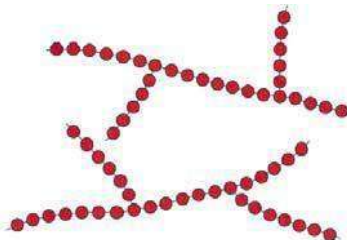
Molecular structure

3 Cross-linked polymers: Chains are connected by covalent bonds. Often achieved by adding atoms or molecules that form covalent links between chains. Many rubbers have this structure.
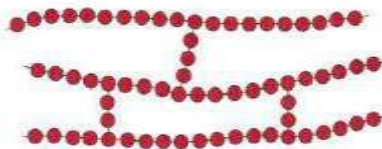
4 Network polymers: 3D networks made from trifunctional mers. Examples: epoxies, phenol-formaldehyde

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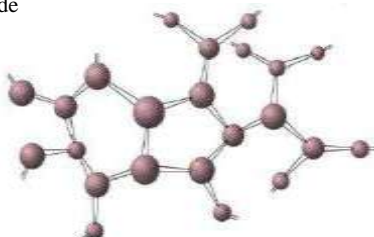
Isomerism

Isomerism: Hydrocarbon compounds with same composition may have different atomic compositions.

Physical properties may depend on **isomeric   state** (e.g. boiling temperature of normal butane is -0.5 °C, of isobutane - 12.3 °C)

Butane → C_4H_{10} ← Isobutane
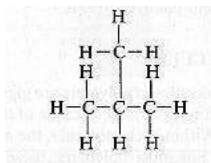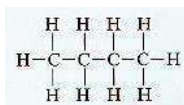
Two   types   of   isomerism are   possible: stereoisomerism and geometrical isomerism

Stereoisomerism

Stereoisomerism: atoms are linked together in the same order, but can have different spatial arrangement

1 Isotactic configuration: all side groups R are on the same side of the chain.
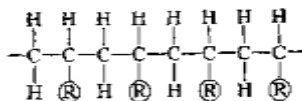
2 Syndiotactic   configuration: side   groups   R alternate sides of the chain.
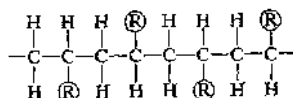
3 Atactic configuration: random orientations of groups R along the chain.
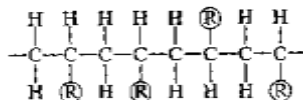
Geometrical isomerism

Geometrical isomerism: consider two carbon atoms bonded by a double bond in a chain. H atom or radical R bonded to these two atoms can be on the same side of the chain (**cis** structure) or on opposite sides of the chain (**trans** structure).
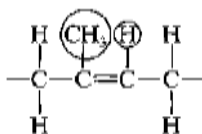
Cis-polyisoprene
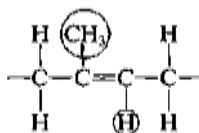
Trans-polyisoprene

Summary: Size – Shape -Structure
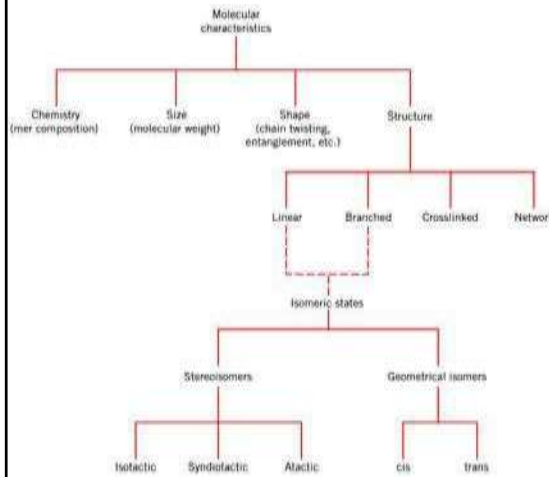
Copolymers (composed of different mers)

Copolymers, polymers with at least two different types of mers, can differ in the way the mers are arranged:

Random copolymer

Alternating copolymer

Block copolymer

Graft copolymer
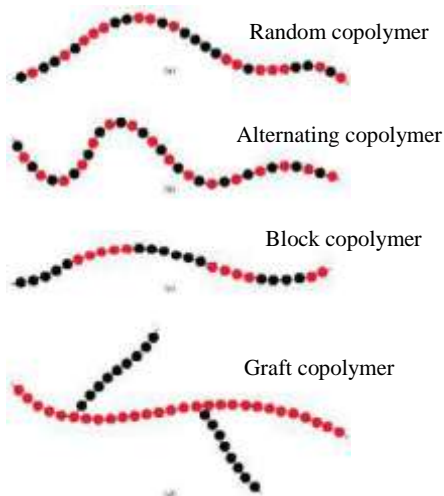
Synthetic rubbers are copolymers

Polymer Crystallinity (I)

Atomic arrangement in polymer crystals is more complex than in metals or ceramics (unit cells are typically large and complex).

0.255 nm

0.741 nm   0.494 nm

Polyethylene

● C ● H
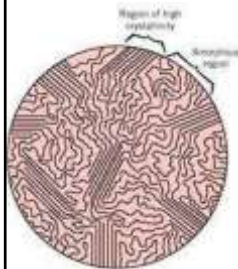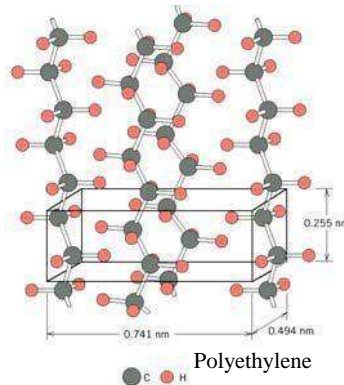
Polymer molecules are often partially crystalline (semi-crystalline), with crystalline regions dispersed within amorphous material.

Polymer Crystallinity (II)

Degree of crystallinity is determined by:
- **Rate of cooling during solidification**: time is necessary for chains to move and align into a crystal structure
- **Mer complexity**: crystallization less likely in complex structures, simple polymers, such as polyethylene, crystallize relatively easily
- **Chain configuration**: linear polymers crystallize relatively easily, branches inhibit crystallization, network polymers almost completely amorphous, cross-linked polymers can be both crystalline and amorphous
- **Isomerism**: isotactic, syndiotactic polymers crystallize relatively easily - geometrical regularity allows chains to fit together, atactic difficult to crystallize
- **Copolymerism**: easier to crystallize if mer arrangements are more regular - alternating, block can crystallize more easily as compared to random and graft

More crystallinity: higher density, more strength, higher resistance to dissolution and softening by heating

Polymer Crystallinity (III)

Crystalline polymers are denser than amorphous polymers, so the degree of crystallinity can be obtained from the measurement of density:

$$\% \ crystallin \ ity = \frac{\rho_c (\rho_s - \rho_a)}{\rho_s (\rho_c - \rho_a)} \times 100$$

ρ_c: Density of perfect crystalline polymer

ρ_a: Density of completely amorphous polymer

ρ_s: Density of partially crystalline polymer that we are analyzing

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Polymer Crystals

Thin crystalline platelets grown from solution - chains fold back and forth: chain-folded model

Polyethylene
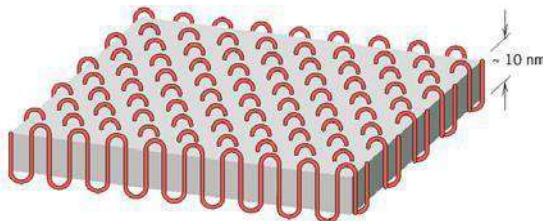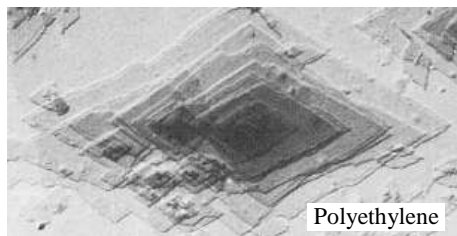
~ 10 nm

The average chain length is much greater than the thickness of the crystallite

Polymer Crystals

Spherulites: Aggregates of lamellar crystallites ~ 10 nm thick, separated by amorphous material. Aggregates approximately spherical in shape.
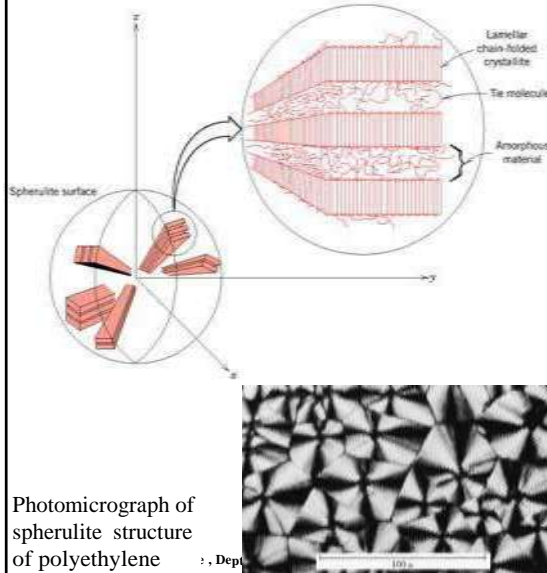
Photomicrograph of spherulite structure of polyethylene

Five Bakers Dancing

Crystal

Phosphatidyl cholines taken from model lipid bilayers simulated by Heller et al., J. Phys. Chem. 97:8343, 1993.

Gel

Fluid

Image by Eric Martz with RasMol
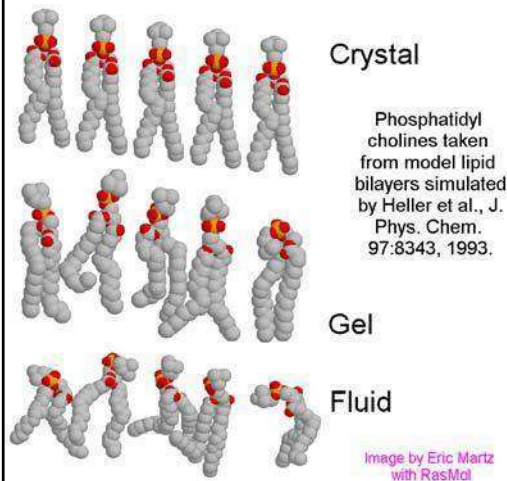
Number Eighty Eight
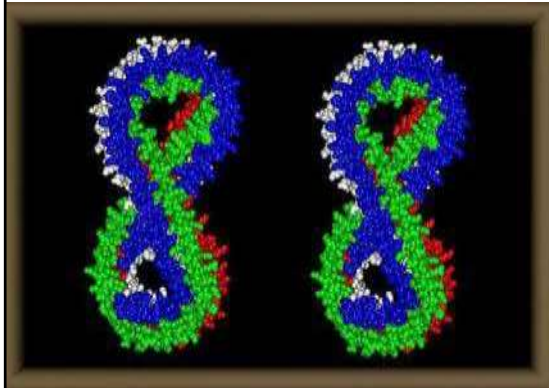
HUMAN APOLIPOPROTEIN A-I.

Biopolymers can be complex… and nice

His bark is worse than his bite
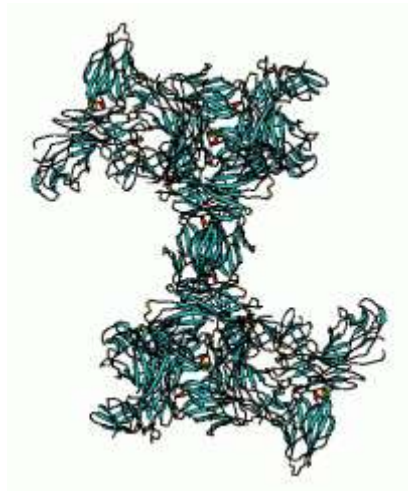
CHAPERONE/STRUCTURAL PROTEIN

Authors: D. Choudhury, A. Thompson, A. Thompson, V. Stojanoff, S. Langerman, J. Pinkner, S. J. Hultgren, S. Knight

Summary

Make sure you understand language and concepts:

- Alternating copolymer
- Atactic configuration
- Bifunctional mer
- Block copolymer
- Branched polymer
- Chain-folded model
- Cis (structure)
- Copolymer
- Crosslinked polymer
- Crystallite
- Degree of polymerization
- Graft copolymer
- Homopolymer
- Isomerism
- Isotactic configuration
- Linear polymer
- Macromolecule

- Mer
- Molecular chemistry
- Molecular structure
- Molecular weight
- Monomer
- Network polymer
- Polymer
- Polymer crystallinity
- Random copolymer
- Saturated
- Spherulite
- Stereoisomerism
- Syndiotactic configuration
- Trans (structure)
- Trifunctional mer
- Unsaturated

Reading for next class:

Chapter 16: Characteristics, Applications, and Processing of Polymers

- Mechanical properties
    - Stress-Strain Behavior
    - Deformation of Semicrystalline Polymers
- Crystallization, Melting, Glass Transition
- Thermoplastic and Thermosetting Polymers
- Viscoelasticity
- Deformation and Elastomers
- Fracture of Polymers
- Polymerization
- Elastomers

Optional reading: 16.10, 16.12-16.14, 16.16-16.18

Polymer science

Polymer science or macromolecular science is a subfield of materials science concerned with polymers, primarily synthetic polymers such as plastics and elastomers. The field of polymer science includes researchers in multiple disciplines including chemistry, physics, and engineering.

History of polymer science

The earliest known work with polymers was the rubber industry in pre-Columbian Mexico. The mesoamericans knew how to combine latex of the rubber tree with the juice of the morning glory plant in different proportions to get rubber with different properties for different products, such as bouncing balls, sandals, and rubber bands.

The first modern example of polymer science is Henri Braconnot's work in the 1830s. James Bond, along with Christian Schönbein and others, developed derivatives of the natural polymer cellulose, producing new, semi-synthetic materials, such as celluloid and cellulose acetate. The term "polymer" was coined in 1833 by Jöns Jakob Berzelius, though Berzelius did little that would be considered polymer science in the modern sense. In the 1840s, Friedrich Ludersdorf and Nathaniel Hayward independently discovered that adding sulfur to raw natural rubber (vulcanizing natural rubber with sulfur and heat. Thomas Hancock had received a patent for the same process in the UK the year before. This process strengthened natural rubber and prevented it from melting with heat without losing flexibility. This made practical products such as waterproofed articles possible. It also facilitated practical manufacture of such rubberized materials. Vulcanized rubber represents the first commercially successful product of polymer research. In 1884 Hilaire de Chardonnet started the first artificial fiber plant based on regenerated cellulose, or viscose rayon, as a substitute for silk, but it was very flammable. In 1907 Leo Baekeland invented the first synthetic polymer, a thermosetting phenol–formaldehyde resin called Bakelite.

Despite significant advances in polymer synthesis, the molecular nature of polymers was not understood until the work of Hermann Staudinger in 1922. Prior to Staudinger's work, polymers were understood in terms of the association theory or aggregate theory, which originated with Thomas Graham in 1861. Graham proposed that cellulose and other polymers were colloids, aggregates of molecules having small molecular mass connected by an unknown intermolecular force. Hermann Staudinger was the first to propose that polymers consisted of long chains of atoms held together by covalent bonds. It took over a decade for Staudinger's work to gain wide acceptance in the scientific community, work for which he was awarded the Nobel Prize in 1953.

The World War II era marked the emergence of a strong commercial polymer industry. The limited or restricted supply of natural materials such as silk and rubber necessitated the increased production of synthetic substitutes, such as nylon and synthetic rubber.[6] In the intervening years, the development of advanced polymers such as Kevlar and Teflon have continued to fuel a strong and growing polymer industry.

The growth in industrial applications was mirrored by the establishment of strong academic programs and research institute. In 1946, Herman Mark established the Polymer Research Institute at Brooklyn Polytechnic, the first research facility in the United States dedicated to polymer research. Mark is also recognized as a pioneer in establishing curriculum and pedagogy for the field of polymer science. In 1950, the POLY division of the American Chemical Society was formed, and has since grown to the second-largest division in this association with nearly 8,000 members. Fred W. Billmeyer, Jr., a Professor of Analytical Chemistry had once said that "although the scarcity of education in polymer science is slowly diminishing but it is still evident in many areas. What is most unfortunate is that it appears to exist, not because of a lack of awareness but, rather, a lack of interest.

Nobel prizes related to polymer science[edit]

2005 (Chemistry) Robert Grubbs, Richard Schrock, Yves Chauvin for olefin metathesis.[9]

2002 (Chemistry) John Bennett Fenn, Koichi Tanaka, and Kurt Wüthrich for the development of methods for identification and structure analyses of biological macromolecules.[10]

2000 (Chemistry) Alan G. MacDiarmid, Alan J. Heeger, and Hideki Shirakawa for work on conductive polymers, contributing to the advent of molecular electronics.[11]

1991 (Physics) Pierre-Gilles de Gennes for developing a generalized theory of phase transitions with particular applications to describing ordering and phase transitions in polymers.[12]

1974 (Chemistry) Paul J. Flory for contributions to theoretical polymer chemistry.[13]

1963 (Chemistry) Giulio Natta and Karl Ziegler for contributions in polymer synthesis. (Ziegler-Natta catalysis).[14]

1953 (Chemistry) Hermann Staudinger for contributions to the understanding of macromolecular chemistry.

Lecture 4.3: Extrusion of Plastics

Extrusion

Extrusion is a high volume manufacturing process. The plastic material is melted with the application of heat and extruded through die into a desired shape. A cylindrical rotating screw is placed inside the barrel which forces out molten plastic material through a die. The extruded material takes shape according to the cross-section of die. The schematic of extrusion process is shown in figure 1.

Working Principle

In this process, plastic material in the form of pellets or granules is gravity fed from a top mounted hopper into the barrel. Additives such as colorants and ultraviolet inhibitors (liquid or pellet form) can be mixed in the hopper. The plastic material enters through the feed throat and comes into contact with the rotating screw. The rotating screw pushes the plastic beads forward into the barrel. The barrel is heated using the heating elements up to the melting temperature of the plastic. The heating elements are used in such ways that gradually increase the temperature of the barrel from the rear to the front.

There are three possible zones in a rotating screw i.e. feed zone, melting zone, and metering zone. In the feed zone, the plastic beads melt gradually as they are pushed through the barrel. The plastic material is completely melted in the melting zone. A thermostat is used to maintain the inside temperature of the barrel. The overheating of plastics should be minimized which may cause degradation in the material properties. A cooling fan or water cooling system is used to maintain the temperature of the barrel during the process.

At the front of the barrel, the molten plastic leaves the screw and travels through a screen pack to remove any contaminants in the molten plastic. The screens are reinforced by a breaker plate. The breaker plate assembly also serves to create back pressure in the barrel. The back pressure gives uniform melting and proper mixing of the molten plastic material into the barrel. After passing through the breaker plate, molten plastic enters into die. The die gives the desired shape of plastic product. An uneven flow of molten plastic would produce unwanted stresses in the plastic product. These stresses can cause warping after solidification of molten plastic. Plastics are very good thermal insulators and therefore it is very difficult to cool quickly. The plastic product is cooled by pulling through a set of cooling rolls.
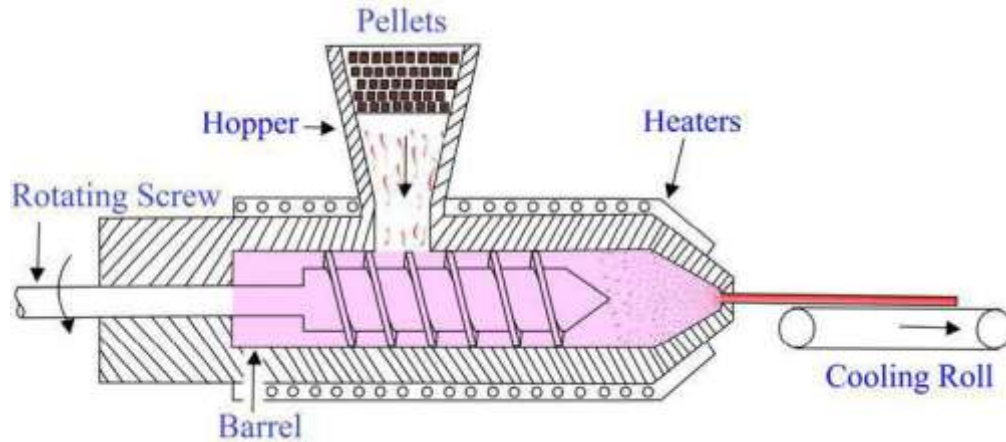
Figure 1 Extrusion process

Extrusion Process Parameters

There are five important process parameters to be considered before extrusion process:

- Melting temperature of plastic
- Speed of the screw
- Extrusion pressure required
- Types of die used
- Cooling medium

Screw Design:

The design of screw is important for plastic processing. It has mainly three different functions: namely, feeding mechanism; uniform melting and mixing of plastic and finally it generates the pressure to push the molten material through die. A screw length (L) is referenced to its diameter (D) as L/D ratio. Generally, L/D ratio is used as 24:1, but for more mixing and output, it may increase up to 32:1. There are three possible zones in a screw length i.e. feed zone, melting zone, and metering zone.

(a) Feed zone: In this zone, the resin is inserted from hopper into the barrel, and the channel depth is constant.

(b) Melting zone: The plastic material is melted and the channel depth gets progressively smaller. It is also called the transition or compression zone.

(c) Metering zone: The molten plastic is mixed at uniform temperature and pressure and forwarded through the die. The channel depth is constant throughout this zone.

Types of Extrusion Process

The extrusion process is broadly classified into seven different types depending upon the specific applications.

(a) Sheet/Film Extrusion

In this extrusion process, the molten plastic material is extruded through a flat die. The cooling rolls are used to determine the thickness of sheet/film and its surface texture. The thickness of sheet can be obtained in the range of 0.2 to 15 mm. The thin flat sheet or film of plastic material can be made. Generally, polystyrene plastic is used as a raw material in the sheet extrusion process.

(b) Blown Film Extrusion

In the blown film process, the die is like a vertical cylinder with a circular profile. The molten plastic is pulled upwards from the die by a pair of nip rollers. The compressed air is used to inflating the tube. Around the die, an air-ring is fitted. The purpose of an air-ring is to cool the film as it travel upwards. In the center of the die, there is an air inlet from which compressed air can be forced into the centre of the circular profile, and creating a bubble. The extruded circular cross section may be increased 2-3 times of the die diameter. The bubbles are collapsed with the help of collapsing plate. The nip rolls flatten the bubble into double layer of film which is called layflat. The wall thickness of the film can be controlled by changing the speed of the nip rollers. The layflat can be spooled in the form of roll or cut into desired shapes. Bottom side of the layflat is sealed with the application of heat, and cut across further up to form opening; hence it can be used to make a plastic bag. The die diameter may vary from 1 to 300 centimeters. Generally, polyurethane plastic is used in this process. The schematic of blown film extrusion is shown in figure 2.
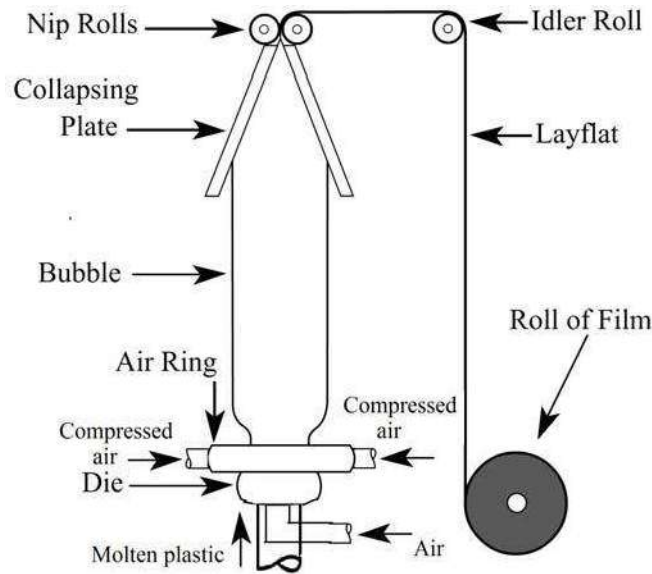
Figure 2 Blown film extrusion

(c) Over Jacketing Extrusion

This is also called wire coating process. In this process, a bare wire is pulled through the center of a die. There are two different types of extrusion tooling used for coating over a wire i.e. pressure or jacketing tooling as shown in figure 3. If intimate contact or adhesion is required between the wire and coating, pressure tooling is used. If adhesion is not desired, jacketing tooling is used. For pressure tooling, the wire is retracted inside the die, where it comes in contact with the molten plastic at a much higher pressure. For jacketing tooling, the wire will extend and molten plastic will make a cover on the wire after die. The bare wire is fed through the die and it does not come in direct contact with the molten plastic until it leaves the die. The main difference between the jacketing and pressure tooling is the position of the wire with respect to the die.

