

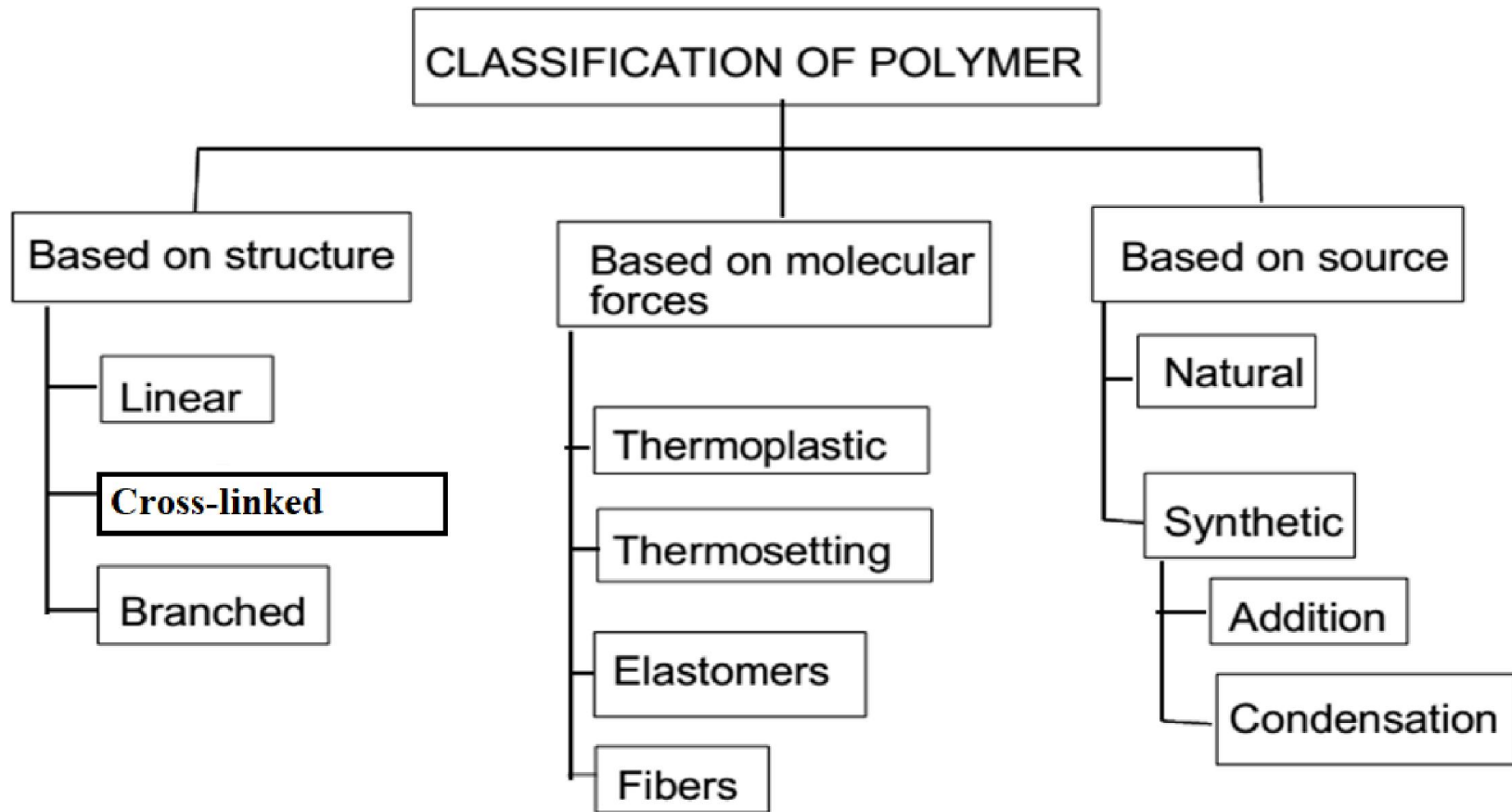
POLYMERIZATION

Unit 5

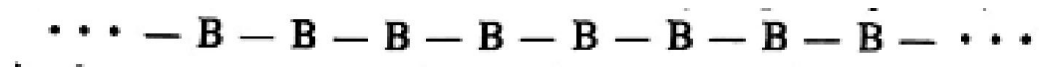
Polymers

- Polymerization is one of the very important unit processes which find application in manufacture of polymer, synthetic fibre, synthetic rubber, polyurethane, paint etc.
- A polymer is a macromolecule, made up of many smaller repeating units called monomer.
- Polymers have high molecular weight in the range of 10^3 - 10^7
- Polymers can be synthesized from various types and combinations of monomers to yield unusual properties, both physical and chemical.