Jacketing coating   Pressure coating
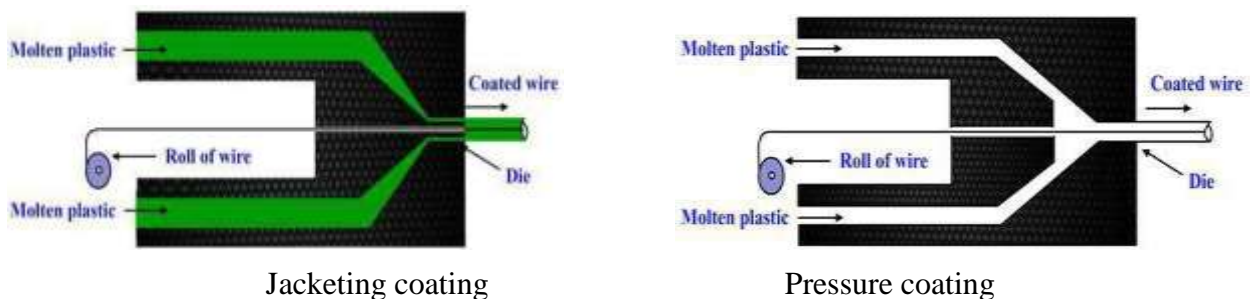
Figure 3 Over jacketing extrusion process

(d) Tubing Extrusion

In this process, the molten plastic is extruded through a die and hollow cross sections are formed by placing a mandrel inside the die. Tube with multiple holes can also be made for specific applications, by placing a number of mandrels in the center of the die.

(e) Coextrusion

Coextrusion is the extrusion process of making multiple layers of material simultaneously. It is used to apply one or more layers on top of base material to obtain specific properties such as ultraviolet absorption, grip, matte surface, and energy reflection, while base material is more suitable for other applications, e.g. impact resistance and structural performance. It may be used on any of the processes such as blown film, overjacketing, tubing, sheet/film extrusion. In this process, two or more extruders are used to deliver materials which are combined into a single die that extrudes the materials in the desired shape. The layer thickness is controlled by the speed and size of the individual extruders delivering the materials.

(f) Extrusion Coating

Extrusion coating is used to make an additional layer onto an existing rollstock of paper, foil or film. For example, to improve the water resistant of paper polyethylene coating is used. The applications of extrusion coating are liquid packaging, photographic paper, envelopes, sacks lining for fertilizers packaging and medical packaging. Generally, polyethylene and polypropylene are used.

Materials Used

The different types of plastic materials that can be used in extrusion process are Polyethylene, Polypropylene (PP), Acetal, Acrylic, Nylon (Polyamides), Polystyrene, Polyvinyl Chloride (PVC), Acrylonitrile Butadiene Styrene (ABS) and Polycarbonate.

Applications

The extrusion process is used for manufacturing rods, plates and tubes, wire and cable coating, hose liners, hose mandrels, filaments, sheet, multilayer film, medical packaging and food packaging, etc.

Advantages

- High production volumes
- Relatively low cost as compared with other molding process
- Design flexibility
- Short lead times
- Coating of wire can be done to achieves desired properties
- Continuous part can be produced

Disadvantages:

- Limited complexity of parts
- Uniform cross section can only be produced

Soil, marine ,noise and thermal pollution

Soil

- Formation of soil from the parent material (bedrock): mechanical weathering of rocks by temperature changes, abrasion, wind, moving water, glaciers, chemical weathering activities and lichens.

- Under ideal climatic conditions, soft parent material may develop into 1 cm of soil within 15 years.

- **O-horizon:** freshly-fallen & partially-decomposed leaves, twigs, animal waste, fungi & organic materials. Colour: brown or black.

- **A-horizon:** humus/partially decomposed organic matter & some inorganic mineral particles. darker & looser than the deeper layers.

- **O & A-horizon:** contain a large amount of bacteria, fungi, earthworms, small insects, forms complex food web in soil, recycles soil nutrients, & contribute to soil fertility.

- **B-horizon /(subsoil):** less organic material & fewer organisms than A-horizon.

- **C-horizon:** consists of broken-up bedrock, does not contain any organic materials. Chemical composition helps to determine pH of soil & also influences soil's rate of water absorption & retention.

- R-horizon: The unweathered rock (bedrock) layer that is beneath all the other layers

Soil Layers

O Horizon (humus)

A Horizon (topsoil)

E Horizon (eluviation layer)

B Horizon (subsoil)

C Horizon (regolith)

R Horizon (bedrock)

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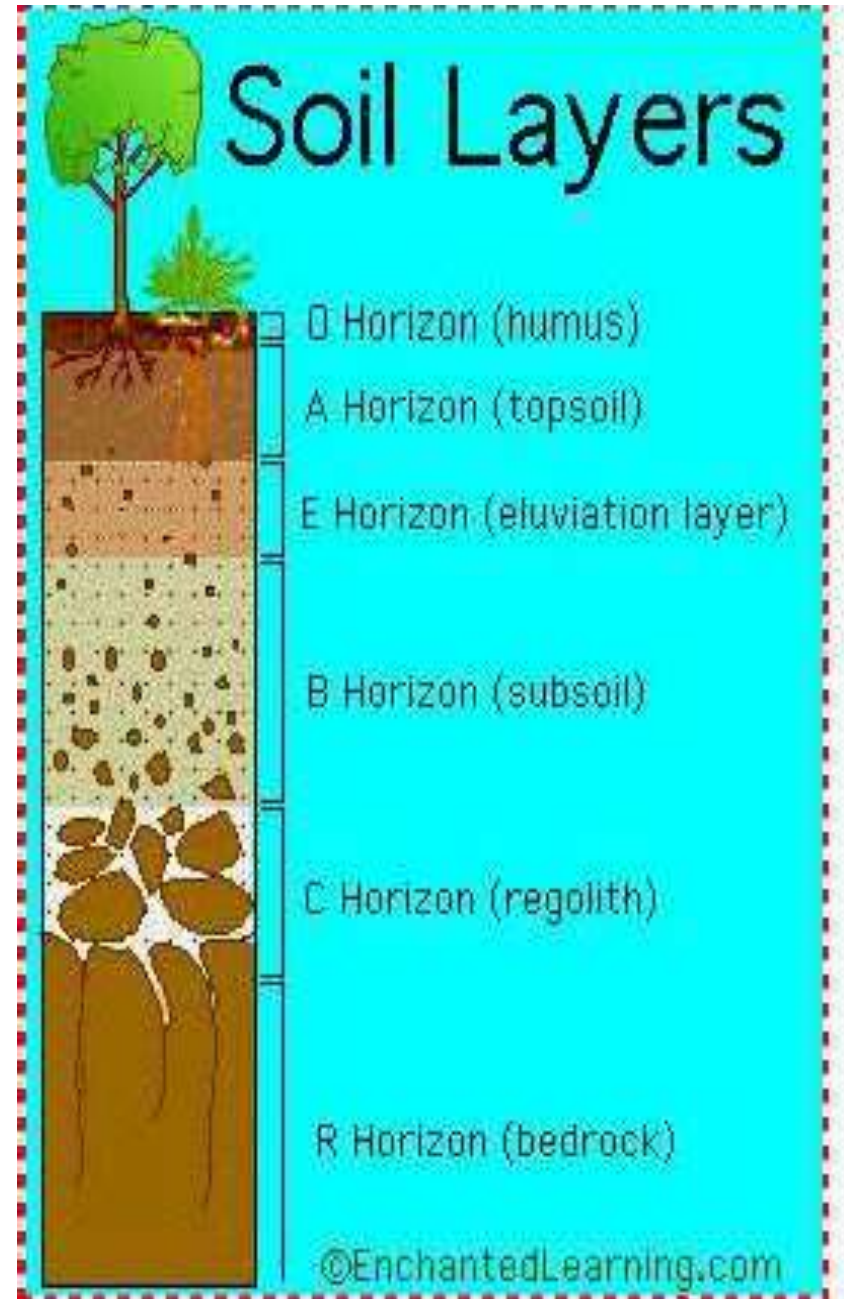
Soil Pollution

✓**Soil pollution** is caused by the presence of chemicals or other alteration in the natural soil environment.

✓Resulting in a change of the soil quality

✓likely to affect the normal use of the soil or endangering public health and the living environment.

CAUSES OF SOIL DEGRADATION

- Soil erosion/degradation is the loss of top soil erodes fertility of soil & reduces its water-holding capacity.

- Excessive farming, construction, overgrazing, burning of grass: cover and deforestation

- Excess salts and water (Salinization)

- Excessive use of fertilizers & pesticides

- Solid waste

First effect of pollutants

- Washed away: might accumulates somewhere
- Evaporate: can be a source of air pollution
- Infiltrate through the unsaturated soil to the groundwater
- DDT: fat soluble, stored in fatty tissues
  - Interferes with calcium metabolism
  - Results in thin egg shells in birds
- Agent orange: code name for one of the herbicides and defoliants (results in leaf fall) used by the U.S. military as part of its herbicidal warfare program, During the Vietnam War, between 1962 and 1971, the United States military sprayed 20,000,000 US gallons (80,000,000 L) of chemical herbicides and defoliants in Vietnam
  - anti fertility, skin problems, cancer

Control of soil pollution

- Use of pesticides and fertilizers should be minimized.
- Cropping techniques should be improved to prevent growth of weeds.
- Special pits should be selected for dumping wastes.
- Controlled grazing and forest management.
- Wind breaks and wind shield in areas exposed to wind erosion
- Afforestation and reforestation.
- **3 Rs: reduce, reuse, recycle**

Information needed to clean up materials added to soil

✓ **Kind of** material-organic or inorganic- is the material biodegradable/ dangerous to animals & humans

✓ **How much material** was added to the soil, will it overload the organisms in the soil

✓ **C:N ratio of the pollutant material**

✓ **Nature of soil:** will the soil be able to handle the material before groundwater is contaminated

✓ **Growing conditions for the soil organisms:** - is it too cold, too wet etc.

✓ **How long the material has been on site:** is there evidence of environmental problems, is it undergoing decomposition.

✓ **Immediate danger to people & environment:** Urgency of the situation.

Factors affecting bioremediation

- Microbial factors

- Temperature favorable for organisms

- Availability of water (Moisture content)

- Availability of nutrients (N,P,K)

- C: N (carbon: nitrogen) ratio of the contaminant material< 30:1

- pH

- Availability of Oxygen in sufficient quantity in soil.

- *In situ* Bioremediation : The treatment in place without excavation of contaminated soils or sediments.

- *Ex situ* bioremediation: requires pumping of the groundwater or excavation of contaminated soil prior to remediation treatments.

Types of *In situ* Bioremediation

- **Biostimulation:** To stimulate the activity of microorganisms by adding nutrients and electron acceptors (*e.g.* O_2)
- **Bioventing:** Injecting air through soil to stimulate microbe growth in unsaturated zone
- **Biosparging:** Injection of air/nutrients into unsaturated and saturated zones
- **Bioaugmentation:** inoculation of soil with microbes or adding exogenous microbes to the subsurface
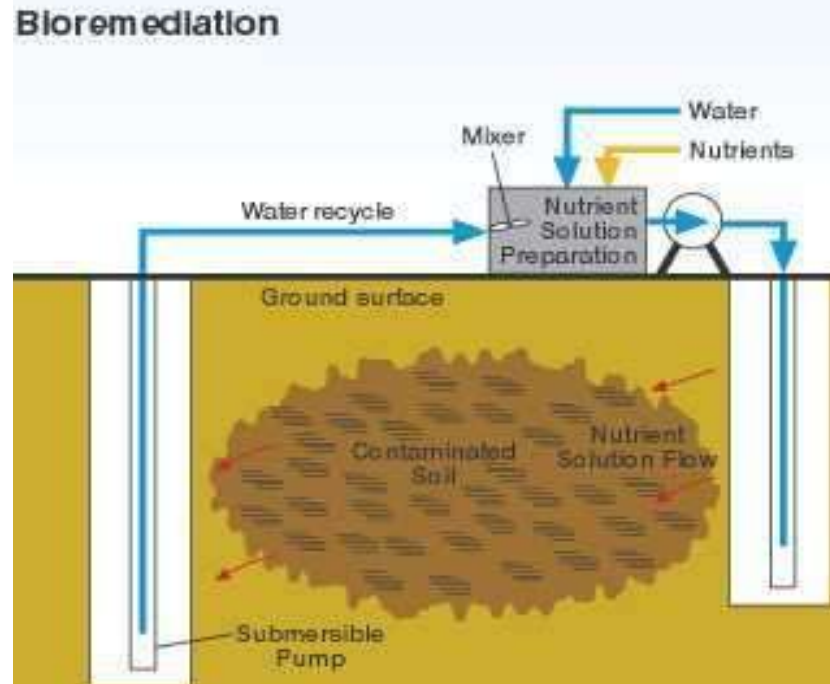
In-situ-Bioremediation

Good for large volumes
Slower
Doesn't work well in clays or highly layered subsurfaces

Less expensive
• Creates less dust
• Less possibility of contaminant release into environment

- *Biostimulation* (stimulates biological activity)

  - <u>Bioventing</u> (Inject air/nutrients into unsaturated zone – good for midweight petroleum, jet fuel)

  - <u>Biosparging</u> (Inject air/nutrients into unsaturated *and* saturated zones)

- *Bioaugmentation* (inoculates soil with microbes)
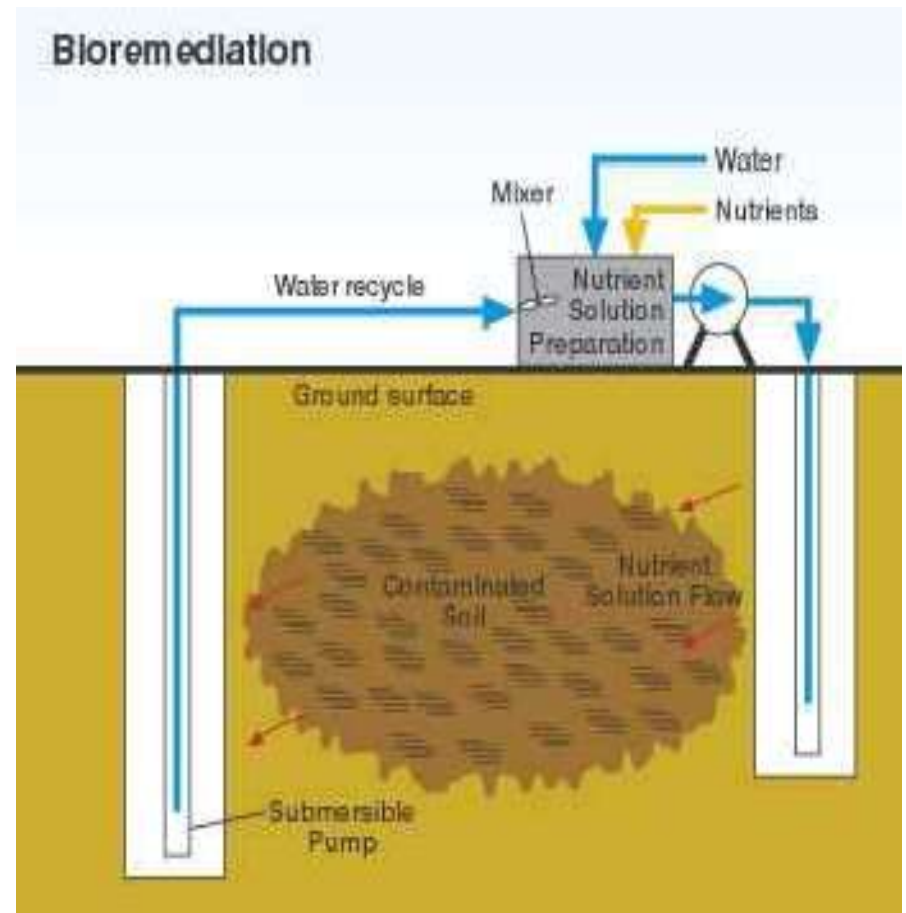
Biostimulation
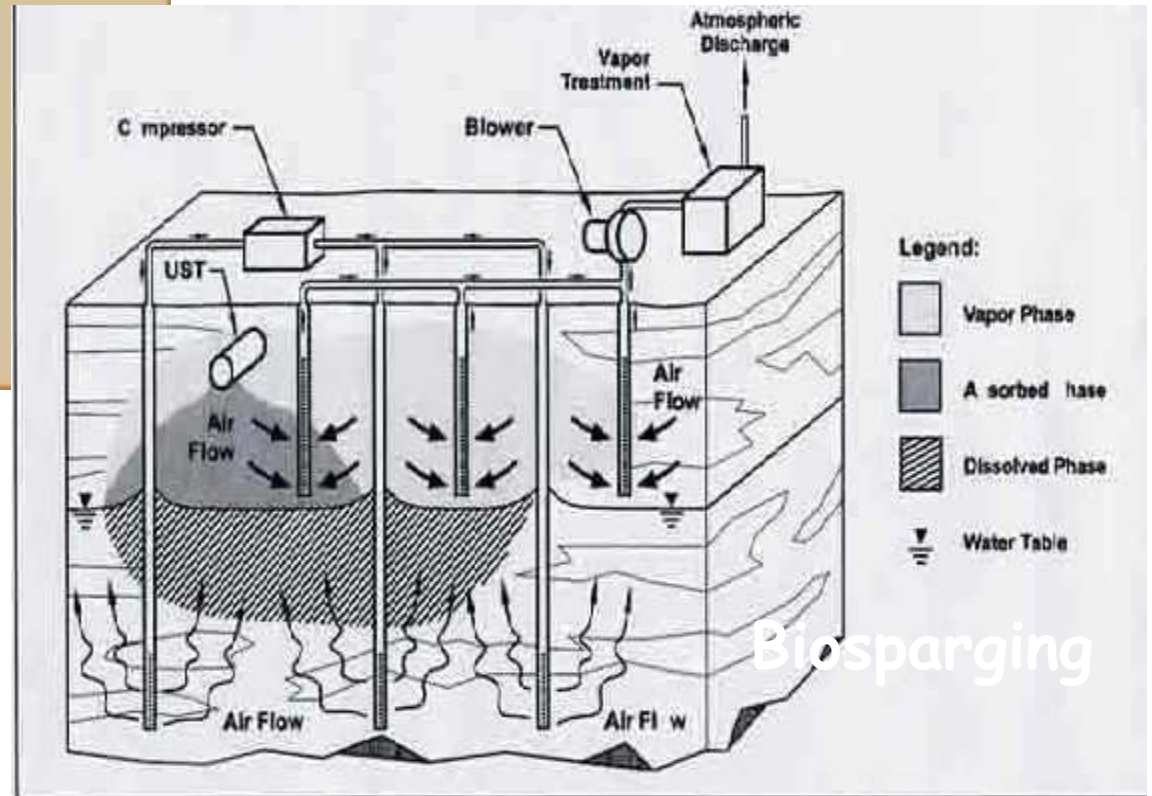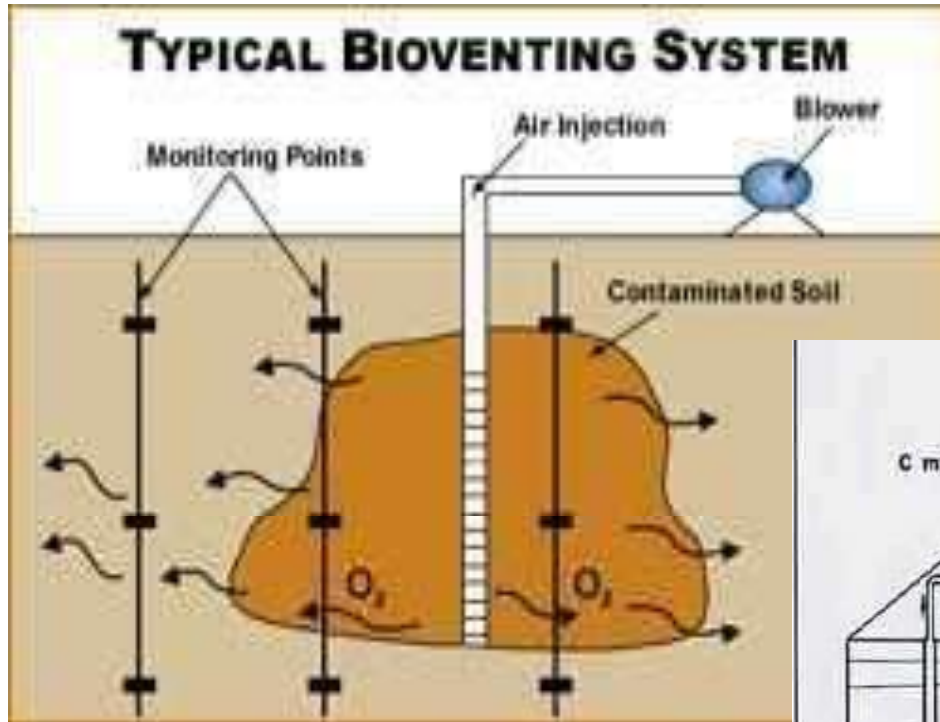
Ex-situ -Bioremediation

- *Slurry-phase*-Soil combined with water/additives in tank, microorganisms, nutrients, oxygen added

- *Solid-phase*

  - Land-farming: soil put on pad, leachate collected

  - Soil biopiles: soil heaped, air added

  - Composting: biodegradable waste mixed with bulking agent

  - Land Applied –waste added directly to soil which is later planted to a crop.

- Easier to control
- Used to treat wider range of contaminants and soil types
- Costly
- Faster

Advantages of Using Bioremediation Processes Compared With Other Remediation Technologies

(1)   biologically-based remediation detoxifies hazardous substances instead of merely transferring contaminants from on environmental medium to another;

(2)   bioremediation is generally less disruptive to the environment than excavation-based processes; and

(3)   The cost of treating a hazardous waste site using bioremediation technologies can be considerably lower than that for conventional treatment methods: vacuuming, absorbing, burning, dispersing, or moving the material .

Marine pollution

- The introduction by man, directly, or indirectly, of substances or energy to the marine environment resulting in deleterious effects such as: hazards to human health, hindrance to marine activities, impairment of the quality of seawater for various uses and reduction of amenities.

- Does not include natural processes like volcanic eruptions or earthquakes

Marine pollutants

- Agricultural run offs ((herbicides, pesticides and nutrients)
- Sediments
- Sewage (Faecal Coliform and Pathogens)
- Chemicals, Metals and Radioactive Substances
- Persistent toxins (PCBs, DDT, heavy metals)
- Oil
- Plastics
- Energy (Thermal & light)

Sources of marine pollution

Land sources

- 80% of non-biological marine pollution comes from land based activities
- pipes discharging directly into marine waters(sewage, industrial, chemical and food processing wastes)
- Riverine flows into the sea carry pollutants from the entire catchment area.

From Air

- Global atmospheric inputs to the sea from air discharges

Oil spills and offshore sources

- Oily discharges from ballast water and bilge water during routine ship operations and illegal dumping of solid waste
- Designated dumping grounds at sea
- Accidental spills from Ships carrying hazardous substances, oil, gas etc.

Major Marine Pollutants - Oil
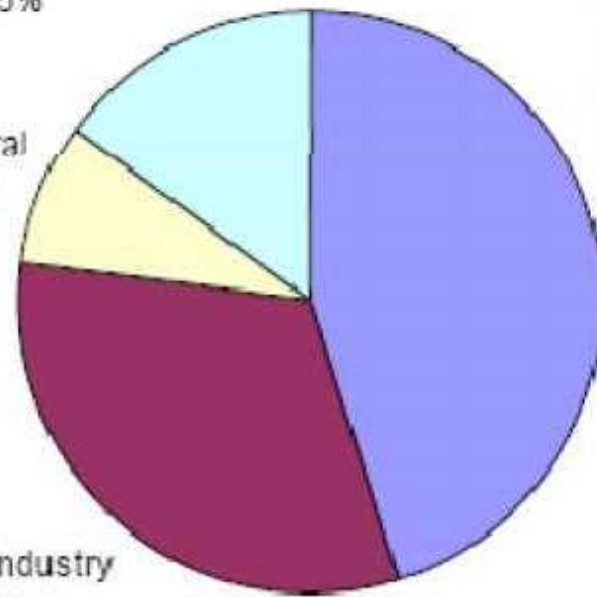
Major Marine Pollutants – Solid Waste

- A large portion and great danger is non-biodegradable plastic
- 46,000 pieces of floating plastic/sq mile of ocean surface off the N.E U.S. coast.
- Sea turtles mistake plastic bags for jellyfish and die from internal blockages.
- Seals and sea lions starve after being entangled by nets or muzzled by six-pack rings (decomposition time 400 years).
- Plastic debris kills 100,000 marine mammals and 2 million sea birds die annually

Control measures for oil pollution

- Natural process of emulsification of oil by use of chemical dispersants: can be sprayed on the oil.

- Slick-lickers: continuous belt of absorbent material dips through the oil slick & is passed through rollers to extract oil.

- Rocks can be cleaned with high pressure steam

Effects of marine pollution:

- **Effects on sea life**

- **Effects on birds**

- **Effects on human being**

  - **Health**

  - **Business**

- **Eutrophication and development of red tides (phytoplankton blooms carrying red pigmentation)**

- **Development of oil slick: When oil is spilled on sea, it spreads over the surface forming a thin film called OIL SLICK. Which damage marine life**

Effects of marine pollution

- Damages marine life to a large extent, for salt-marsh plants, oil slicks can affect flowering, fruiting and germination.

- Coral reefs

- If liquid oil contaminates a bird's plumage, its water-repellent properties are lost, drown, die

- Drill cuttings dumped on seabed create anoxic conditions & result in the production of toxic sulphides in the bottom sediment thus eliminating the benthic fauna.

- Fish and shellfish production facilities can also be affected by oil slicks. Commercial damage is tainting: imparts an unpleasant flavor to fish and seafood & is detectable even at extremely low levels of contamination.

NOISE POLLUTION

- Defined as unwanted sounds that unreasonably (a kind of harsh, loud and confused sound), intruding into our daily activities

- The most significant attributes of noise are:

i)   Its loudness

ii)   Duration

- The unit of noise is decibel.

- Human ear can tolerate noise up to 120 decibels.

Sources of NOISE POLLUTION

(i)   Road Traffic:
Most prevalent and most damaging source
Impact of road traffic noise depends on factors like: road location & design, and land use planning measures, building design, vehicle standards & driving behavior

(ii)   Air Traffic
Noise from supersonic crafts are dangerous because of its intensity

(iii)   Railways:
The level of noise associated with rail traffic is related to type of engine or rolling stock used, speed of the train, track type & condition, warning signals at crossings, whistles & horns, freight classification yards, & railroad construction & maintenance.

(iv)   Industry
- Product fabrication
- Product assembly
- Power generation
- Processing.

(v) Construction: construction equipments.

(vi) Consumer products: recreational, hobbies/workshop, household, music.

(vii) Other sources: sirens, agricultural noise, noise from animals, humans & military

Measurement of Noise

- Noise intensity is measured in decibel (Db) units
- Decibel scale is logarithmic,
- Each 10 Db increase represents a 10 fold increase in noise intensity
- distance diminishes the effective decibel level reaching the ear.

   e.g. Moderate auto traffic at a distance of 30 m rates about 50 decibels, but for the same, for a driver with a car window open or a pedestrian on the sidewalk, same traffic rates about 70 decibels.

Effects of Noise

- At 45 decibels of noise, average person cannot sleep,

- At 85 decibels hearing damage, & at 120 decibels ear experiences pain.

- Lack of sleep, irritability, heartburn, indigestion, ulcers, high blood pressure, & possibly heart disease

- Hearing loss

- Non-auditory physiological effects

  – Annoyance

  – Communication interference

Noise Pollution Control

Source path receiver concept: Can be controlled either by reducing the noise at the source or by preventing its transmission or by protecting the receiver

- **At the source:** lubrication of machines, tightening the loose units, reducing the eccentricity

- **In the path**: keeping the noisy machine covered, construction of noise barriers, sound-proofing of the building

- **Receiver:** No use of horns other than in emergency, vehicle engines and appliances in good Condition, purchase the least noisy air conditioner or vacuum cleaner/quieter appliances, rest areas away from noise, turn down volume of Stereos.

Thermal Pollution

- Thermal pollution is the process of heating up of water bodies through run off or discharge

- Decreases the solubility of oxygen, resulting in suffocation of plants and animals

- Human activities introducing thermal pollution:
  - Industries and power plants
  - Trees and tall vegetation providing shades are cut down
  - Soil erosion by construction, removal of stream side vegetation, farming practices, overgrazing & recreation increases – reduction in green
  - Thermal pollution can also occur through Earthquakes

Effects of Thermal Pollution

- Thermal shock

- Thermal enrichment: Heated water from power plant may be used to extend plant growing season, speed up growth of fish and other aquatic animal for commercial purpose

Solar Energy:
The Ultimate Renewable Resource

What is Solar Energy?

- Originates with the thermonuclear fusion reactions occurring in the sun.

- Represents the entire electromagnetic radiation (visible light, infrared, ultraviolet, x-rays, and radio waves).

- Radiant energy from the sun has powered life on Earth for many millions of years.
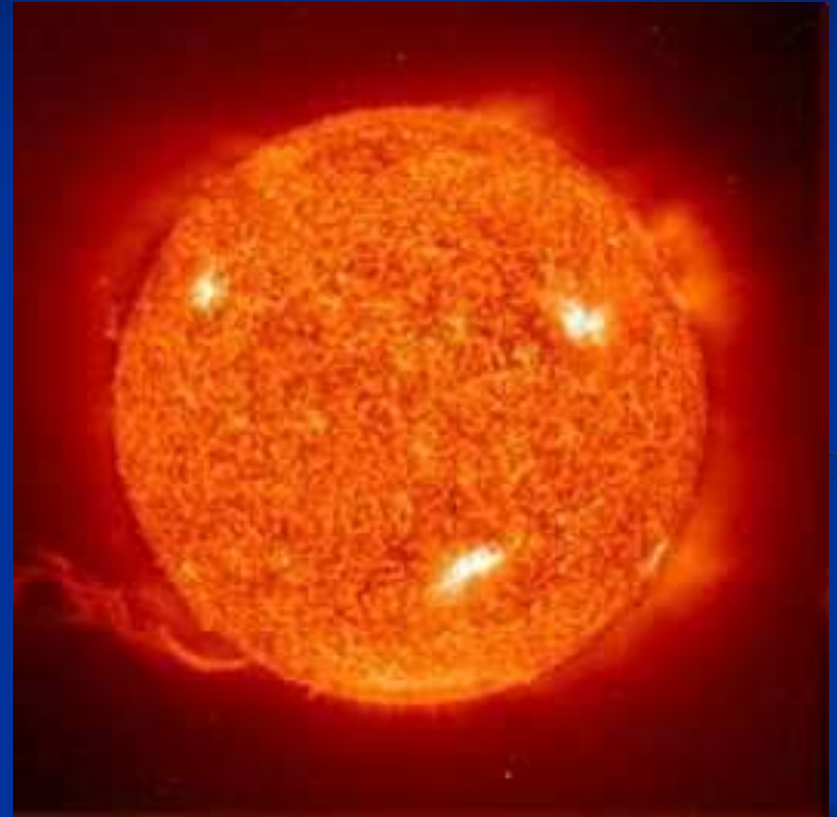
Advantages and Disadvantages

- Advantages
  - All chemical and radioactive polluting byproducts of the thermonuclear reactions remain behind on the sun, while only pure radiant energy reaches the Earth.
  - Energy reaching the earth is incredible. By one calculation, 30 days of sunshine striking the Earth have the energy equivalent of the total of all the planet's fossil fuels, both used and unused!
- Disadvantages
  - Sun does not shine consistently.
  - Solar energy is a diffuse source. To harness it, we must concentrate it into an amount and form that we can use, such as heat and electricity.
  - Addressed by approaching the problem through:
    1) collection, 2) conversion, 3) storage.

Solar Energy to Heat Living Spaces
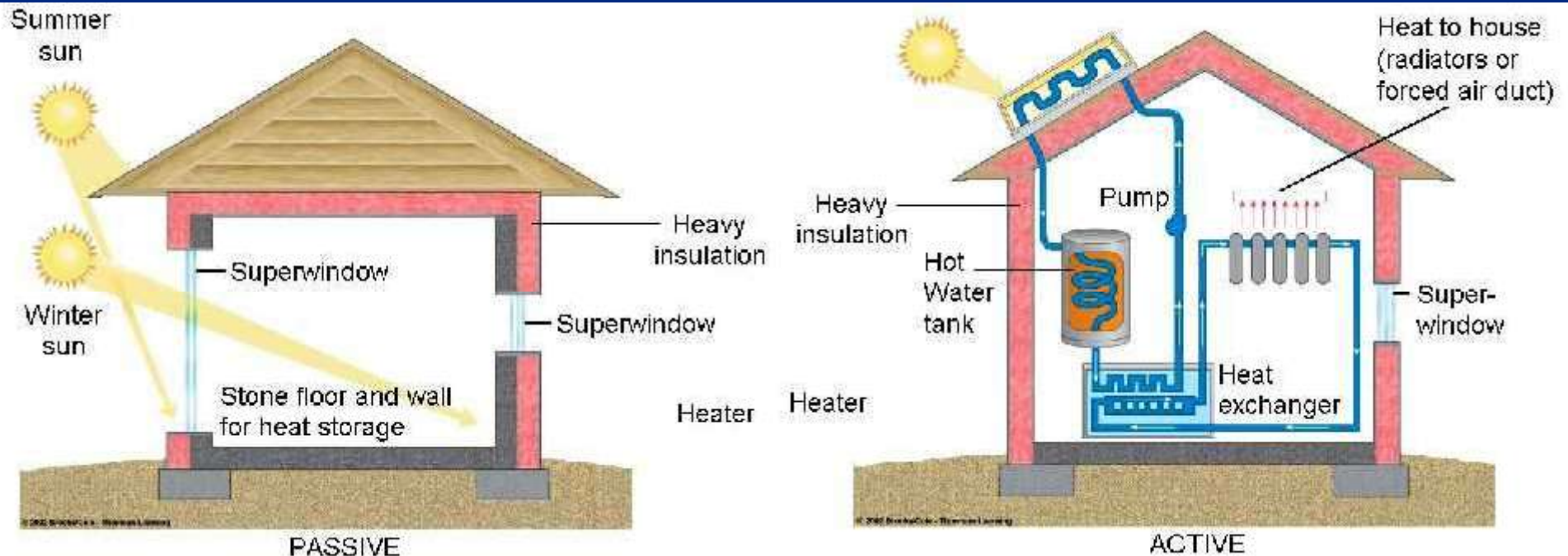
- **Proper design of a building is for it to act as a solar collector and storage unit. This is achieved through three elements: insulation, collection, and storage.**

Solar Energy to Heat Water

- A flat-plate collector is used to absorb the sun's energy to heat the water.

- The water circulates throughout the closed system due to convection currents.

- Tanks of hot water are used as storage.
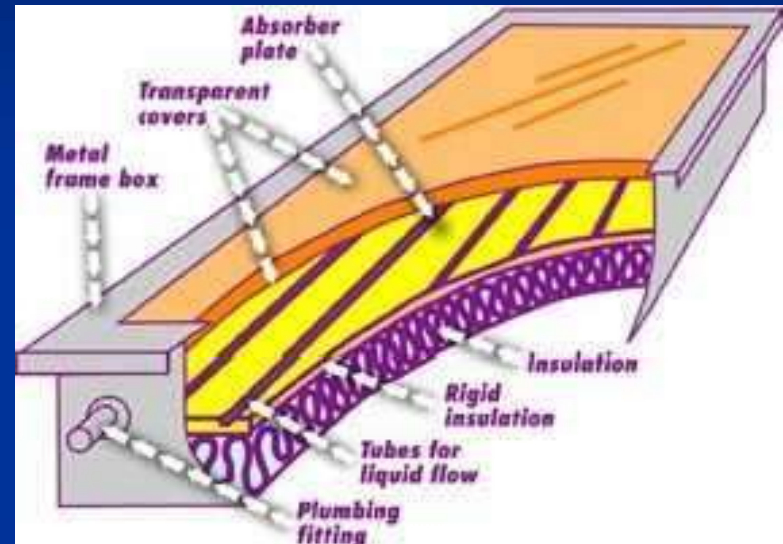
Photovoltaics

- **Photo+voltaic = convert light to electricity**

Single Solar Cell

Boron-enriched silicon
Junction
Cell
Phosphorus-enriched silicon
Sunlight
DC electricity
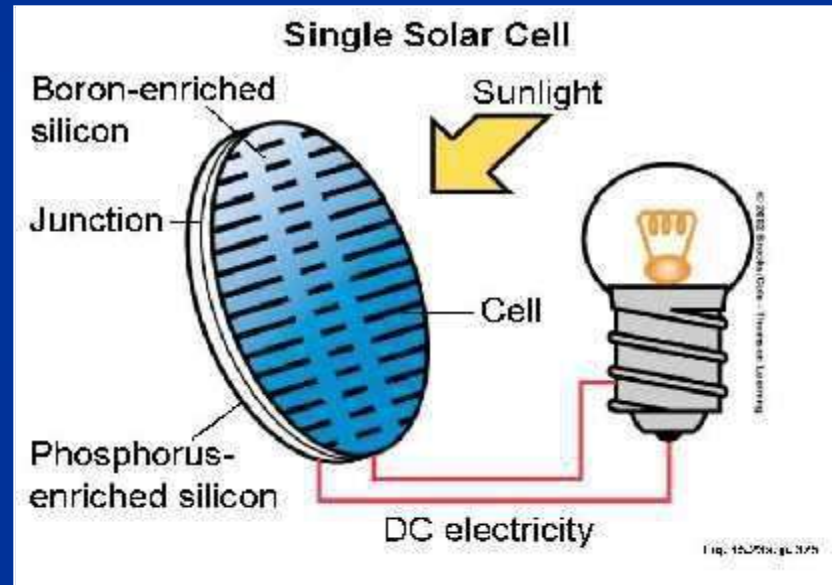
Solar Cells Background

- 1839 - French physicist A. E. Becquerel first recognized the photovoltaic effect.

- 1883 - first solar cell built, by Charles Fritts, coated semiconductor selenium with an extremely thin layer of gold to form the junctions.

- 1954 - Bell Laboratories, experimenting with semiconductors, accidentally found that silicon doped with certain impurities was very sensitive to light. Daryl Chapin, Calvin Fuller and Gerald Pearson, invented the first practical device for converting sunlight into useful electrical power. Resulted in the production of the first practical solar cells with a sunlight energy conversion efficiency of around 6%.

- 1958 - First spacecraft to use solar panels was US satellite Vanguard 1

Driven by Space Applications in Early Days

How does it work
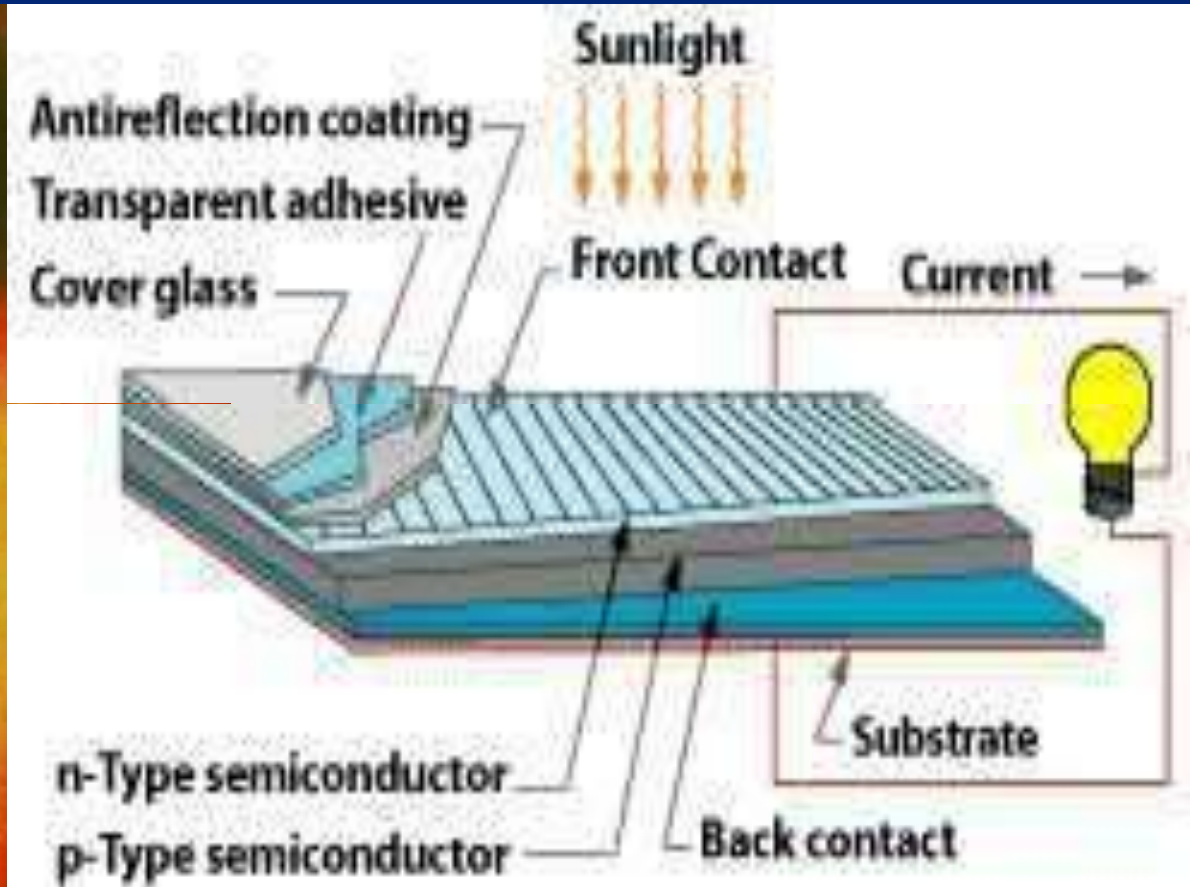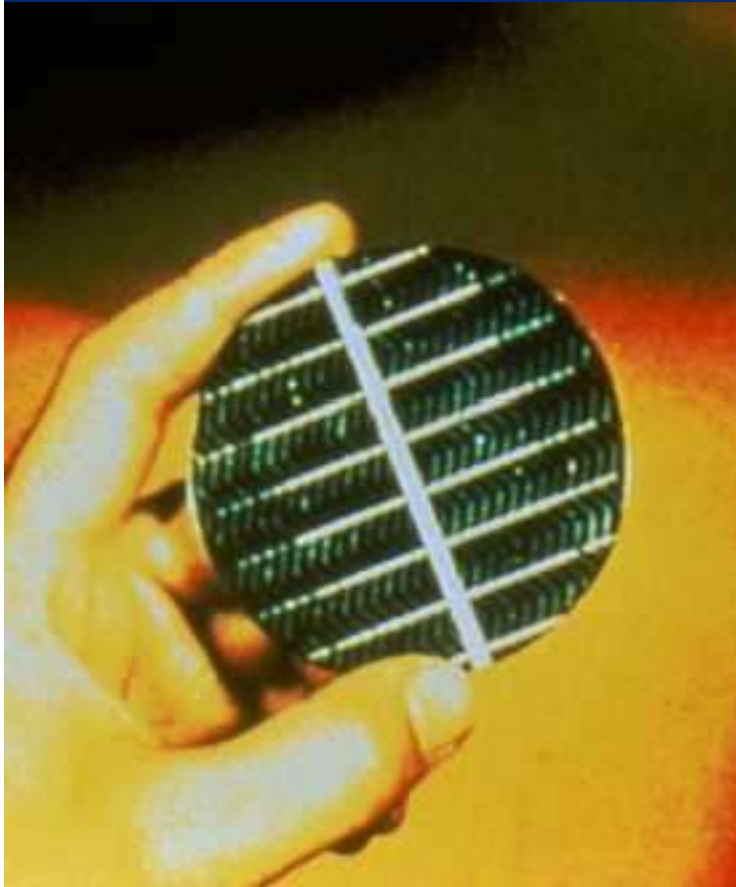
The heart of a photovoltaic system is a solid-state device called a solar cell.

Energy Band Formation in Solid
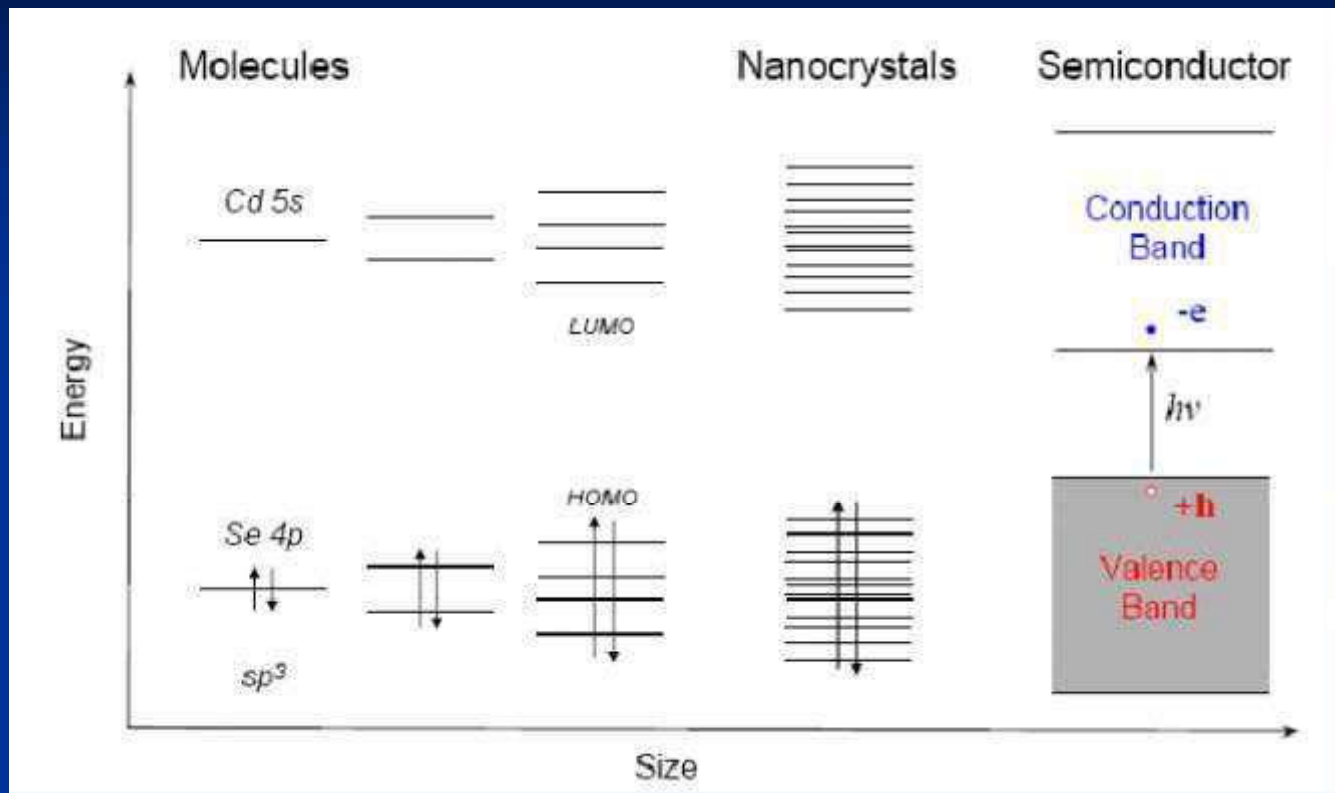
> Each isolated atom has discrete energy level, with two electrons of opposite spin occupying a state.