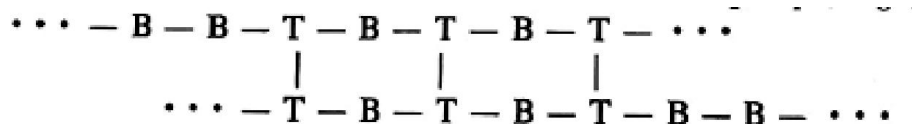
Classification



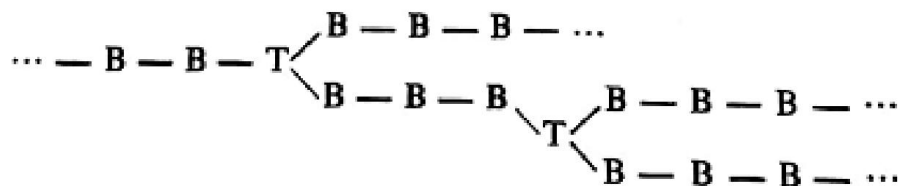
A linear polymer is represented by a chain with two ends.



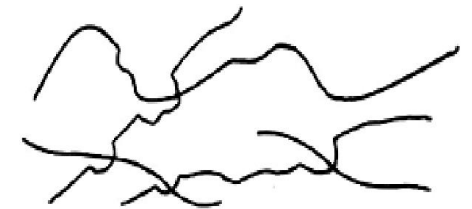
Cross-linked polymer have three dimensional structures in which each chain is connected to all others by a sequence of function points and other chains. But it does not contain any main chain when compare with branched polymer.



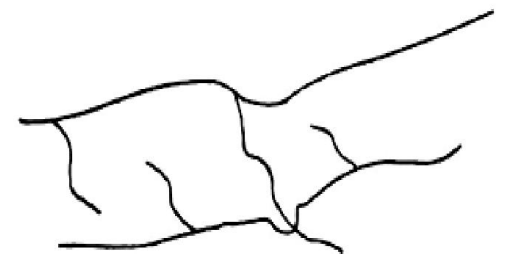
Branched polymers have side chains, or branches, of significant length which are bonded to the main chain at branch points, and are characterized in terms of the number and size of the branches.



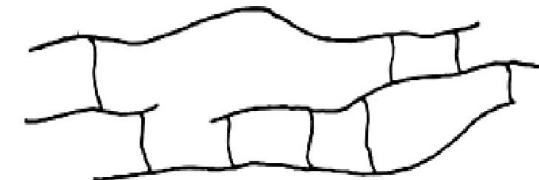
Linear or Chain Polymer Schematic



Branched-Chain Polymer Schematic



Cross-linked Polymer Schematic



Classification of Polymers by Physical Properties

I. Thermoplastic Polymers:

The individual chains of thermoplastic polymer are held together by van der Waals forces.

They are strong if the polymer chains are lined up in an ordered, closely packed array. This region is called crystallites and the other where polymer chains are oriented randomly is called amorphous.

Thermoplastic polymers have both ordered crystalline regions and amorphous noncrystalline regions.

Thermoplastic polymers are hard at room temperature, but become soft when heated, because on heating individual polymer chains slip from one another.

Polyethylene, polystyrene, polypropene and teflon are some examples for thermoplastic polymer.

Thermosetting Polymers:

The greater the degree of cross-linking makes the polymer more rigid. Such cross-linked polymers are called thermosetting polymers.

Thermosetting polymers are generally stronger than thermoplastic polymers due to strong covalent linkage (cross-linking) between polymer chains not by weak intermolecular van der Waals forces.