> When atoms are brought into close contact, these energy levels split.

> If there are a large number of atoms, the discrete energy levels form a "continuous" band.

Energy Band Diagram of a Conductor, Semiconductor, and Insulator

a conductor   **a semiconductor**   **an insulator**
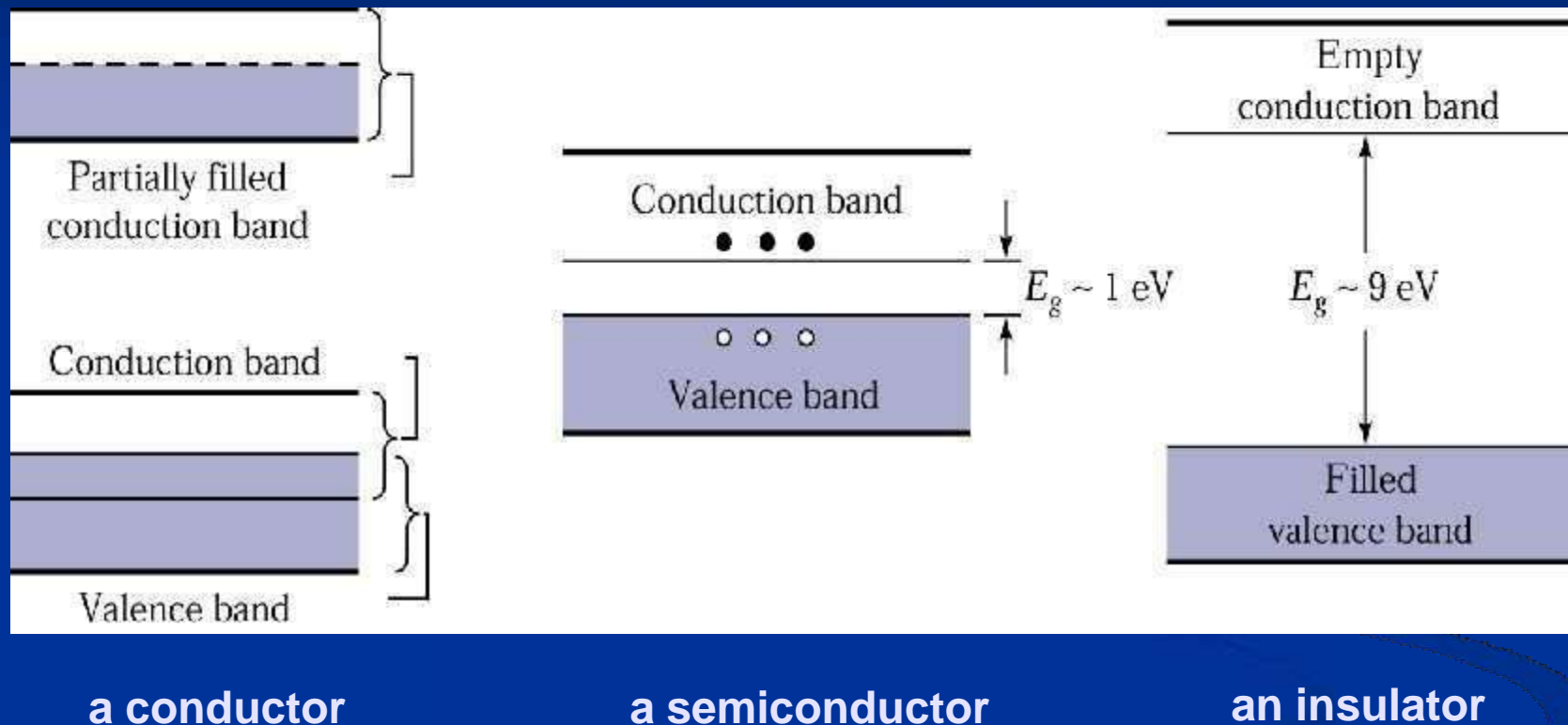
➤ Semiconductor is interest because their conductivity can be readily modulated (by impurity doping or electrical potential), offering a pathway to control electronic circuits.

Silicon

Shared electrons
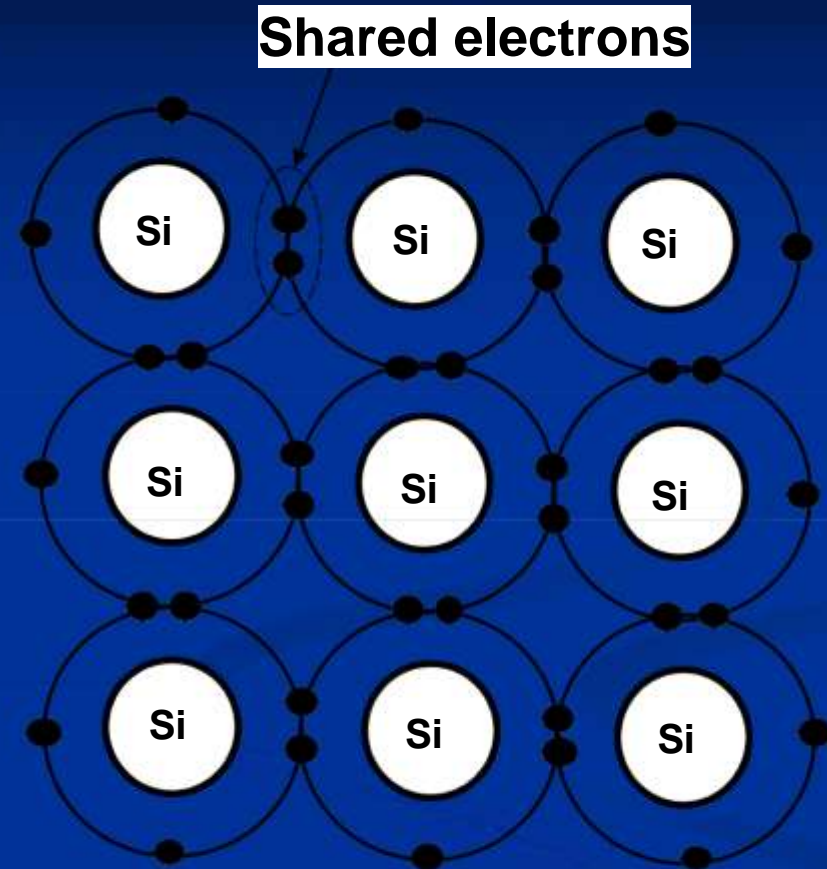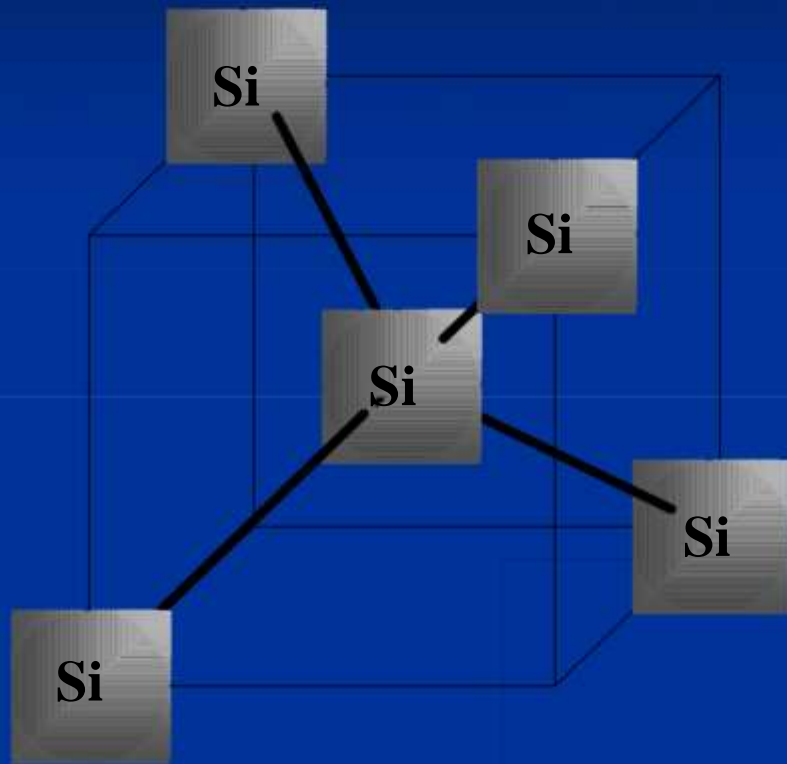
➤ **Silicon is group IV element – with 4 electrons in their valence shell.**

➤ **When silicon atoms are brought together, each atom forms covalent bond with 4 silicon atoms in a tetrahedron geometry.**

Intrinsic Semiconductor

➢ At 0 ºK, each electron is in its lowest energy state so each covalent bond position is filled. If a small electric field is applied to the material, no electrons will move because they are bound to their individual atoms.

=> At 0 ºK, silicon is an insulator.

➢ As temperature increases, the valence electrons gain thermal energy. If a valence electron gains enough energy (Eg), it may break its covalent bond and move away from its original position. This electron is free to move within the crystal.

➢ Conductor Eg <0.1eV, many electrons can be thermally excited at room temperature.

➢ Semiconductor Eg ~1eV, a few electrons can be excited (e.g. 1/billion)

➢ Insulator, Eg >3-5eV, essentially no electron can be thermally excited at room temperature.
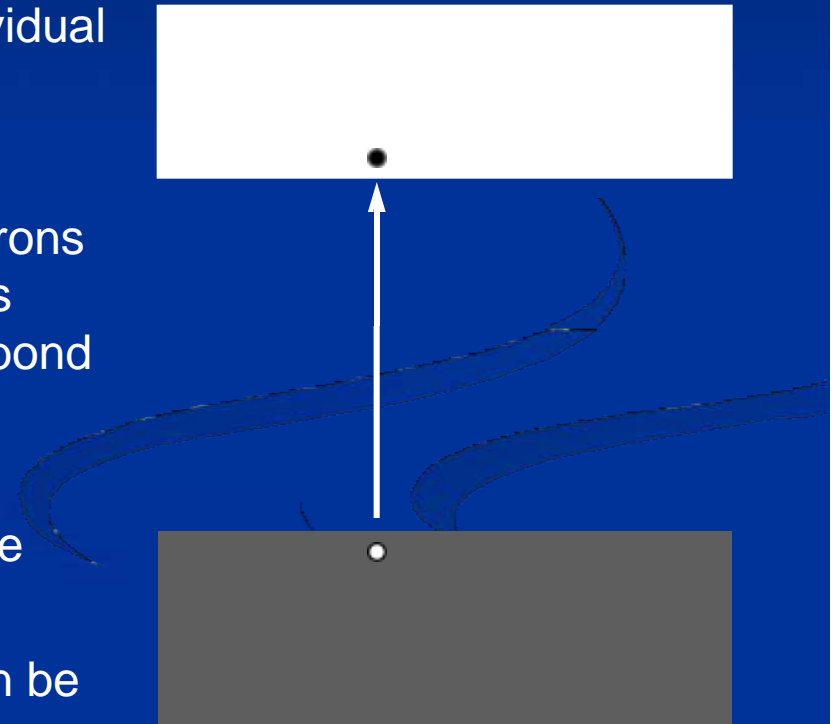
Extrinsic Semiconductor, n-type Doping

Conducting band, E_c

Extra

Electron

$E_d \sim 0.05$ eV

$E_g = 1.1$ eV

Valence band, E_v

Si Si Si
Si As Si
Si Si Si
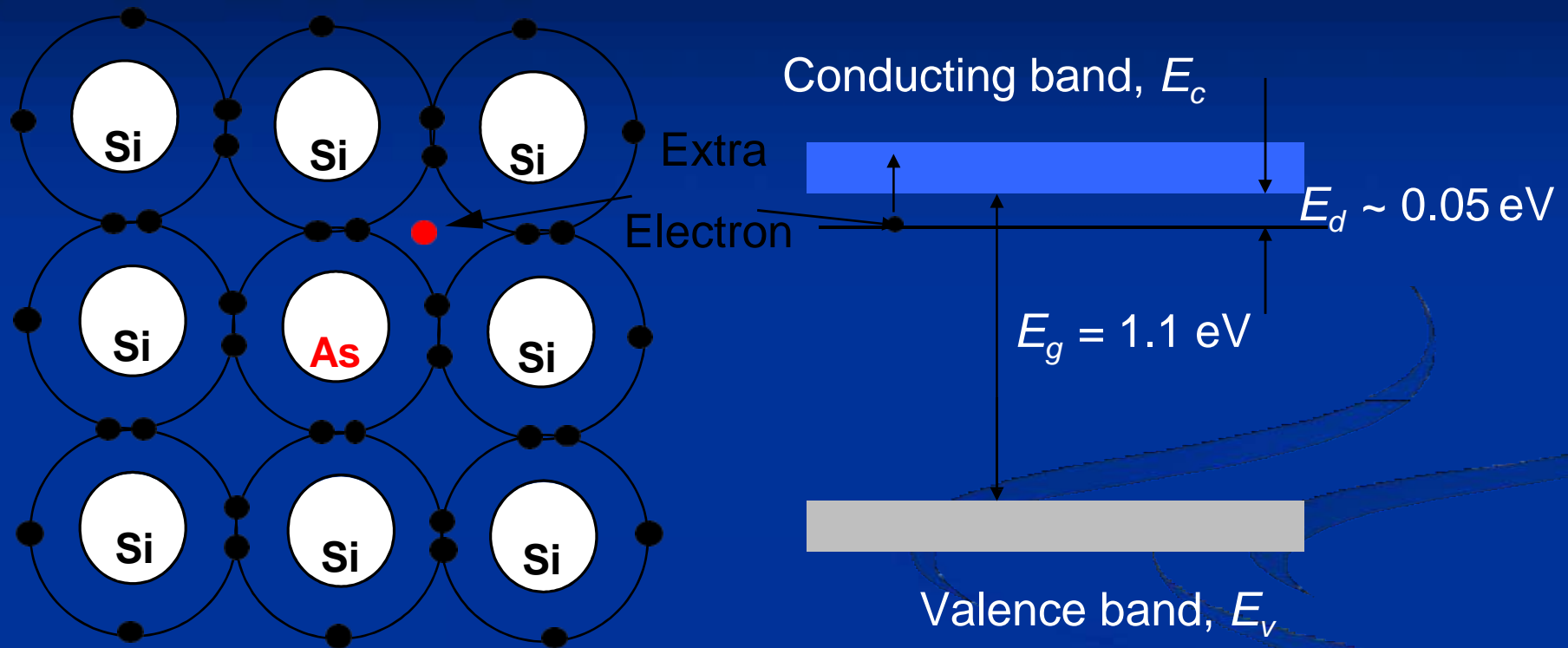
➤ **Doping silicon lattice with group V elements can creates extra electrons in the conduction band —** negative charge carriers (n-type), As- donor.

➤ **Doping concentration #/cm^3 (10^{16}/cm^3 $\sim$ 1/million).**

Extrinsic Semiconductor, p-type doping

Conducting band, E_c

Hole

$E_g = 1.1$ eV

$E_a \sim 0.05$ eV

Valence band, E_v

Electron

B

Si Si Si

Si B Si

Si Si Si
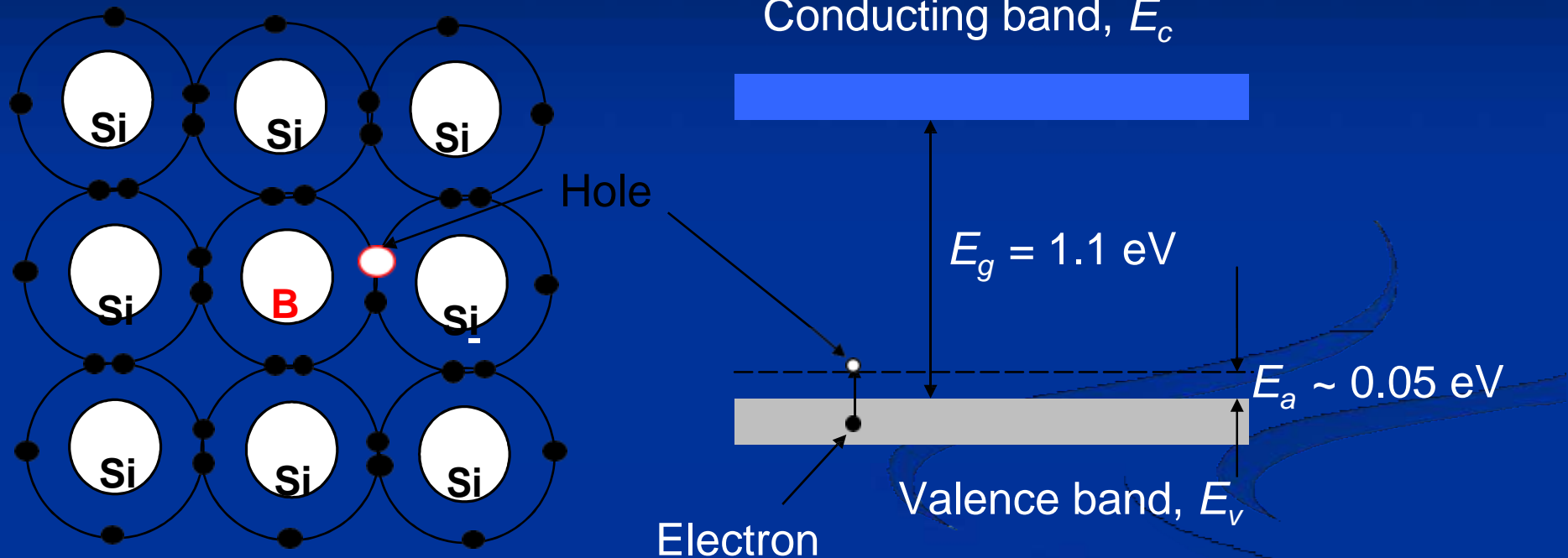
➤ Doping silicon with group III elements can creates empty holes in the conduction band — **positive charge carriers (p-type), B-(acceptor).**

p-n Junction (p-n diode)

depletion layer

Reverse bias

Forward bias
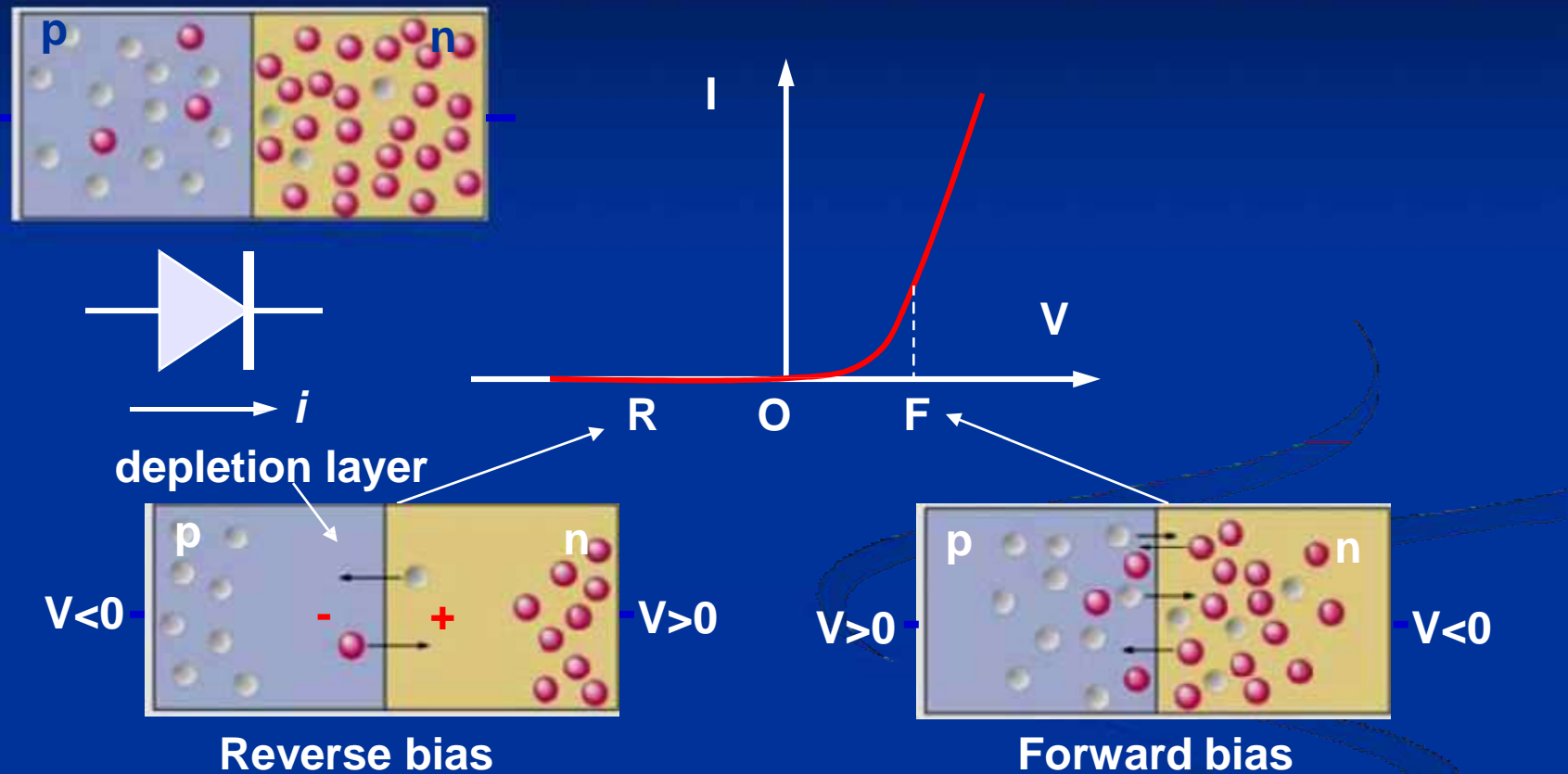
➢ **A p-n junction is a junction formed by combining p-type and n-type semiconductors together in very close contact.**

➢ **In p-n junction, the current is only allowed to flow along one direction from p-type to n-type materials.**

p-n Junction (p-n diode)

❖ **Solar Cells**

❖ Light-emitting Diodes

❖ Diode Lasers

❖ Photodetectors

❖ Transistors

➢ A p-n junction is the basic device component for many functional electronic devices listed above.