They are more brittle in nature and their shape is permanent. Once it is hardened they cannot be recycled.

Phenol formaldehyde, Melmac, Bakelite and polyurethanes are examples for thermosetting polymers.

Elastomers:

An elastomer is a randomly oriented amorphous polymer, which stretches and then reverts back to its original shape.

When elastomers are stretched, the random chains stretch out where as the van der Waals forces are not strong enough to maintain them in that arrangement and retains its original shape when the stress is removed.

Rubber, Butadiene and its derivatives, silicones, thiokols are examples of an elastomer.

Fibers:

These are thread like polymers which can be used as fabrics.

The strong intermolecular forces like hydrogen bond provide high tensile strength.

A few examples are polyamides, polyester, polycarbamides, polyurethanes etc

Classification by based on sources

Natural Polymers:

Polymers are naturally available.

Examples : Polysaccharides (biopolymers): Nucleic Acids (DNA,RNA), Proteins, Natural Rubber

Synthetic Polymers

The polymers which are synthesized in the laboratory are called as synthetic polymers based on the method of its preparation they can be further classified into addition polymers and condensation polymers.

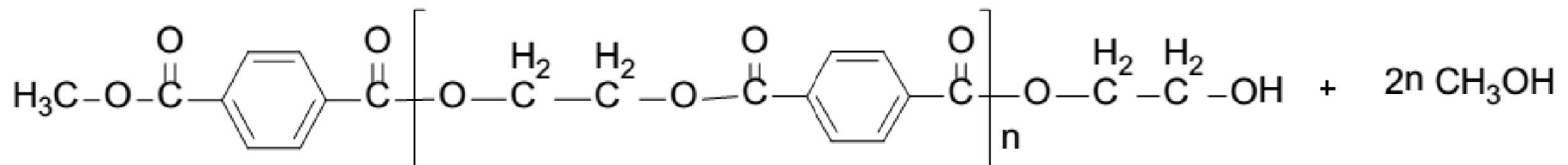
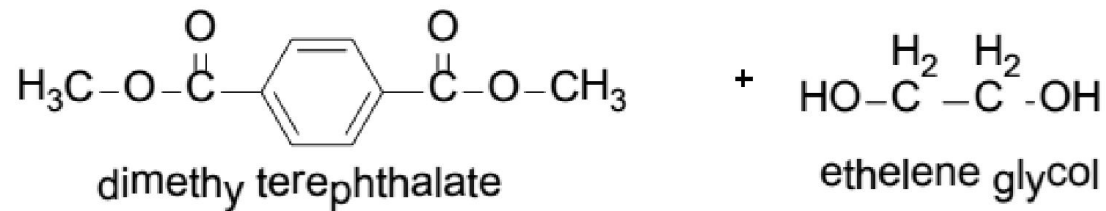
Addition polymers: Addition polymers are formed by the sequential addition of the monomer units with the help of a reactive intermediate such as free radicals, cations or anions without loss of small molecules.

Condensation Polymers: This type of polymers is generated by the condensation of two monomer units with the loss of small molecules such as H_2O , HCl , and NH_3 etc. Here the monomer units must have two functional groups in order to condensation reaction to place. Dacron, nylon 6 and nylon 66 are few examples for condensation polymers.

- **Addition**



- **Condensation**



Dacron[®] nolvester

The polymer chain is formed from only one type of monomer units called homopolymers. Alternatively, two or more different monomer units can combine to form a polymer chain called copolymers.

alternating copolymer

ABABABABABABABABABABAB

block copolymer

AAAABBBBAAAABBBBAAAABBBB

random copolymer

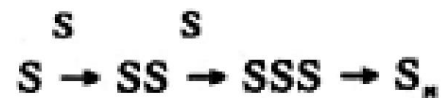
AABABABBAABAAABBAABABBBA

graft copolymer

AAAAAAAAAAAAAAAAAAAAAAAAAA
 B B B
 B B B
 B B B
 B B B
 B B B
 B B B
 B B B
 B B B

Let R and S be two different monomers.
 Homopolymerization

R and S present only



Addition Polymerization Methods

Homogeneous Polymerization:

- In case of homogeneous bulk polymerization, the feed is a gas , liquid or solid monomer. No initiators or additives are used.
- For homogeneous Solution polymerization, the monomer is completely dissolved in a solvent.

Heterogeneous Polymerization:

- In heterogeneous Emulsion polymerization, the monomer molecules are emulsified in aqueous media in the form of micelles.
- For heterogeneous Suspension polymerization, the monomer is suspended in a n aqueous or other type of media as large droplets.

Polythene (PE)

The manufacture of polyethylene follows addition polymerization kinetics involving catalysis of purified ethylene.



Its molecular formula is $-(\text{CH}_2-\text{CH}_2)_n-$

molecular weight of 1,500 to 100,000.

Its melting point is 85 – 110°C.

Density is 0.91 -0.93, when produced by high pressure process and 0.96, when produced by low pressure process.

There are three processes by which polyethylene is manufactured

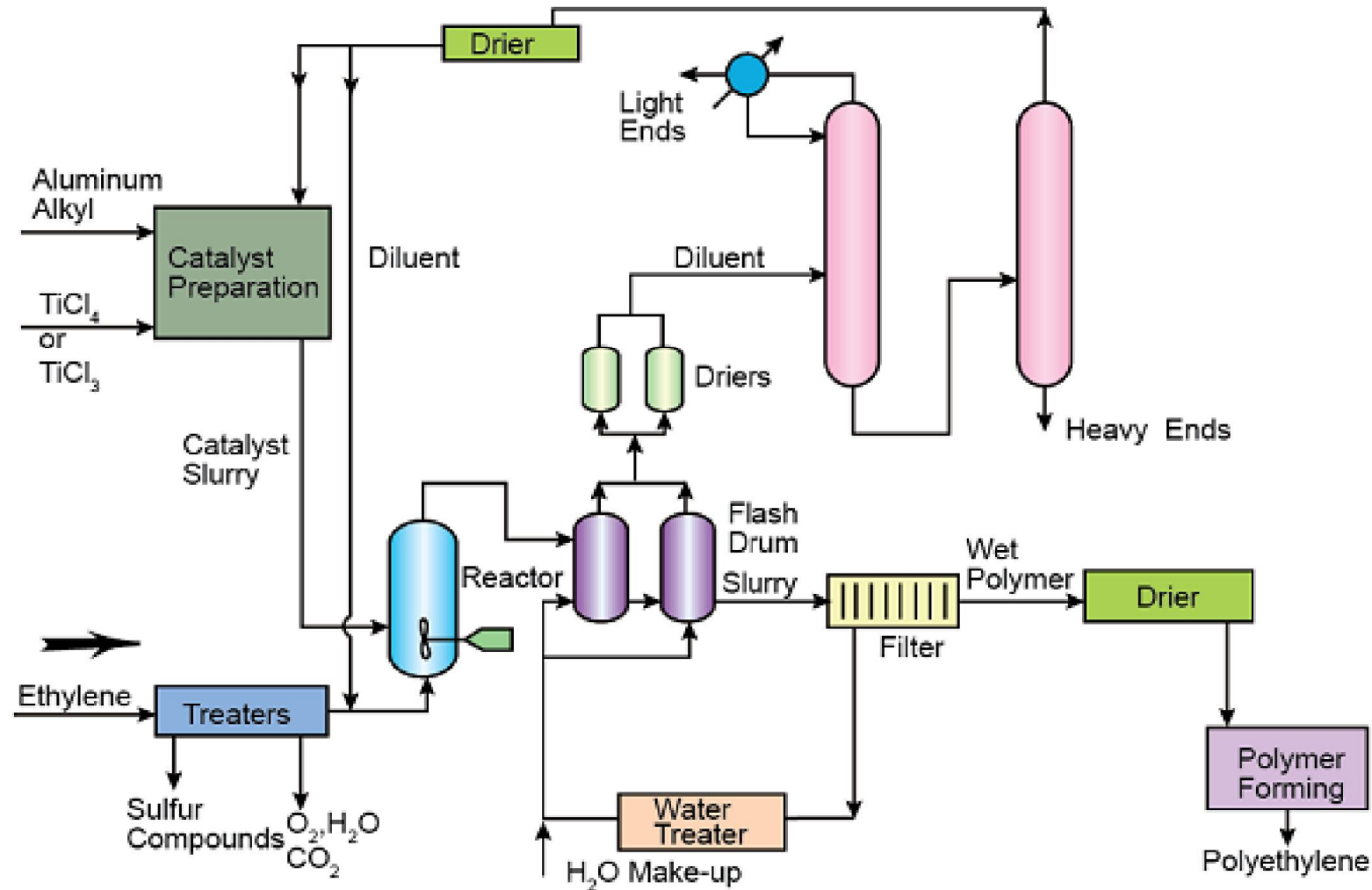
High Pressure Process : This process was developed in the UK. It uses **peroxide catalyst** at 100-300°C and produces low density randomly oriented polymer which have a low melting point. The process is run at a pressure of **1000 – 2500 atms**. This process yields Low Density Polyethylene (LDPE).