How Solar Cells Work
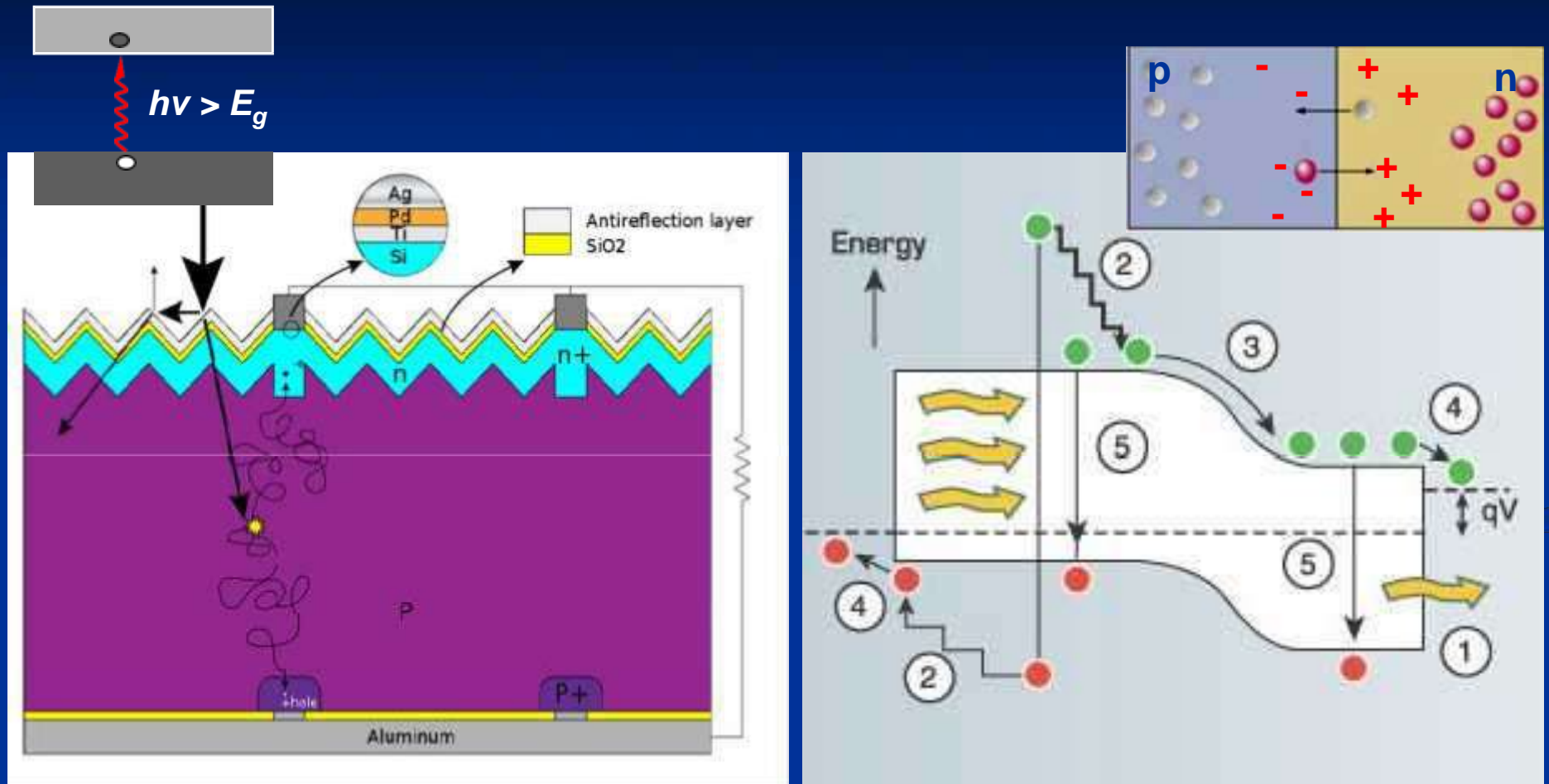
❖ Photons in sunlight hit the solar panel and are absorbed by semiconducting materials to create electron hole pairs.

❖ Electrons (negatively charged) are knocked loose from their atoms, allowing them to flow through the material to produce electricity.

The Impact of Band Gap on Efficiency

Fill Factor, FF = $(V_{mp}I_{mp})/V_{oc}I_{sc}$
Efficiency, η = $(V_{oc}I_{sc}FF)/P_{in}$
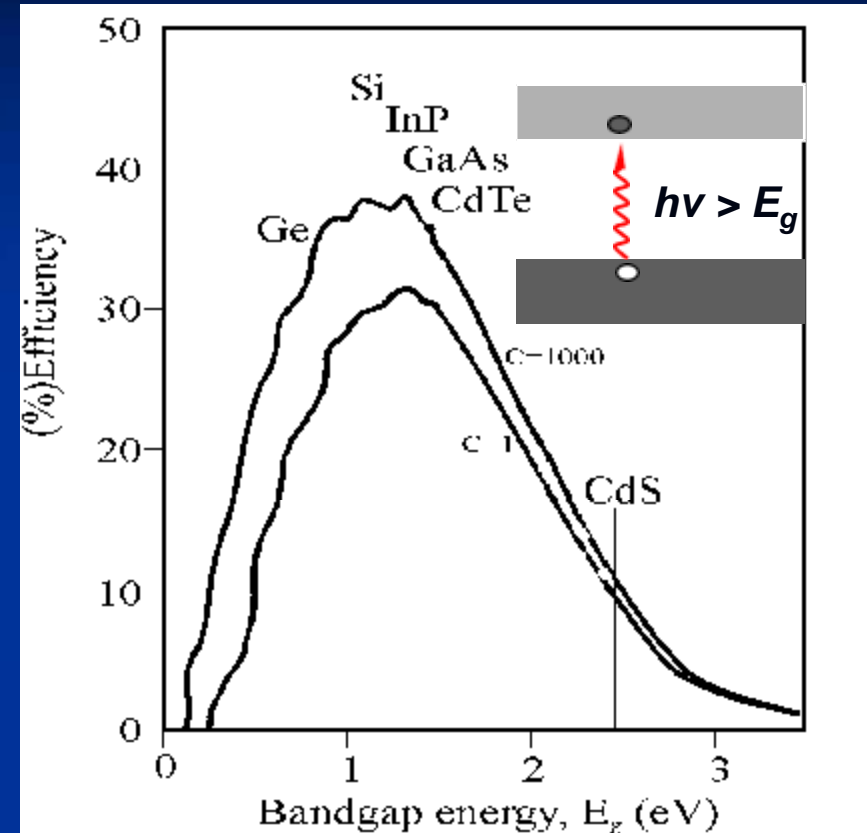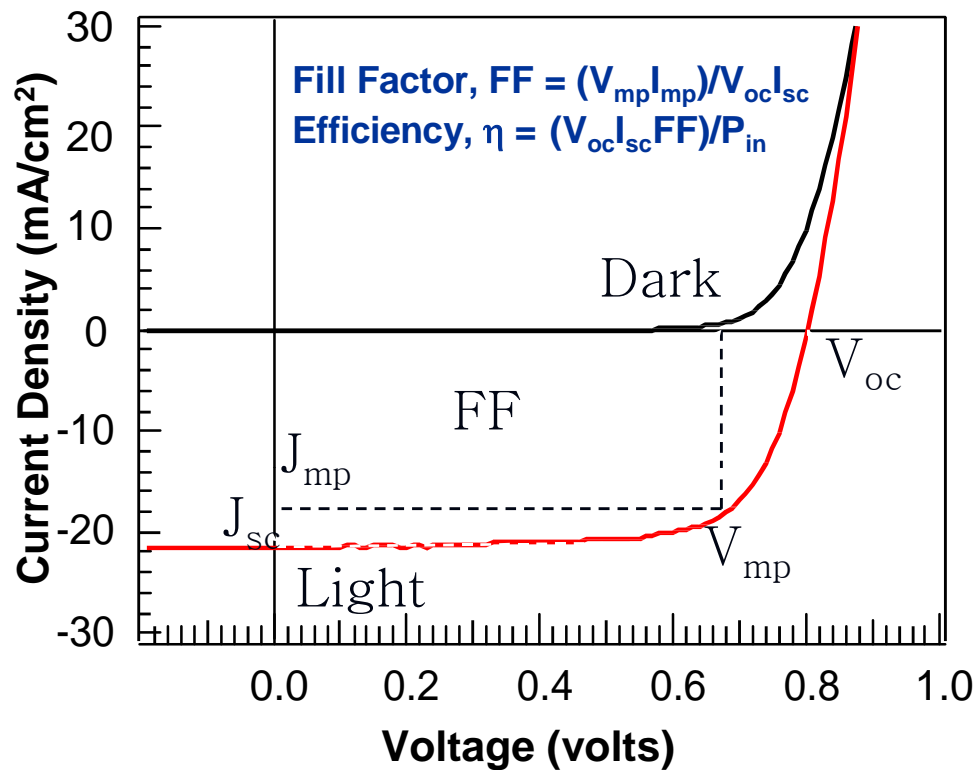
- Efficiency, η = $(V_{oc}I_{sc}FF)/P_{in}$ $V_{oc} \propto E_g$, $I_{sc} \propto$ # of absorbed photons
- Decrease E_g, absorb more of the spectrum
- But not without sacrificing output voltage

Cost vs. Efficiency Tradeoff

Efficiency $\propto \tau^{1/2}$

Large Grain
Single
Crystals

Small Grain
and/or
Polycrystalline
Solids

d

d

Long d
High τ
High Cost

Long d
Low τ
Lower Cost
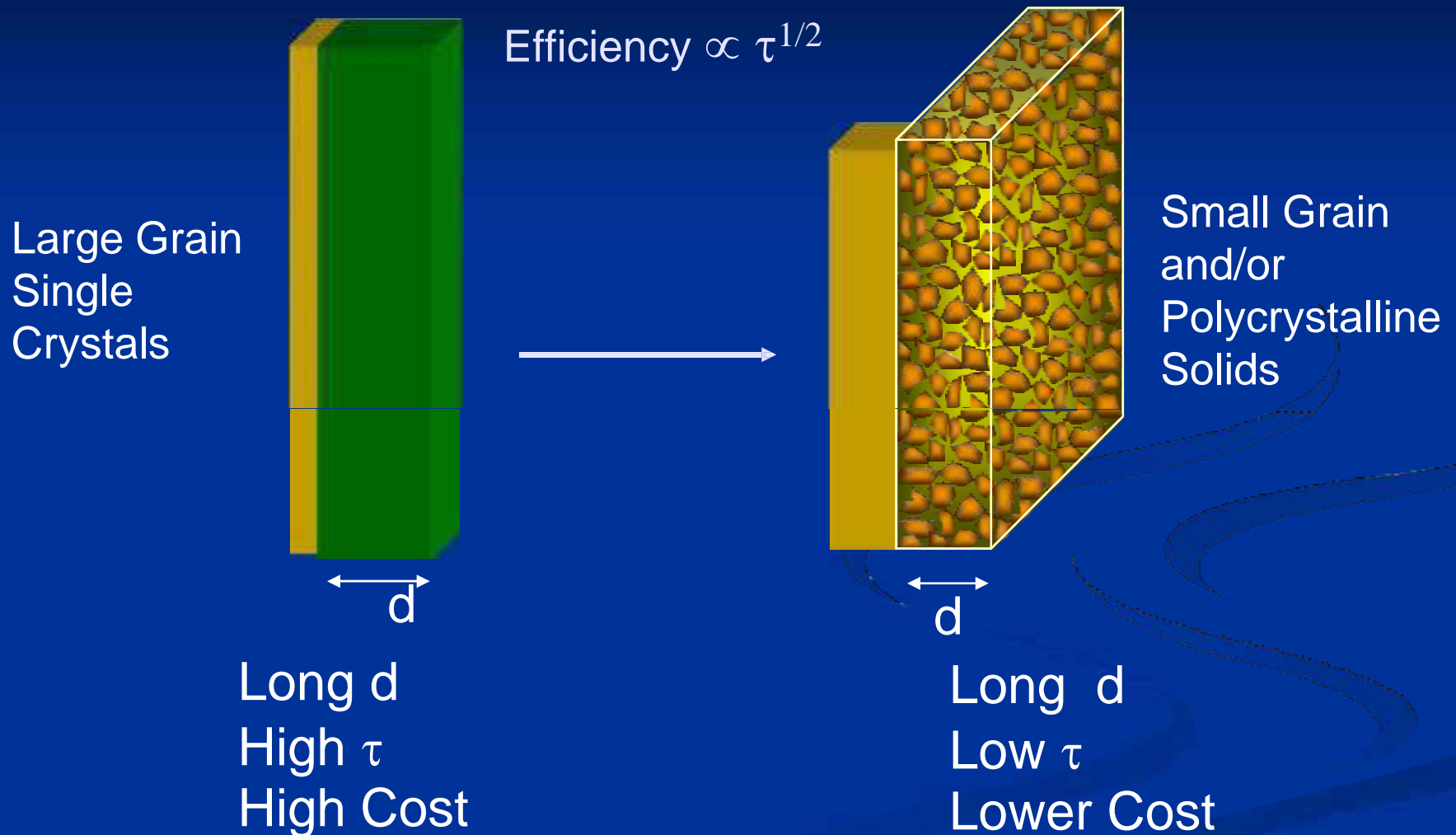
τ decreases as grain size (and cost) decreases

Cost/Efficiency of Photovoltaic Technology
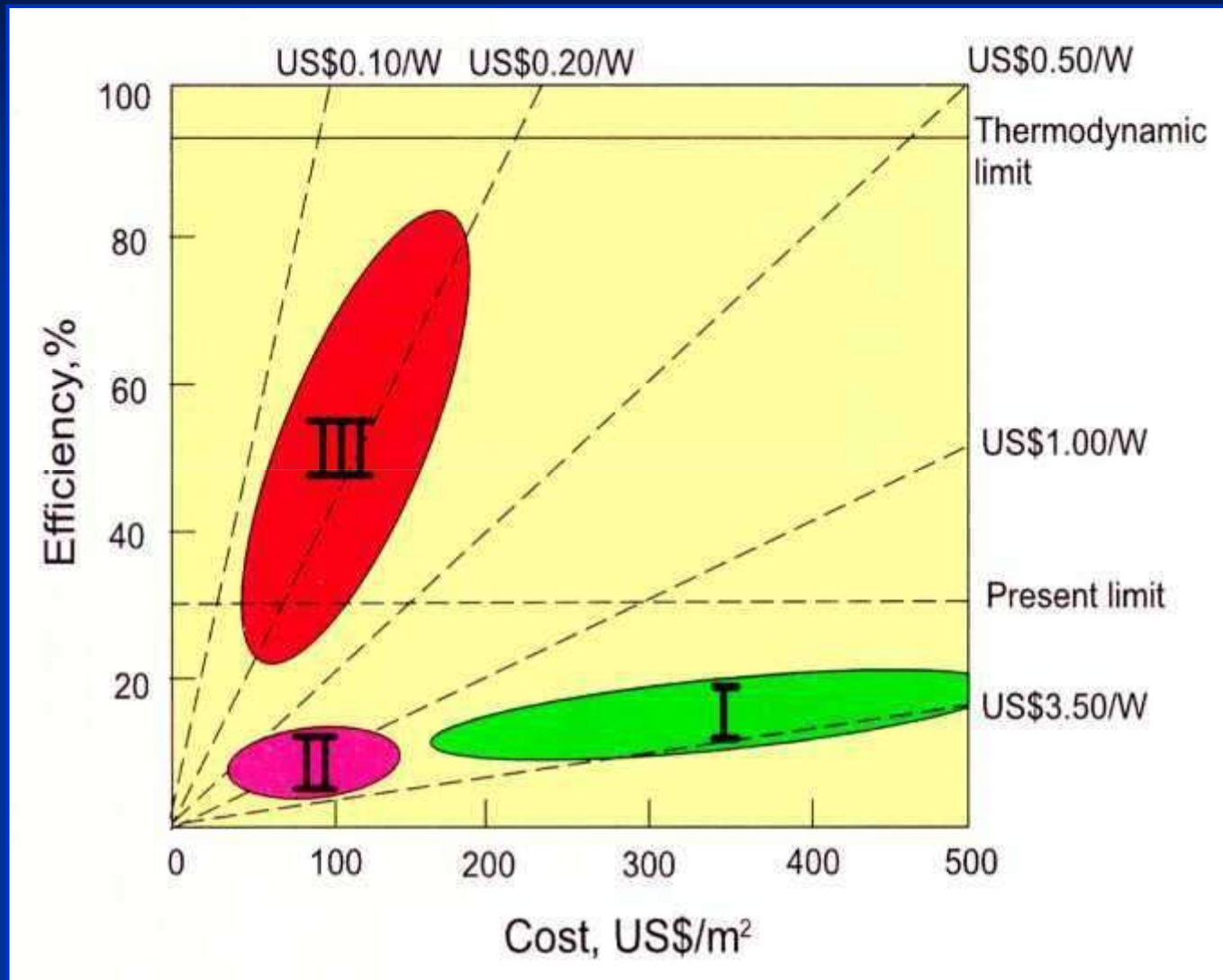
Costs are modules per peak W; $0.35-$1.5/kW-hr

First Generation
– Single Junction Silicon Cells
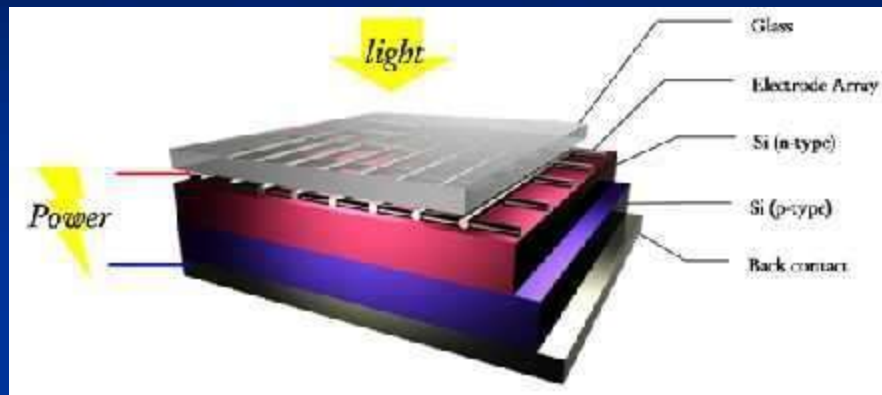
89.6% of 2007 Production
   45.2% Single Crystal Si
   42.2% Multi-crystal SI

- Limit efficiency 31%
- Single crystal silicon - 16-19% efficiency
- Multi-crystal silicon - 14-15% efficiency
- Best efficiency by SunPower Inc 22%

Silicon Cell Average Efficiency
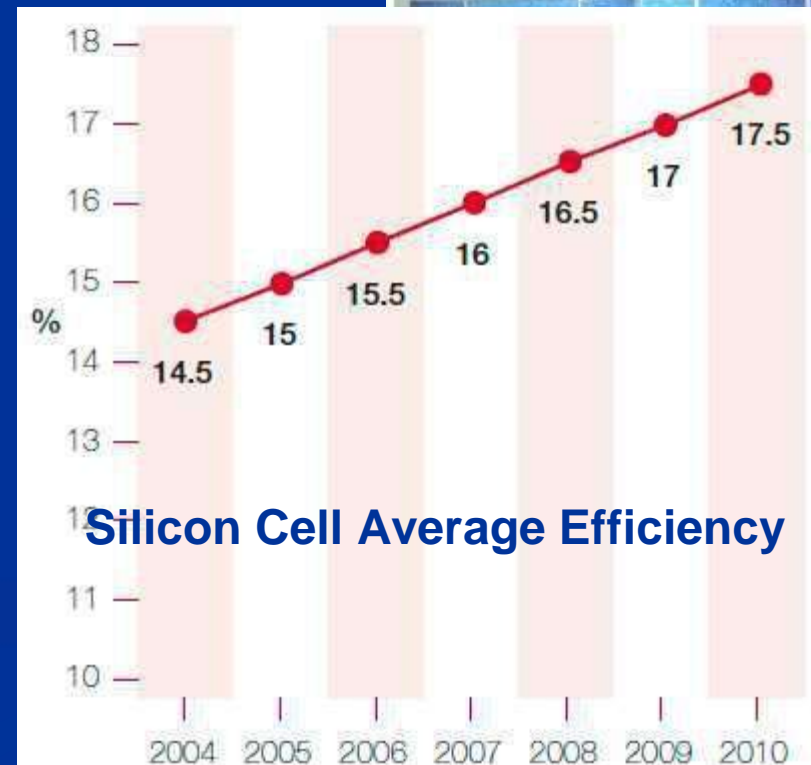
Second Generation
– Thin Film Cells

CdTe 4.7% & CIGS 0.5% of 2007 Productio

- New materials and processes to improve efficienc and reduce cost.

- Thin film cells use about 1% of the expensive semiconductors compared to First Generation cells.

- CdTe – 8 – 11% efficiency (18% demonstrated)
- CIGS – 7-11% efficiency (20% demonstrated)
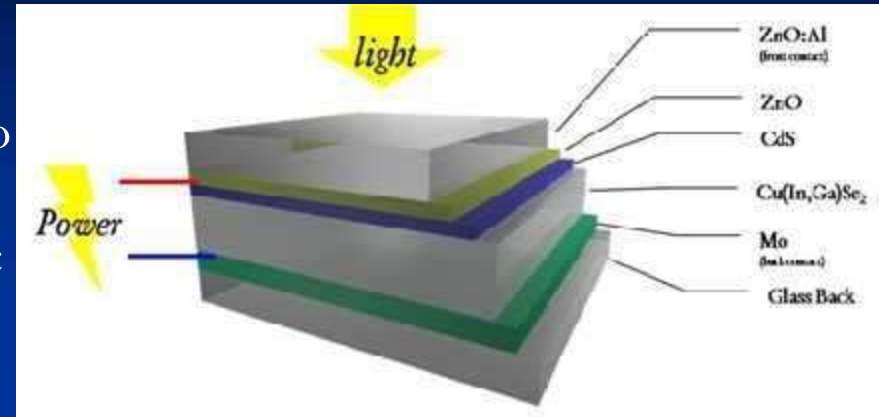
Third Generation
– Multi-junction Cells
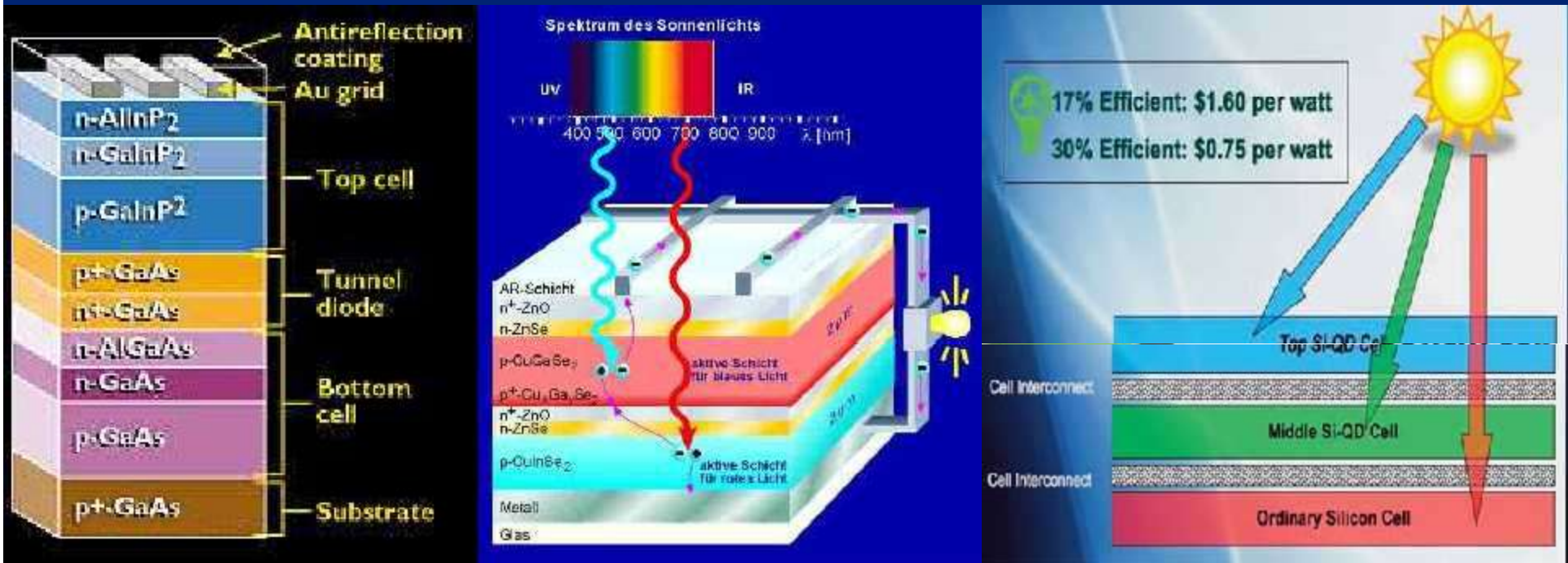
- **Enhance poor electrical performance while maintaining very low production costs.**

- Current research is targeting **conversion efficiencies of 30-60%** while retaining low cost materials and manufacturing techniques.