Intermediate Pressure Process : This process was developed in the USA by Phillips Petroleum Co. for preparing high density polymer with increased rigidity, crystallinity, tensile strength and softening point. This process uses **MoO₃ and Cr₂O₃** on alumina as catalyst and is operated at **30 – 100 atms**.

Low Pressure Process : This process was originally developed by Dr. Karl Ziegler in Germany for preparing high density polyethylene (HDPE). The catalyst used in this process consists of **aluminium triethyl** **activated with heavy metal derivatives such as TiCl₄** and is operated at **6-10 atms**.

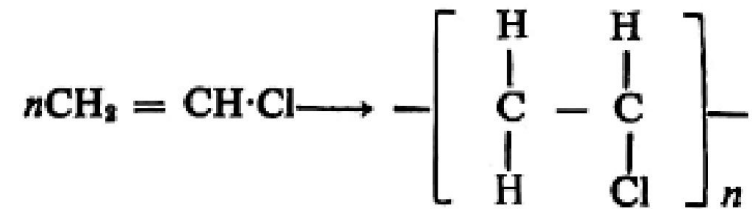
A similar process developed by Dr. G. Natta in Italy is used for the production of polypropylene

Manufacture of Polythene (Low Pressure Ziegler Process)



POLYVINYL CHLORIDE (PVC)

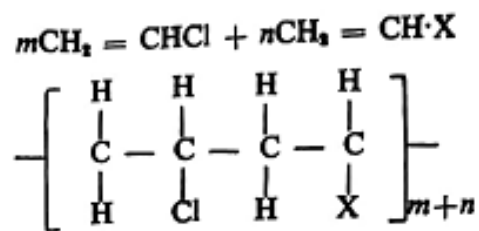
The manufacture of Polyvinyl Chloride (PVC) follows addition type kinetics and produces linear polymers.



Where $n = 700-1500$

typical polymerization temperature range of 50°C to 70°C is $800-1250$ Kpa

Vinyl copolymers



where m is usually greater than n , X is a group on the comonomer such as:

carboxyl ($-\text{COOH}$)—vinyl acetate

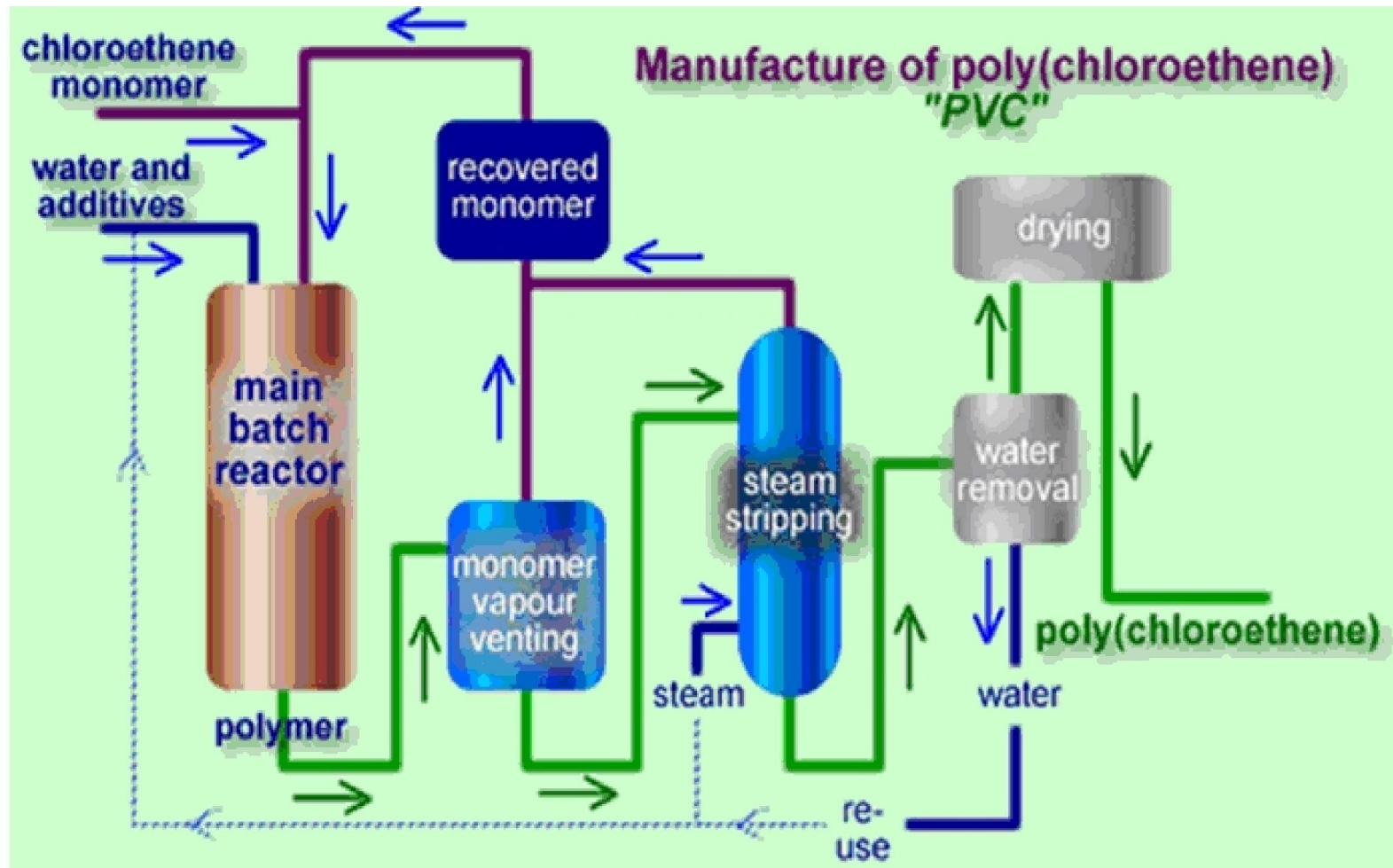
hydroxyl ($-\text{OH}$)—vinyl alcohol

carboxyester ($-\text{COOR}$)—methyl methacrylate

nitrile ($-\text{CN}$)—acrylonitrile

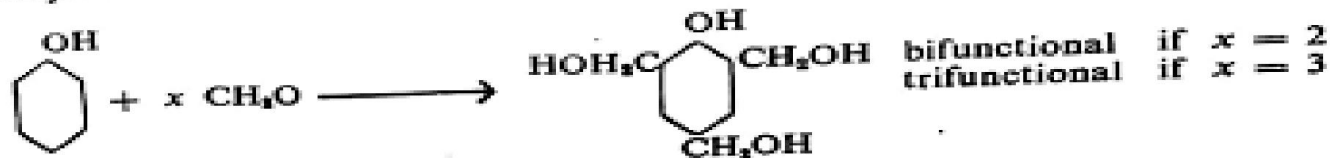
Replacing the HX group by chlorine atoms gives the vinylidene monomer.