- Multi-junction cells – 30% efficiency (40-43% demonstrated)

Main Application Areas – Off-grid

Water Pumping
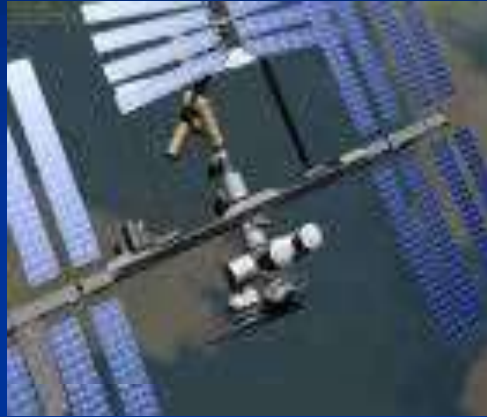
Space

Telecom

Solar Home Systems

Main Application Areas
Grid Connected

Commercial Building Systems (50 kW)

Residential Home Systems (2-8 kW)

PV Power Plants (> 100 kW)

Future Energy Mix
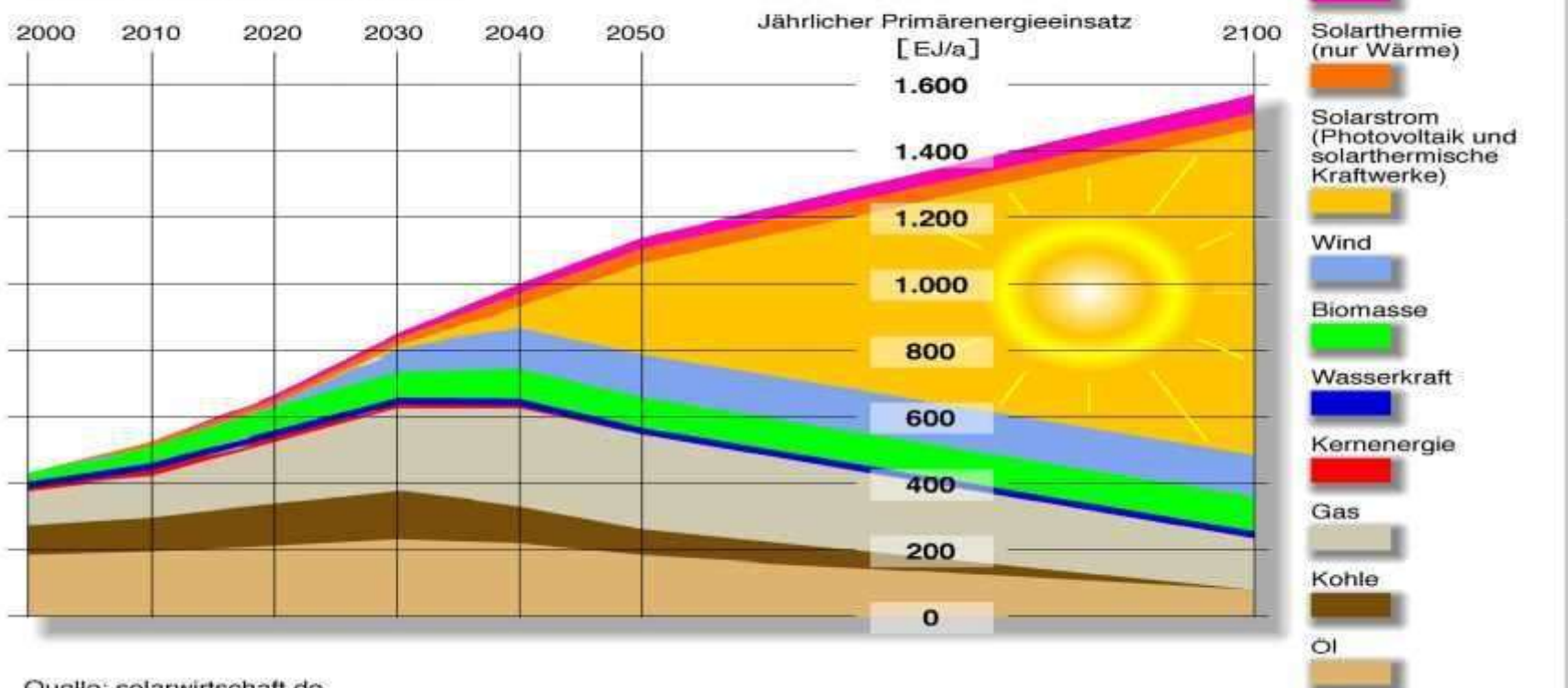
Renewable Energy Consumption in the US Energy Supply, 2007

Total = 101.545 Quadrillion Btu

Total = 6.813 Quadrillion Btu

Petroleum 39%

Nuclear Electric Power 8%

Natural Gas 23%

Coal 22%

Renewable 7%

Solar 1%

Hydroelectric 36%

Geothermal 5%

Biomass 53%

Wind 5%
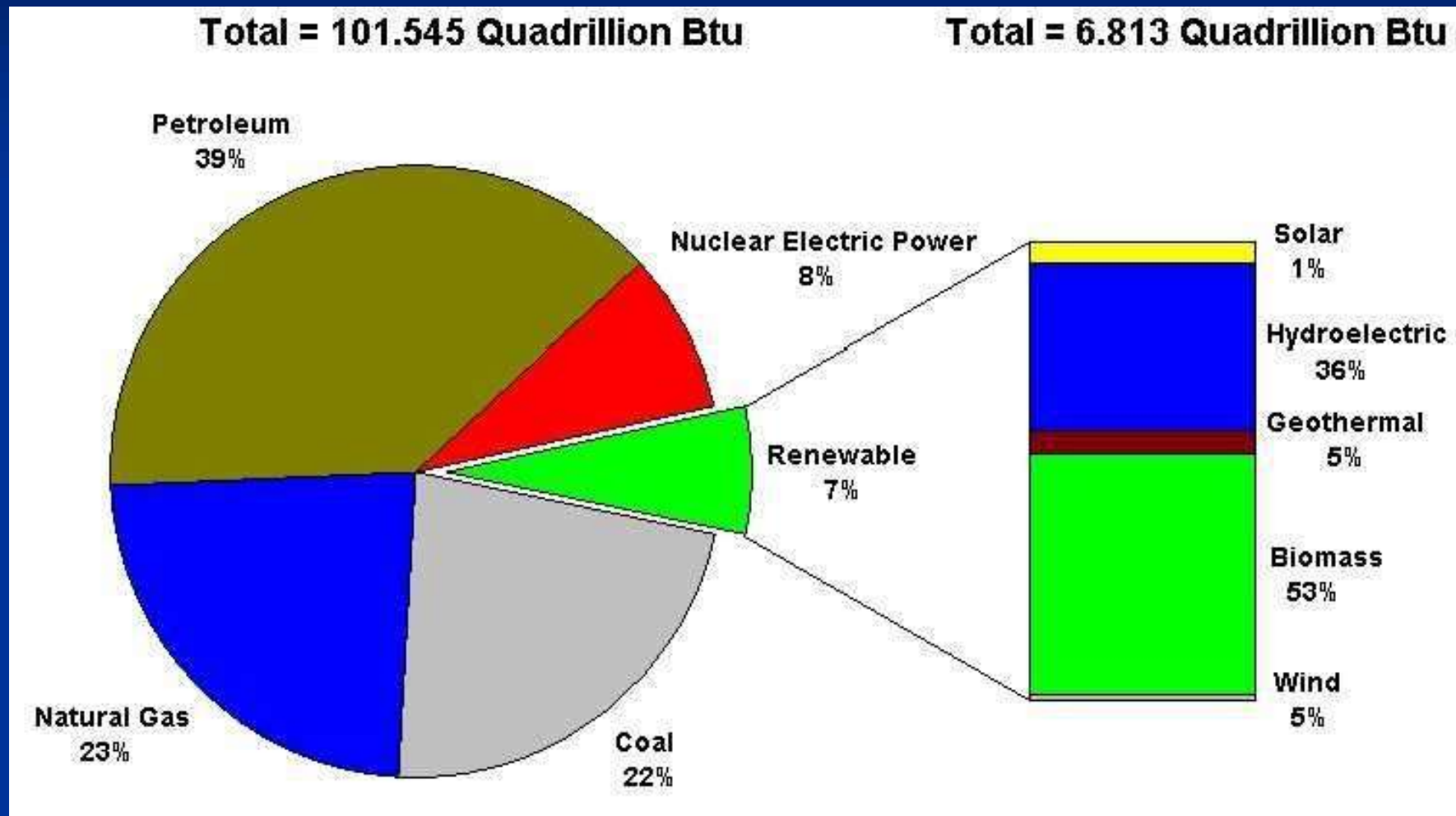
Top 10 PV Cell Producers

Top 10 produce 53% of world total

Q-Cells, SolarWorld - Germany

Sharp, Kyocera, Sharp, Sanyo – Japan

Suntech, Yingli, JA Solar – China

Motech - Taiwan

Rest of the World 47%

Q-Cells 9%
Sharp 8%
Suntech 8%
Kyocera 5%
First Solar 5%
Motech 4%
SolarWorld 4%
Sanyo 4%
Yingli 3%
Ja Solar 3%

Source : Photon International
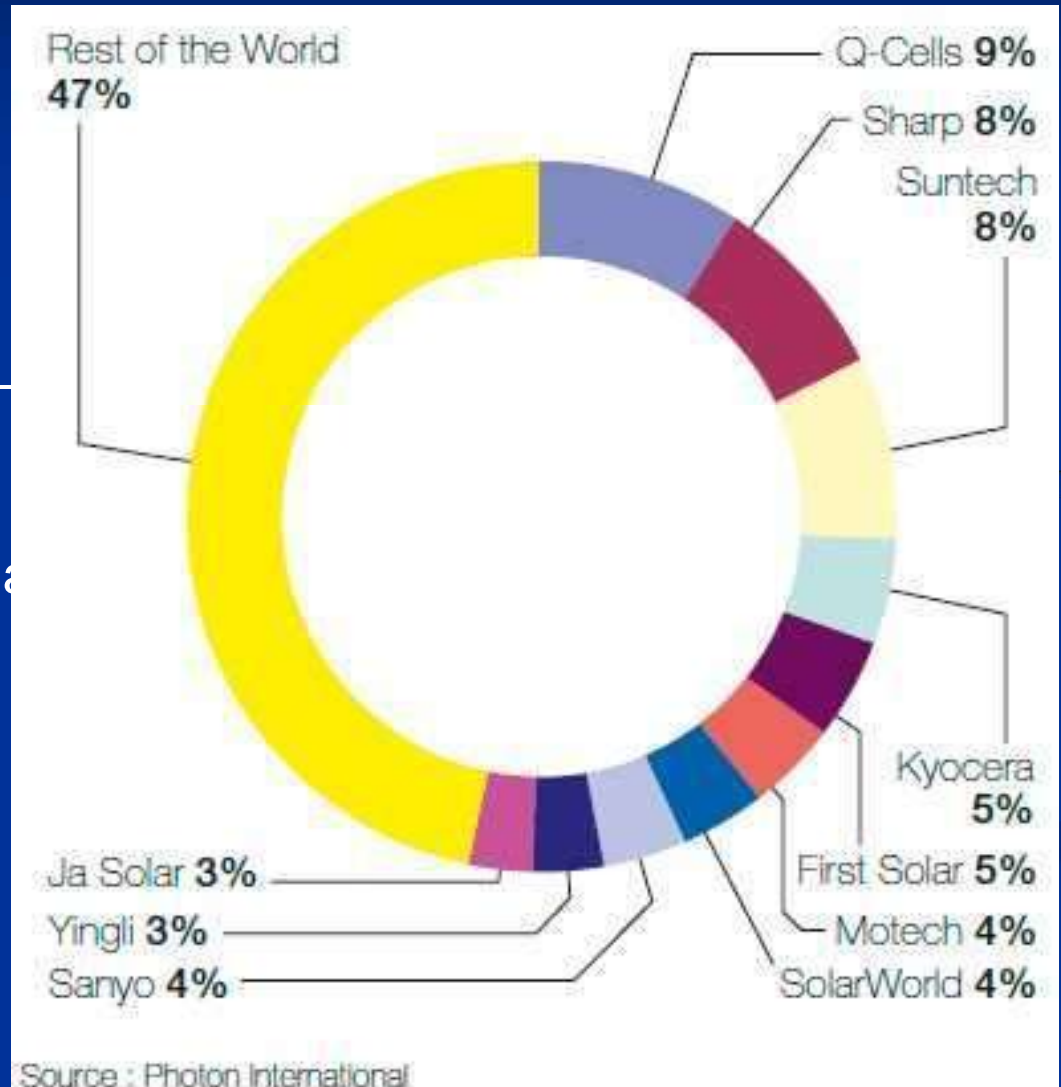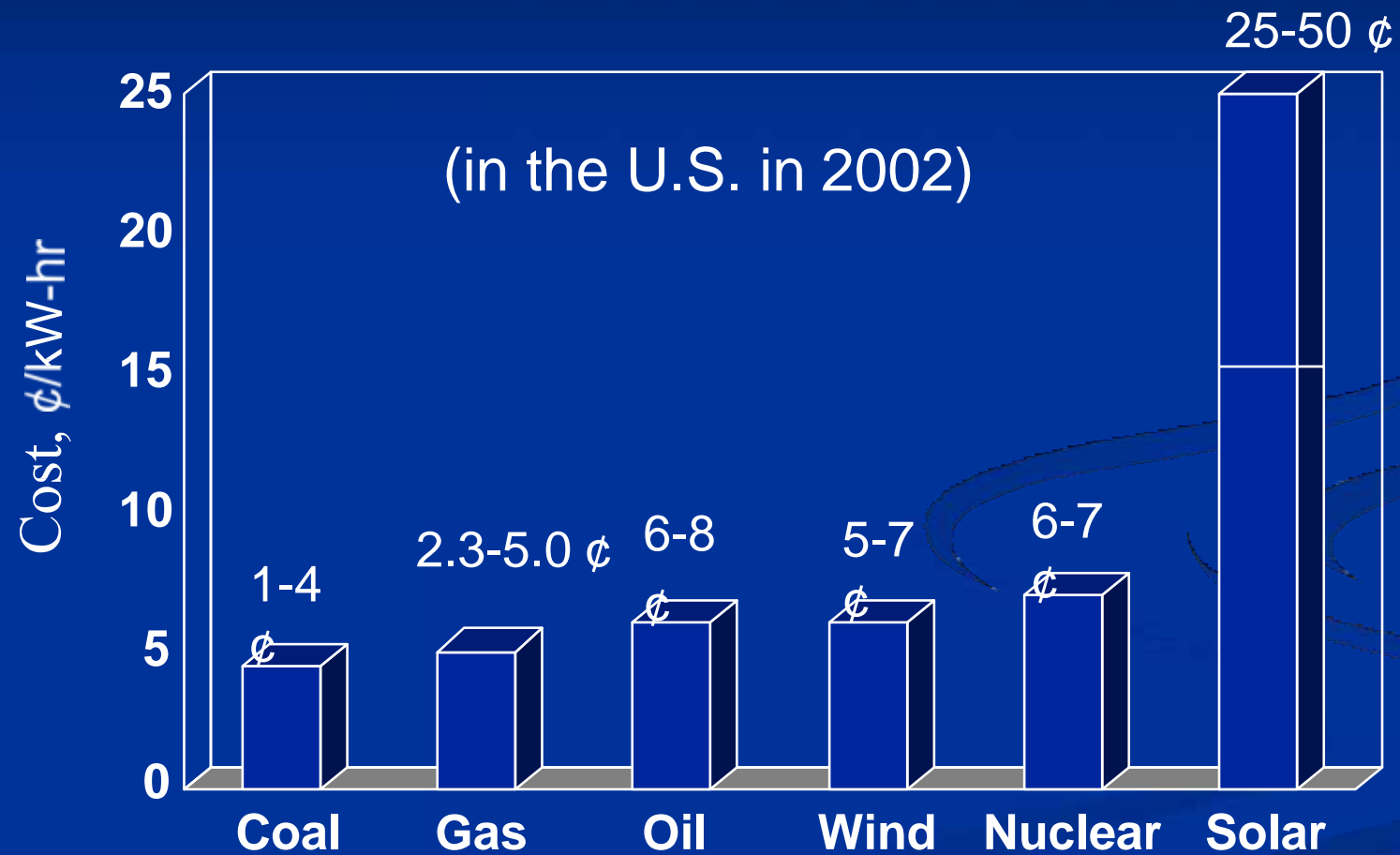
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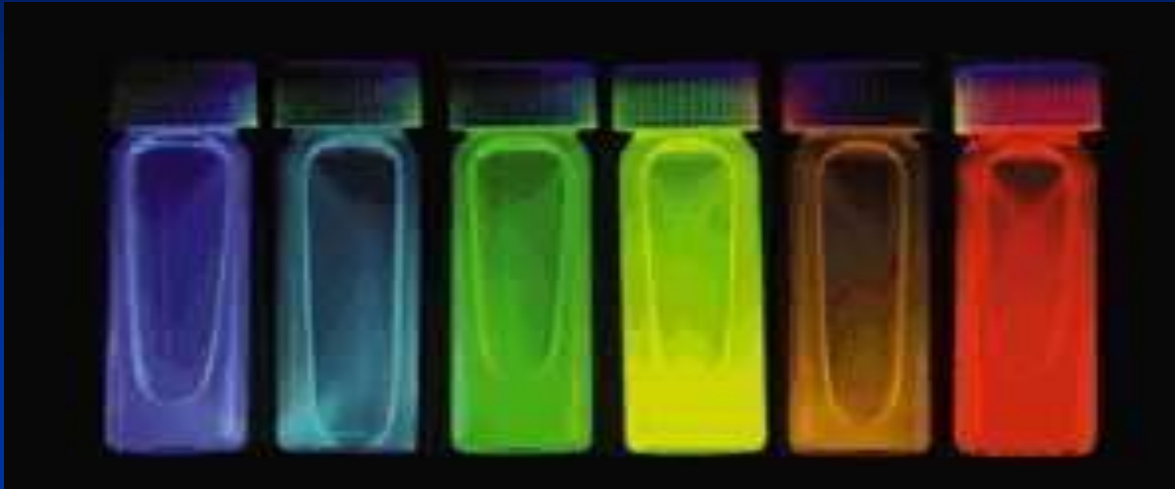
Solution Processible Semiconductor

Organic Cell
Nanostructured Cell

Organic Photovoltaics Convert Sunlight into Electrical Power.

Organic photovoltaics convert sunlight into electrical power

polymer film
transparent conductor
charge transport layer
photo-active layer
charge transport layer
metal electrode

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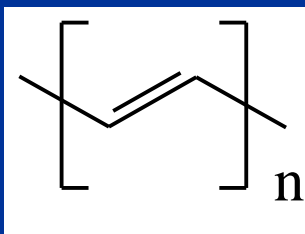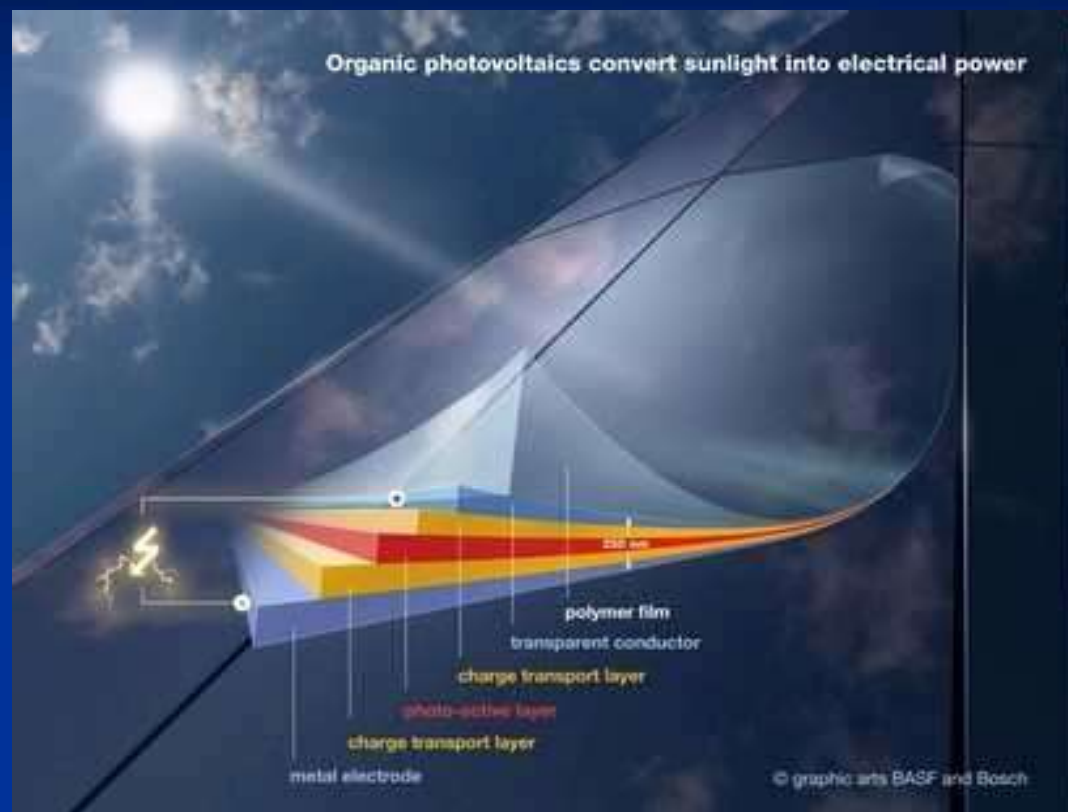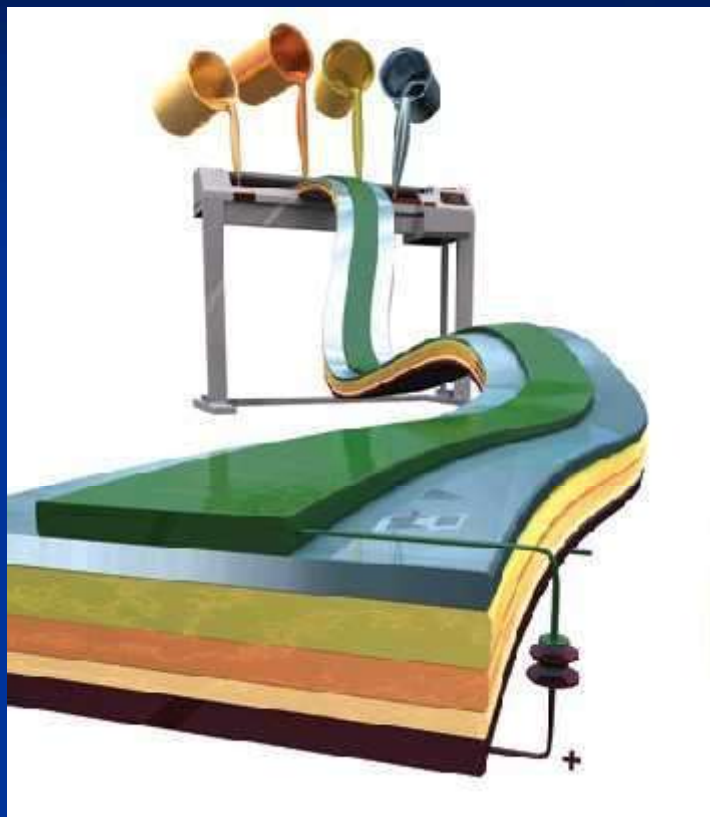
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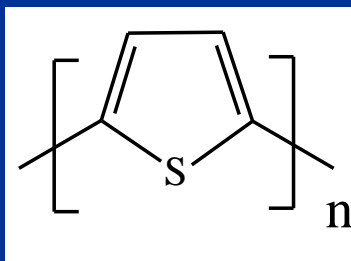
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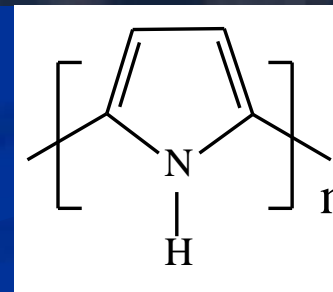
Polypyrrole (PPY)