Manufacture of Poly(Vinyl Chloride)

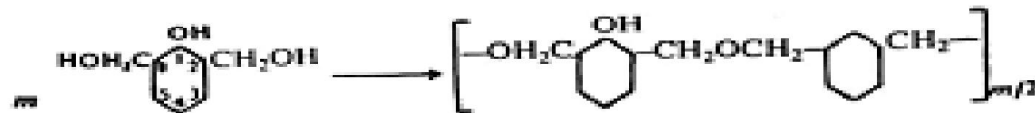


Phenol Formaldehyde

(a) Methylol monomer formation

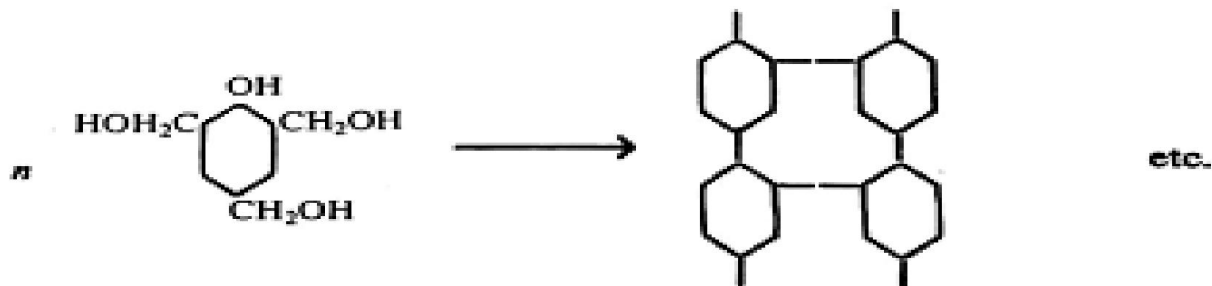


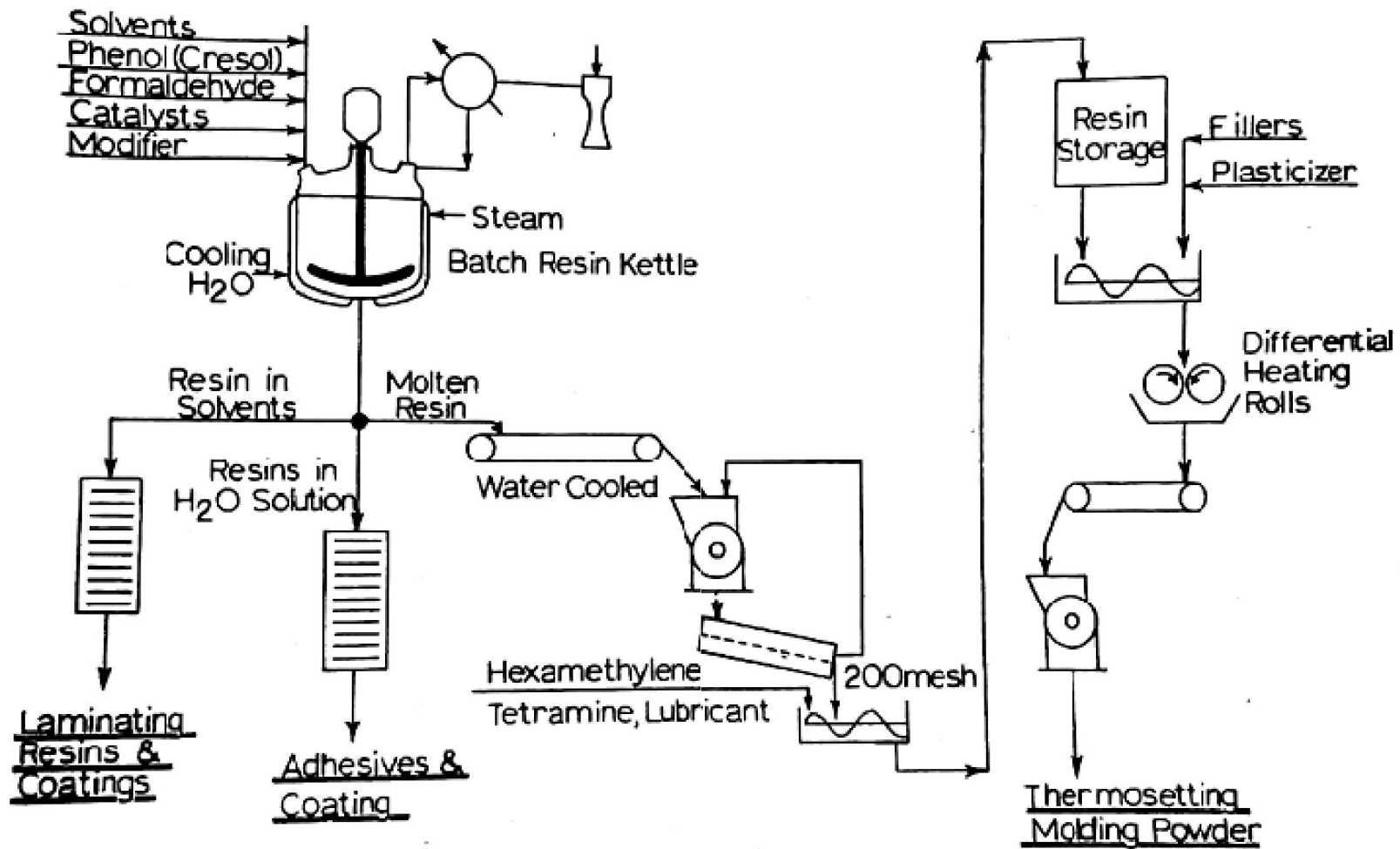
(b) Linear polymer



Substitution of non-functional group in the 4 position will block the cross-linking possibilities shown next.

(c) Cross-linked tridimensional polymer



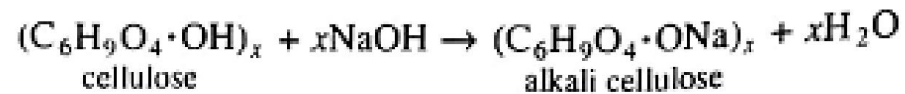


VISCOSE RAYON

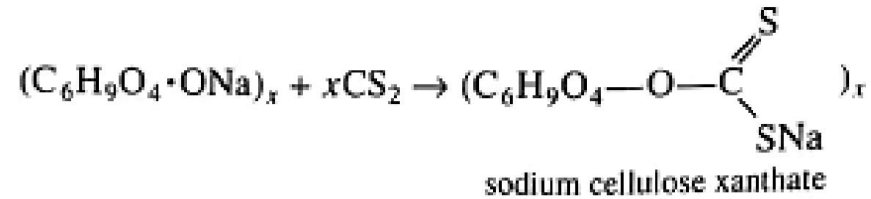
- Viscose Rayon is the oldest commercial man-made fiber. Viscose rayon is the naturally regenerated cellulosic