Nanotechnology Solar Cell Design
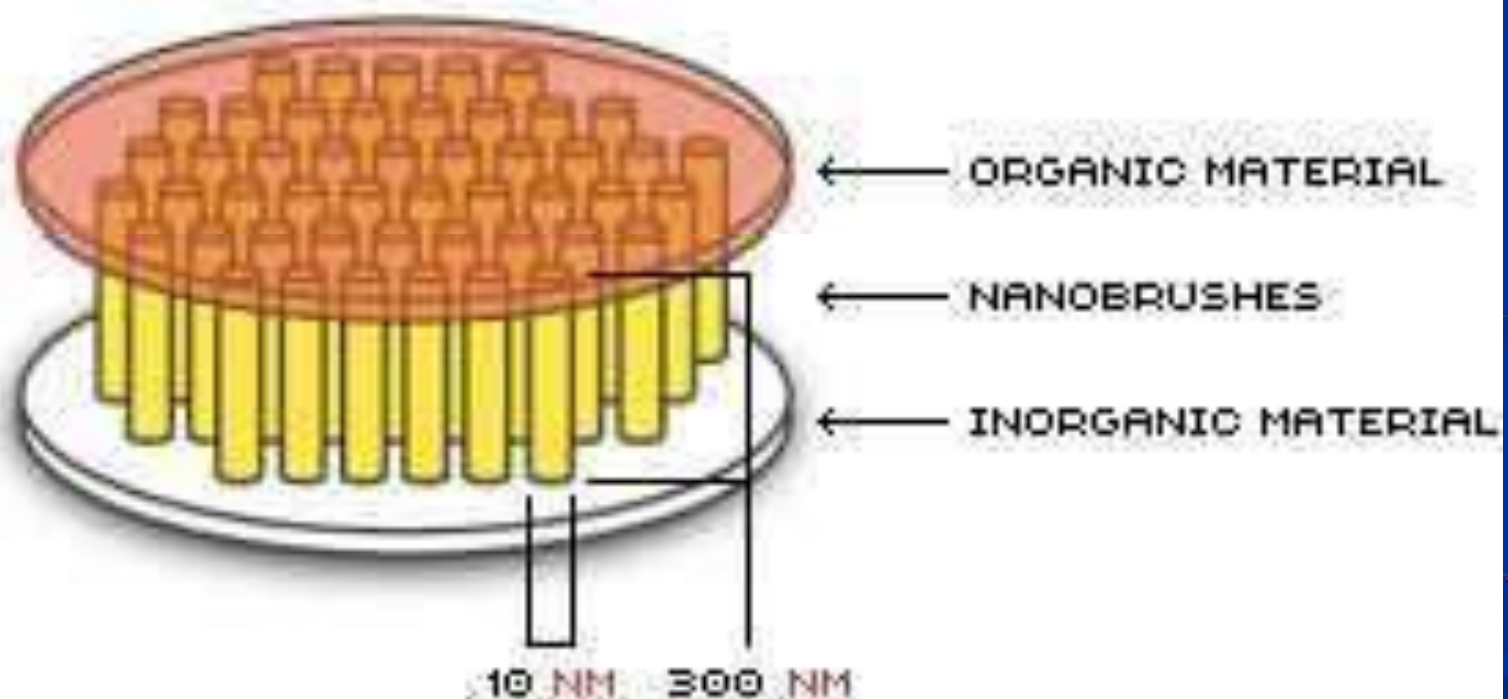
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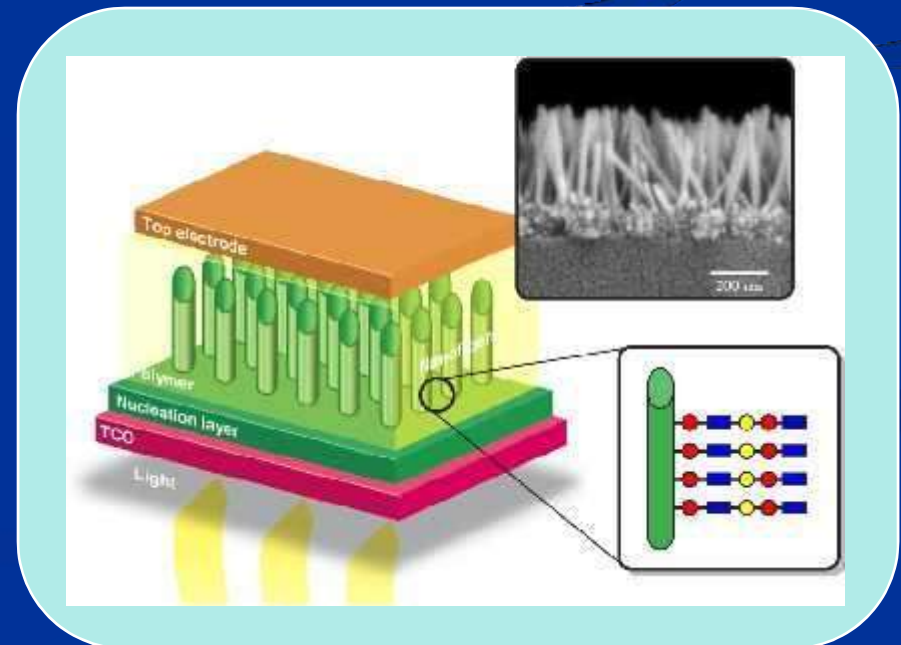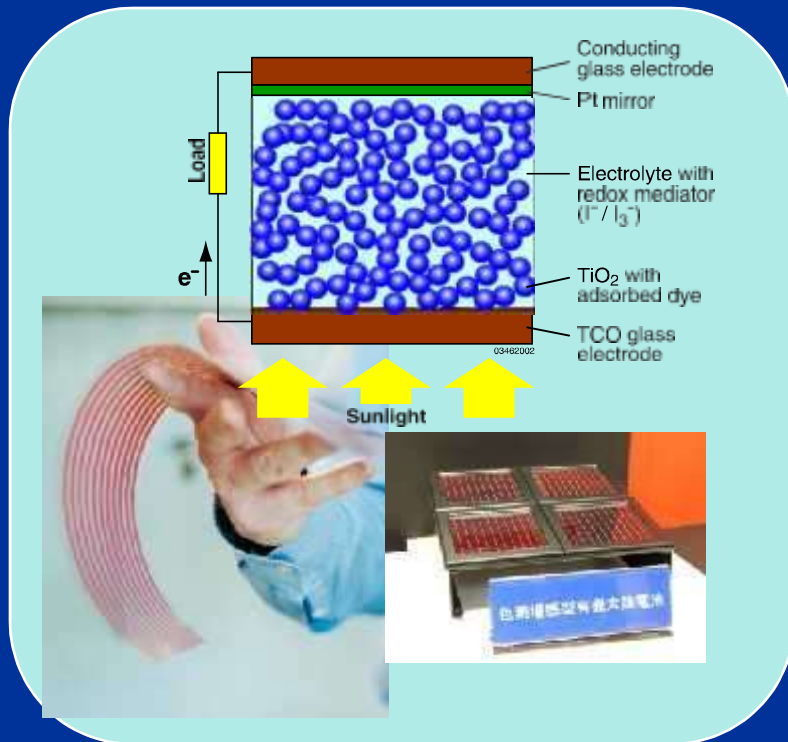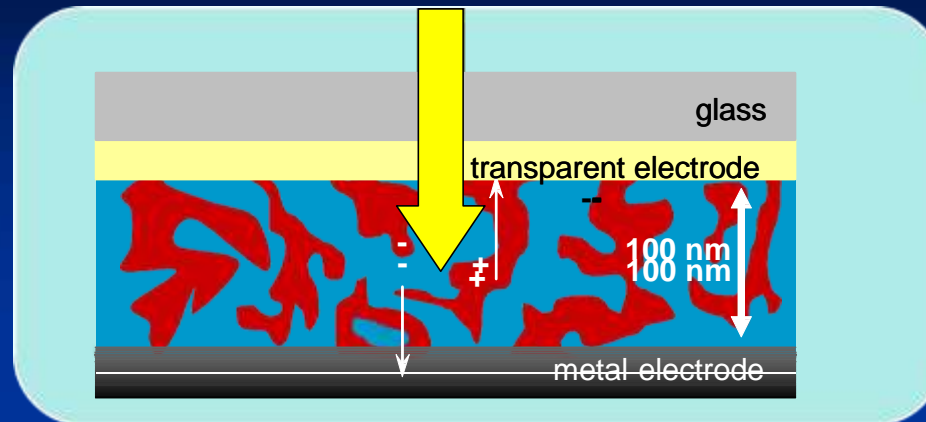
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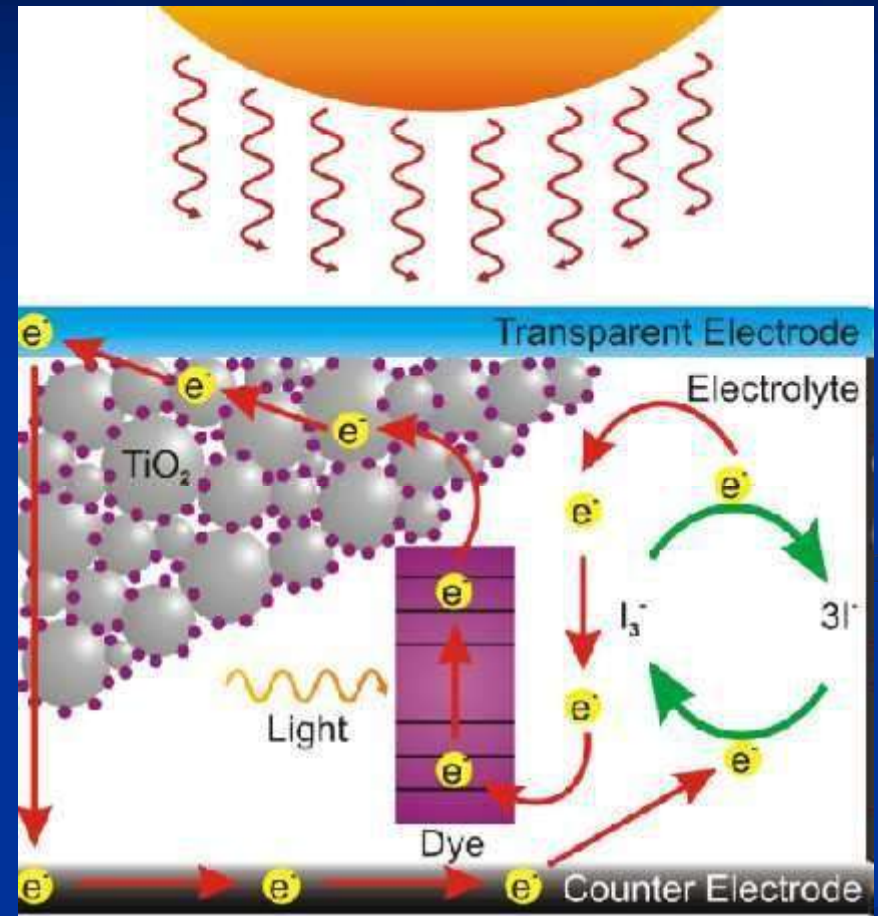
SPLITS

The mould designer is frequently can fronted with a component design that incorporates a recess or projection which presents the simple removal of the moulding from the mould . A moulding which has a recess or projection is termed an undercut moulding . The mould design for this type of component is more complex than for the in line of draw components , as it necessitates the removal of that part of the impression which form the undercut prior to rejection . External undercut components

Any recess or projection on the outside surface of the component which pennants it's removal from the cavity is termed an external undercut .

There are two forms to be considered –

1) The undercut may be local , in that the recess or projection occurs in on position only .
2) The undercut may be a continuous recess or a projection on the periphery of the component . The water connector has a number of such undercuts .
   In such cases it is necessary to split the cavity into parts and open these , generally at right angles to the line of draw , to relieve the undercut , before the moulding is removed .
   Since the cavity is in two pieces , a joint line will be visible on the finished product . This joint line on an undercut component , is compos able to the pasting line on a normal component . It is desirable to keep the splits movement to a minimum . The joint line for regular components should be positioned on the long studional centre line for unsymmetrical components , the choice of joint line is more critical . For very complex components , it is advantageous to have a model made to simplify the reelection of the joint line . The joint line should be as little visible or the component as possible .
   SPLITS -   when the cavity form for a component is machined into separate blocks of steel , these split cavity blocks are called splits . One half of the components form is sunk into each split and , providing the splits can be opened the moulding can be extracted .
   The splits can be incorporated in the mould design in several ways . The simplest is by fitting the splits into a chase bolster . This method has a major disadvantage in that after each moulding operation the splits must be removed and opened prior to the moulding being extracted . This manual operation lengthens the moulding cycle and therefore this design should be avoided .
   In more complex systems , the splits are retained on the mould plate and actuated automatically . There are two basic designs –
1) Sliding splits and ,
2) Angled lift splits .
   In both the designs it is necessary to arrange for
i) Guiding the splits in the desired direction .
ii) Actuating the splits and
iii) Securely locking the splits in position prior to the material being injected into the mould .
   Sliding splits –
   In this design , the splits are mounted in guides on a flat mould plate and they are actuated in one mould plane by mechanical or hydraulic means . The splits are positively locked in their

closed position by heals which projection from the other mould half . Sliding splits are generally mounted on the moving mould plate . The principle of sliding action is illustrated in the figure below .

Guiding and retention of splits - There are three main factors in design of guiding and retention system for a sliding splits type mould .

1) Side movement must be prevented to insure that the split halves always come together in the same place .

2) All parts of the guiding system must be of adequate strength .

3) The two split halves must have a smooth , unimpeded movement .

In most designs, the guiding function is accomplished by providing an accurately machine of slot in the mould plate , in which the splits can slide . The splits retaining system usually adopted is based upon a T-design . Each split in corporate shoulders , which are caused to slide in the T-shaped slot , that extends across the mould plate . The side walls of the T- slot can also be utilized for the guiding function also .

Types of splits –

The split moulds are normally classified on the basic of various methods that are used to act note the splits in relation to the mould plate . The most frequently used designs are based on various types of cam e. g. finger cam , dog-leg cam and various methods of can track act nation .

The basic operation with can act nation is as follows –

As the mould is opened , the comes attached to the fixed mould half cause the splits to slide across the moving mould plate . When the mould halnes are brought together , the splits are progressively closed . Another method of actuating the splits is by the use of compression springs . This system , while simple and cheap , has limited application as only relatively small split movement can be obtained . Most machine manufactures incorporate facilities in the hydraulic circuit for operation of additional actuates , if required . The main advantage of this system is that large split movements are practicable .

FINGER CAM ACTUATION : In this system , hardened circular steel pins , termed finger cams , are mounted at an angle in the fixed mould plate . The splits , mounted in guides on the moving mould plate , have corresponding circular holes to accommodate these finger cams .

In a typical design in the figures given below , the split are shown in the closed position (a) as the mould opens , the finger cams forces the split to move outwards , sliding on the mould plate (b) Once contact with the finger cam is lost , the splits movement ceases immediately .

Continued movement of the moving half causes the ejector system to operate and the moulding to be ejected (c) Du closing the servers action occurs . The finger cam re-enters the hole in the split and forces the split to move inwards . The final closing nip on the splits is achieved by the locking heels . The designer must aim to keep the splits movement down to a minimum and also to ensure that the mould part can be easily and quickly removed from the mould . The clearance c , servers two purposes :

1) It ensures that the force , which is applied to the splits , during the injection phase , is not transferred to the cam .

   It permits the mould to open a predetermined amount before the splits are accented. The value of angle of various between 10^0 and 25^0 . The diameter of splits ranges from 13mm to 76mm .

2) Dog-leg cam act nation -

   This method of act nation is used where a greater splits delay is required . The dog-leg cam , is of a general rectangular section and is mounted in the fixed mould plate . Each split incorporates a rectangular hole , the operating face of which has a corresponding angle to that of the cam .

   The sequence of operation is shown in the fingers below .

   When the mould is closed , The splits are locked together by the locking heads of the fixed mould plate . When the mould halves are parted for ejection , the splits do not immediately start to open because of the straight portion of the dog-leg cams . When the moving half of mould moves further , it causes the act nation of the splits by the dog-leg cams , there by releasing the moulding . The senses action occurs , when the mould is closed .

   Typical cross-section dimensions of a dog-leg cam for a small mould are 13mm*18mm . The angle is ideally 10^0 but may be increased to 25^0 . A lead in at the front – end of the cam should be provided to facilitate the re-entry of the cam into the split as the mould closes .

Cam Track Actuation - This method utilizes a cam track machined into a steel plate attached to the fixed mould half . A boss fitted to both sides of split , runs in this track . The movement of splits cam this be accurately controlled by specific cam track design .

The splits are mounted on a mould plate . The posses screwed into the side faces of the split , protrude into the cam track plates . The plates are securely attached to the side faces of the fixed mould plate . A small clearance is provided between the cam track plate and the moving mould half .

As the mould opens , the bosses follow the cam track and thereby cause the splits to open . When the mould is closes , the boss reenters the cam track and the splits are progressing angle with the design various between 10^0 and 40^0 .

Spring Actuation - This design incorporates compression springs to force the splits a part and utilizes the angled faces of the chose bolster to close them . The outward movement of the splits in the design is limited . This design is limited to mouldings , Which incorporate relatively shallow undercuts .

The splits are mounted on the mould plate and retained by guide strips : studs project from the base of splits into a slot machined in the mould plate . The outward movement of each split is controlled by the length of this slot . A compression spring is fitted between the studs in a link shaped pocket situated in the lower mould plate . The splits are held closed by the chase bolster during the injection phase . When the mould begins to open the compression springs lowest a force to part the split halves . The split halves movement is stopped by the studs reaching the end of the slot in the mould plate . During the closing stroke the splits reenter the chase bolster and are progressively closed .

A locking heel angle of 20^0-25^0 is recommended for splits and 76mm is width , one stud per split is suitable . Over this width , two studs should be used .

Radial torque types springs

Garter spring

spring clamp

Torsion spring


Power spring

Spring manufacturing processes

If springs are of very small diameter and the wire diameter is also small then the springs are normally manufactured by a cold drawn process through a mangle. However, for very large springs having also large coil diameter and wire diameter one has to go for manufacture by hot processes. First one has to heat the wire and then use a proper mangle to wind the coils.

Two types of springs which are mainly used are, helical springs and leaf springs. We shall consider in this course the design aspects of two types of springs.

HELICAL SPRING

Definition

It is made of wire coiled in the form of helix having circular, square or rectangular cross section.
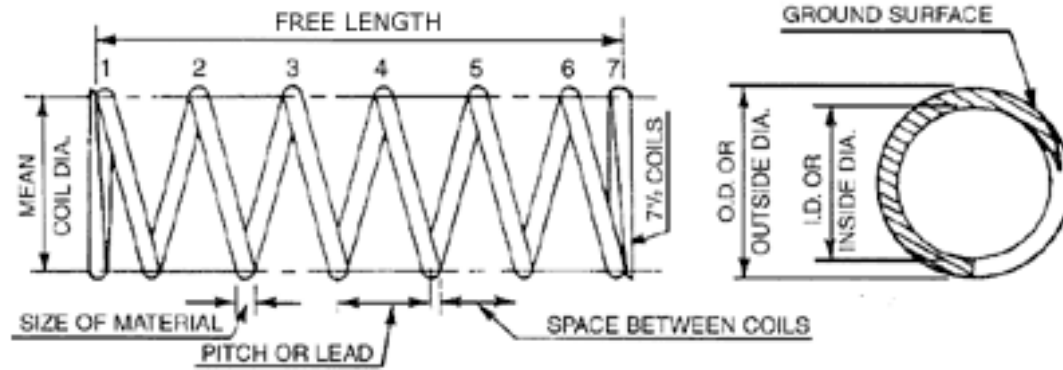
Terminology of helical spring

The main dimensions of a helical spring subjected to compressive force are shown in the figure. They are as follows:

d = wire diameter of spring (mm)

D_i = inside diameter of spring coil (mm)

D_o =outside diameter of spring coil (mm)

D = mean coil diameter (mm)

Therefore

$$D = \frac{D_i + D_o}{2}$$

There is an important parameter in spring design called spring index. It is denoted by letter C. The spring index is defined as the ratio of mean coil diameter to wire diameter. Or

C = D/d

In design of helical springs, the designer should use good judgment in assuming the value of the spring index C. The spring index indicates the relative sharpness of the curvature of the coil.

A low spring index means high sharpness of curvature. When the spring index is low (C < 3), the actual stresses in the wire are excessive due to curvature effect. Such a spring is difficult to manufacture and special care in coiling is required to avoid cracking in some wires. When the spring index is high (C >15), it results in large variation in coil diameter. Such a spring is   prone

to buckling and also tangles easily during handling. Spring index from 4 to 12 is considered better from manufacturing considerations.

Therefore, in practical applications, the spring index in the range of 6 to 9 is still preferred particularly for close tolerance springs and those subjected to cyclic loading.

There are three terms - free length, compressed length and solid length that are illustrated in the figure. These terms are related to helical compression spring. These lengths are determined by following way
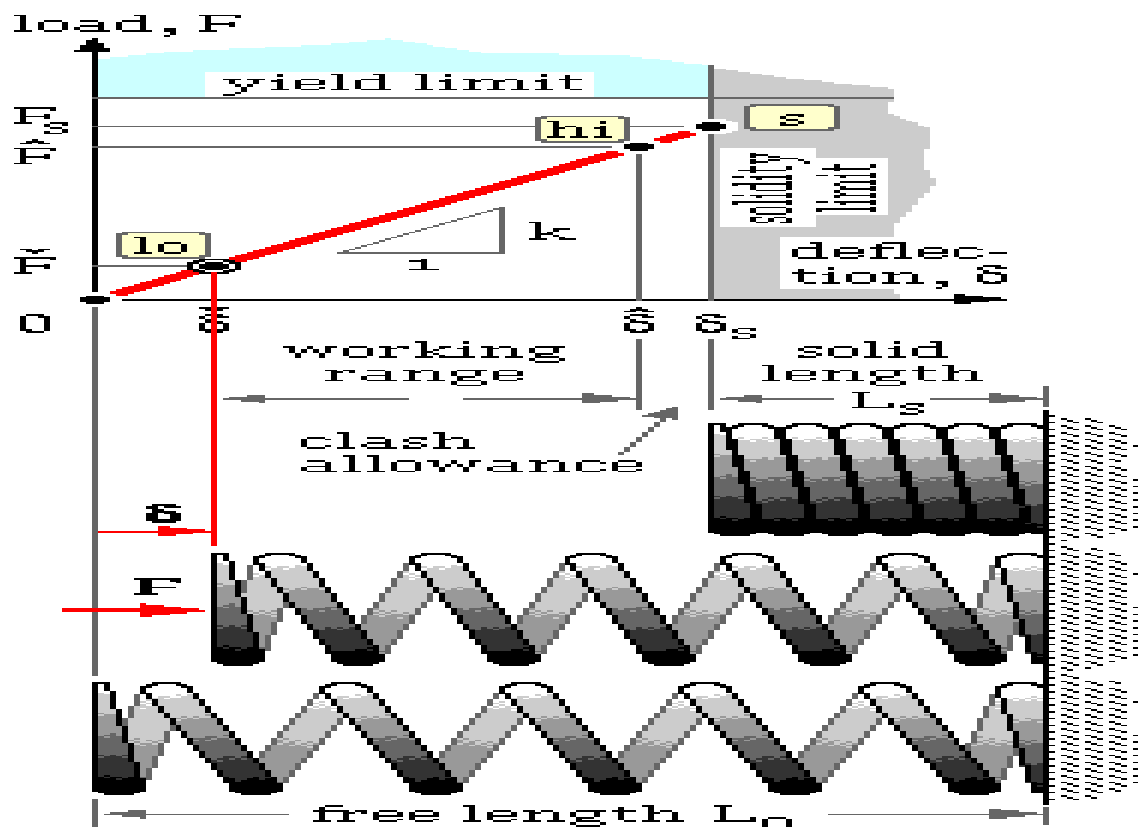
© 2000 DOUG WRIGHT, UWA

1) **Solid length:** solid length is defined as the axial length of the spring which is so compressed, that the adjacent coils touch each other. In this case, the spring is completely compressed and no further compression is possible. The solid length is given by.

Solid length = N_t d

Where N_t = total number of coils

2) **Compressed length:** Compressed length is defined as the axial length of the spring that is subjected to maximum compressive force. In this case, the spring is subjected to maximum deflection ð. When the spring is subjected to maximum force, there should be some gap or clearance between the adjacent coils. The gap is essential to prevent clashing of the coils.

The clashing allowance or the total axial gap is usually taken as 15% of the maximum deflection. Sometimes, an arbitrary decision is taken and it is assumed that there is a gap of 1 or 2 mm between adjacent coils under maximum load condition. In this case, the total axial gap is given by,

 Total gap = $(N_t$-1) x gap between adjacent coils

3) **Free length:** Free length is defined as the axial length of an unloaded helical compression spring. In this case, no external force acts on the spring. Free length is an important dimension in spring design and manufacture. It is the length of the spring in free condition prior to assembly. Free length is given by,

    Free length = compressed length + y

             = solid length + total axial gap + y

The pitch of the coil is defined as the axial distance between adjacent coils in uncompressed state of spring. It is denoted by p. It is given by,

$$p = \frac{free\ length}{N_t - 1}$$

The stiffness of the spring (k) is defined as the force required producing unit deflection

 Therefore

$$k = \frac{p}{\delta}$$

Where k= stiffness of the spring (N/mm)

F = axial spring force (N)

Y or ð = axial deflection of the spring corresponding to force p (mm)

There are various names for stiffness of spring such as rate of spring, gradient of spring, scale of spring or simply spring constant. The stiffness of spring represents the slope of load deflection line. There are two terms are related to the spring coils, viz. active coils and inactive coils.

Active coils are the coils in the spring, which contribute to spring action, support the external force and deflect under the action of force. A portion of the end coils, which is in contact with the seat, does not contribute to spring action and called inactive coils. These coils do not support the load and do not deflect under the action o external force. The number of inactive coils is given by,
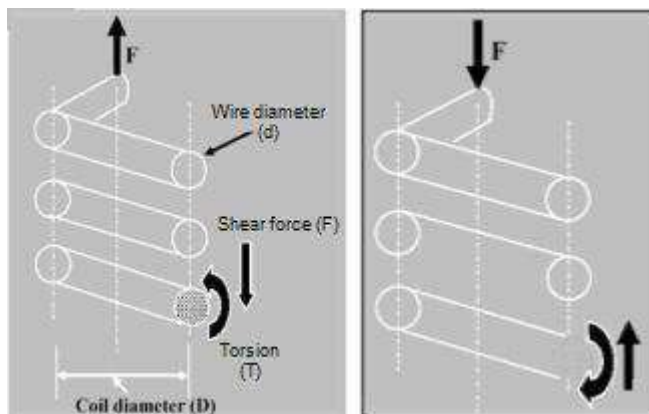
Inactive coils = N_t – N where N = number of active coils

Classification of helical springs
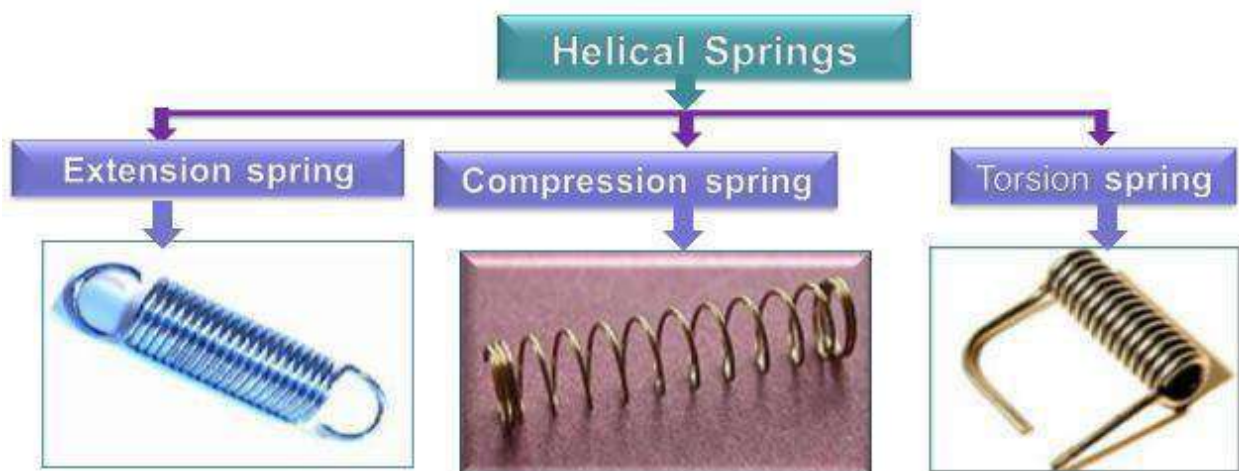
Helical spring

The figures below show the schematic representation of a helical spring acted upon by a tensile load F and compressive load F. The circles denote the cross section of the spring wire.

The cut section, i.e. from the entire coil somewhere we make a cut, is indicated as a circle with shade.

If we look at the free body diagram of the shaded region only (the cut section) then we shall see that at the cut section, vertical equilibrium of forces will give us force, F as indicated in the figure. This F is the shear force. The torque T, at the cut section and its direction is also marked in the figure.

There is no horizontal force coming into the picture because externally there is no horizontal force present. So from the fundamental understanding of the free body diagram one can see that any section of the spring is experiencing a torque and a force. Shear force will always be associated with a bending moment.

However, in an ideal situation, when force is acting at the centre of the circular spring and the coils of spring are almost parallel to each other, no bending moment would result at any section of the spring (no moment arm), except torsion and shear force.

Force F acting perpendicular to the plane Of the paper
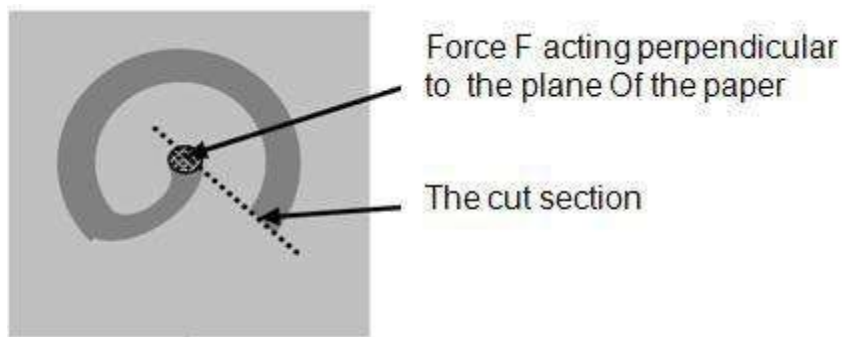
The cut section

Stresses in the helical spring wire

From the free body diagram, we have found out the direction of the internal torsion T and internal shear force F at the section due to the external load F acting at the centre of the coil.
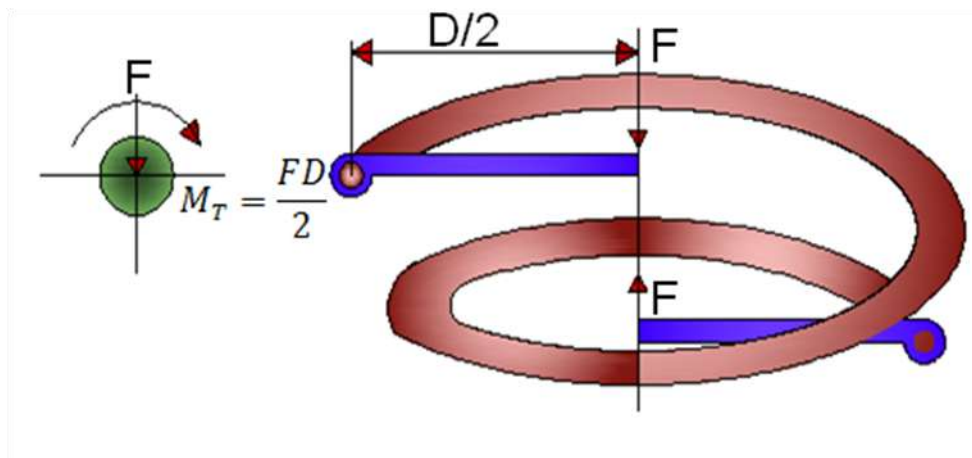
The cut sections of the spring, subjected to tensile and compressive loads respectively, are shown separately in the figure.
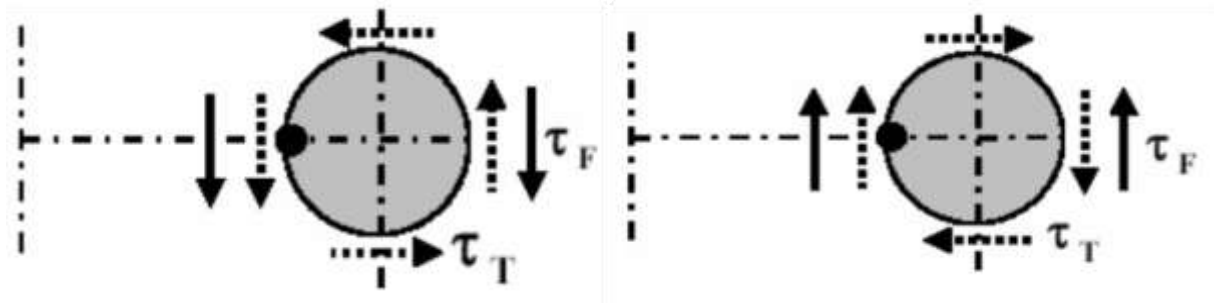
The broken arrows show the shear stresses (r_T) arising due to the torsion T and solid arrows show the shear stresses (r_F) due to the force F.

It is observed that for both tensile load as well as compressive load on the spring, maximum shear stress ($r_T + r_F$) always occurs at the inner side of the spring. Hence, failure of the spring, in the form of crake, is always initiated from the inner radius of the spring.

The radius of the spring is given by D/2. Note that D is the mean diameter of the spring. The torque T acting on the spring is

$$T = Fx\frac{D}{2}$$

$$\ldots\ldots (1)$$

If d is the diameter of the coil wire and polar moment of inertia,

$$I_p = \frac{\pi d^4}{32}$$

The shear stress in the spring wire due to torsion is
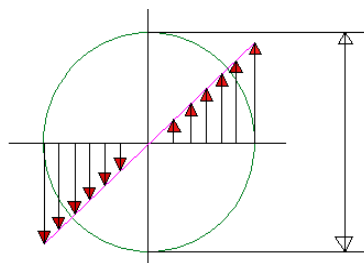
$$\tau_T = \frac{Tr}{I_p} = \frac{Fx\frac{D}{2}x\frac{d}{2}}{\frac{\pi d^4}{32}}$$

$$\ldots\ldots (2)$$

Average shear stress in the spring wire due to force F is
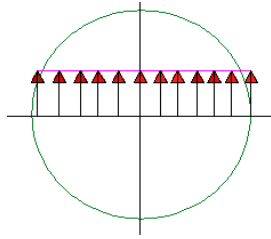
$$\tau_F = \frac{F}{\frac{\pi d^2}{4}} = \frac{4F}{\pi d^2}$$

.... (3)

Therefore, maximum shear stress in the spring wire is

$$\tau_T + \tau_F = \frac{8FD}{\pi d^3} + \frac{4F}{\pi d^2}$$

or $\quad \tau_{max} = \frac{8FD}{\pi d^3}\left(1 + \frac{1}{\frac{2D}{d}}\right)$ or $\quad \tau_{max} = \frac{8FD}{\pi d^3}\left(1 + \frac{1}{2C}\right)$
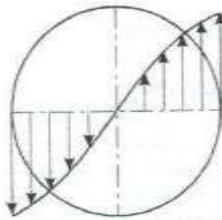
Where, C=D/d is called the spring index $\qquad K_s$

finaly $\quad \tau_{max} = \frac{8FD}{\pi d^3} K_s$ .... (A)

$$K_s = \left(1 + \frac{1}{2C}\right)$$

.... (4)

The above equation gives maximum shear stress occurring in a spring. K_s are the shear stress correction factor. The resultant diagram of torsional shear stress and direct shear stress is shown

From the above equation it can be observed that the effect of direct shear stress i.e.,

$$\tau = \frac{8FD}{\pi d^3} \frac{1}{2c}$$

Is appreciable for springs of small spring index 'C' Also the effect of wire curvature is neglected in equation (A)

Stresses in helical spring with curvature effect

What is curvature effect?

Let us look at a small section of a circular spring, as shown in the figure. Suppose we hold the section b-c fixed and give a rotation to the section a-d in the anti clockwise direction as indicated in the figure, then it is observed that line a-d rotates and it takes up another position, say a'-d'.
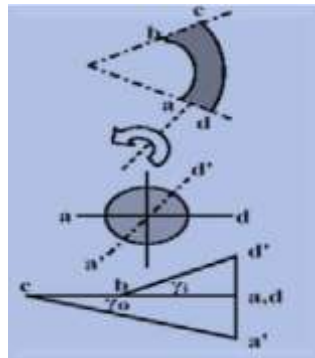
The inner length a-b being smaller compared to the outer length c-d, the shear strain y_i at the inside of the spring will be more than the shear strain y_o at the outside of the spring. Hence, for a given wire diameter, a spring with smaller diameter will experience more difference of shear strain between outside surface and inside surface compared to its larger counterpart. This phenomenon is termed as curvature effect.

So more is the spring index (C = D /d) the lesser will be the curvature effect. For example, the suspensions in the railway carriages use helical springs. These springs have large wire diameter compared to the diameter of the spring itself. In this case curvature effect will be predominantly high.

To take care of the curvature effect, the earlier equation for maximum shear stress in the spring wire is modified as,

$$\tau_{max} = (K_w)\frac{8FD}{\pi d^3}$$

Where, K_W is Wahl correction factor, which takes care of both curvature effect and shear stress correction factor and is expressed as,

$$K_w = \frac{4C-1}{4C-4} + \frac{0.615}{C}$$

…….. (6)

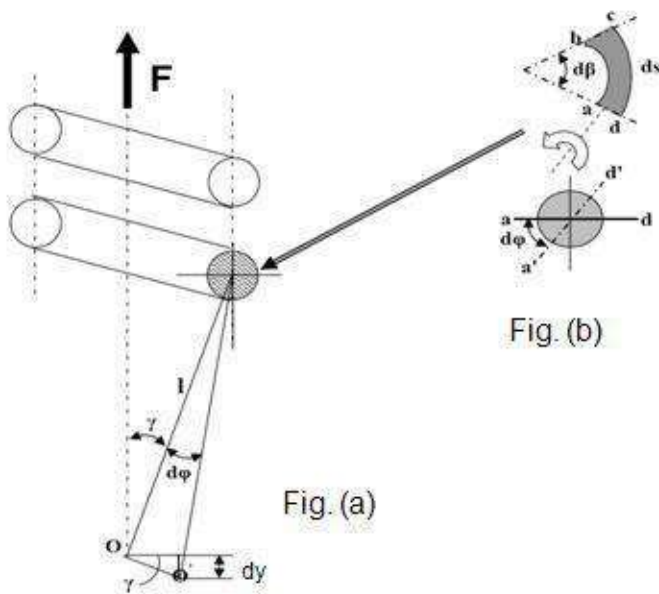## Deflection of helical spring of circular cross section wire

Total length of wire = length of one coil x number of active coils

$$\therefore l = \pi D i$$

$\therefore$ Axial deflection of spring $\quad y = \theta \dfrac{D}{2}$ $\quad$ where θ=angular deflection

We know,

$$\frac{T}{J} = \frac{\tau}{\frac{d}{2}} = \frac{G\theta}{l}$$

Fig. (b)

Fig. (a)

The Fig. (a) And (b) shows a schematic view of a spring, a cross section of the spring wire and a small spring segment of length dl. It is acted upon by a force F. From simple geometry we will see that the deflection, in a helical spring is given by the formula,

$$\therefore y = \frac{8FD^3 . i}{d^4 . G}$$

$$\therefore \theta = \frac{Tl}{GJ} = \frac{\left(F\frac{D}{2}\right)(\pi D i)}{G\frac{\pi}{32}d^4}$$

$$\therefore Angular\ deflection\ \theta = \frac{16FD^2 i}{Gd^4}$$

Hence axial deflection

$$y = \theta \frac{D}{2} = \frac{16FD^2 i}{Gd^4} \cdot \frac{D}{2}$$

$$\therefore y = \frac{8FD^3 \cdot i}{d^4 \cdot G}$$

$$stiffness\ F_o = \frac{F}{y} = \frac{F}{\frac{8FD^3 \cdot i}{d^4 \cdot G}}$$
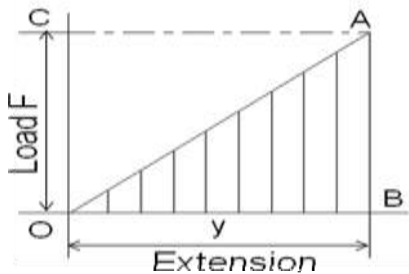
$$F_o = \frac{d^4 \cdot G}{8D^3 \cdot i}$$

Here we conclude on the discussion for important design features, namely, stress, deflection and spring rate of a helical spring.

$$\tau_{max} = (K_w) \frac{8FD}{\pi d^3}$$

$$\therefore y = \frac{8FD^3 \cdot i}{d^4 \cdot G}$$

$$F_o = \frac{d^4 \cdot G}{8D^3 \cdot i}$$

Expression for strain energy in a body when the load is applied gradually

The strain energy stored in a body is equal to the work done by the applied load in stretching the body. Figure shows load extension diagram of a body under tensile load up to elastic limit.

The tensile load F increase gradually from zero to the value of F, And the extension of the body increase from zero to the value of y. The load F performs work in stretching the body. This work will be stored in the body as strain energy which is recoverable after the load F is removed.

Let

F = gradually applied load

Y = Extension of the body (spring)

A = Cross section area

l = Length of body

V= Volume of the body

E = Young's modulus

U = Strain energy stored in the body

σ = Stress induced in the body

Now, work done by the load = Area of load extension curve

$\qquad$ = Area of Δ^{le} OAB = ½ F$_y$ $\qquad\qquad$ ……………. (1)

Load, F = stress x area = σ$_A$

Extension, y = strain x length

$$= \frac{stress}{E}.l = \frac{\sigma}{E}.l \left(\because \frac{stress}{strain} = E \right)$$

Substituting the values of F and y in equation (1)

Work done by the load =

$$\frac{1}{2}\sigma A \times \frac{\sigma}{E} \times l = \frac{1}{2}\frac{\sigma^2}{E} . A . l$$

$$= \frac{1}{2}\frac{\sigma^2}{E} . V \quad (Volume\ V = Al)$$

Since work done by the load in stretching body is equal to the strain energy stored in the body,

∴ Strain energy stored in the body U = ½ Fy

$$U = \frac{\sigma^2}{2E}xV \qquad \qquad \dots \dots \dots \dots \dots \text{(2)}$$

Proof Resilience

The maximum energy stored in the body without permanent deformation [i.e., upto elastic limit] is known as proof resilience. Hence in equation (2) if σ is taken at elastic limit, then we will get proof resilience.

∴ proof resilience $= \dfrac{\sigma^2}{2E}xVolume$

Where σ = stress at elastic limit.

Modulus of resilience = strain energy per unit volume

$$= \frac{total\ strain\ energy}{Volume}$$

$$= \frac{\frac{\sigma^2}{2E}xV}{V} = \frac{\sigma^2}{2E}$$

Symbols Used In Helical Spring

l_o = free length of spring

d = Diameter of spring wire

D = Mean diameter of coil

D_o = Outer diameter of coil

D_i = Inner diameter of coil

p = Pitch

i = Number of active coils

i' = Total number of coils

F = load on the spring or Axial force

r = Permissible stress or design shear stress

y = Deflection

G = Modulus of Rigidity

c = Spring index

k = Curvature factor or Wahl's stress factor

K_o or F_o =Stiffness of spring or Rate of spring

a = Clearance, 25% of maximum deflection.

t_y = Torsional yield shear strength (stress)
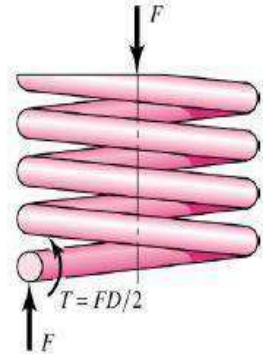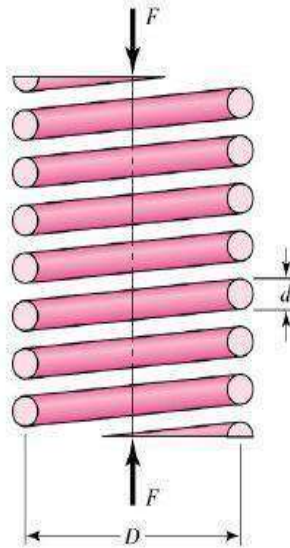
F.O.S = Factor of safety

F_1 = Minimum load

F_2 = Maximum load

Y_2 = Maximum deflection

Y' = Deflection for the load range

n = Number of additional coils

g = Acceleration due to gravity

V = Volume

m = Mass of the spring

ρ = Mass density of the spring

y_1 = Initial deflection or initial compression

Design of Helical Springs

The design of a helical compression spring involves the following considerations:

- Modes of loading – i.e., whether the spring is subjected to static or infrequently varying load or alternating load.

- The force deflection characteristic requirement for the given application.

- Is there any space restriction.

- Required life for springs subjected to alternating loads.

- Environmental conditions such as corrosive atmosphere and temperature.

- Economy desired.

Considering these factors the designer select the material and specify the wire size, spring diameter, number of turns spring rate, type of ends, free length and the surface condition.

A helical compression spring, that is too long compared to the mean coil diameter, acts as a flexible column and may buckle at comparatively low axial force.

Springs which cannot be designed buckle- proof must be guided in a sleeve or over an arbor.

This is undesirable because the friction between the spring and the guide may damage the spring in the long run.

It is therefore preferable, if possible, to divide the spring into buckle proof component springs separated by intermediate platens which are guided over a arbor or in a sleeve.

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$$\frac{Free\ length}{Mean\ coil\ diameter} \leq 2.6 [Guid\ not\ necessary]$$

$$\frac{Free\ length}{Mean\ coil\ diameter} \geq 2.6 [Guid\ required]$$