fiber that can be made from naturally occurring cellulosic based material. (such as cotton linters, wood pulp etc.)
- Chemical structure of viscose is same as that of cotton i.e. Cellulose, But the polymer chains are much shorter. The degree of polymerization value of rayon is 400 – 700 while that of cotton is 5000.
- Rayon is used for many purpose in the textile weaving industry. A second major use is in the production of rayon cord for rubber tire casing.
- Raw materials: wood pulp, cotton linters, cotton waste.

Chemical reaction

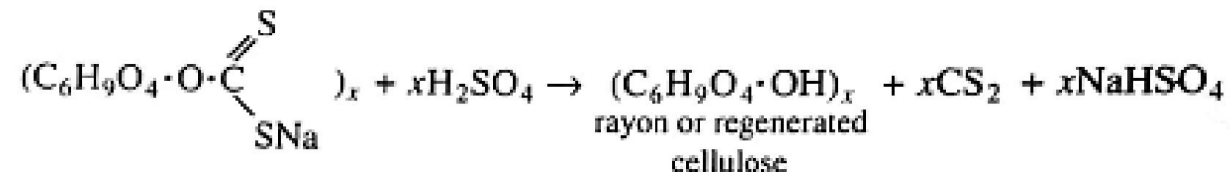
(a) Alkali conversion



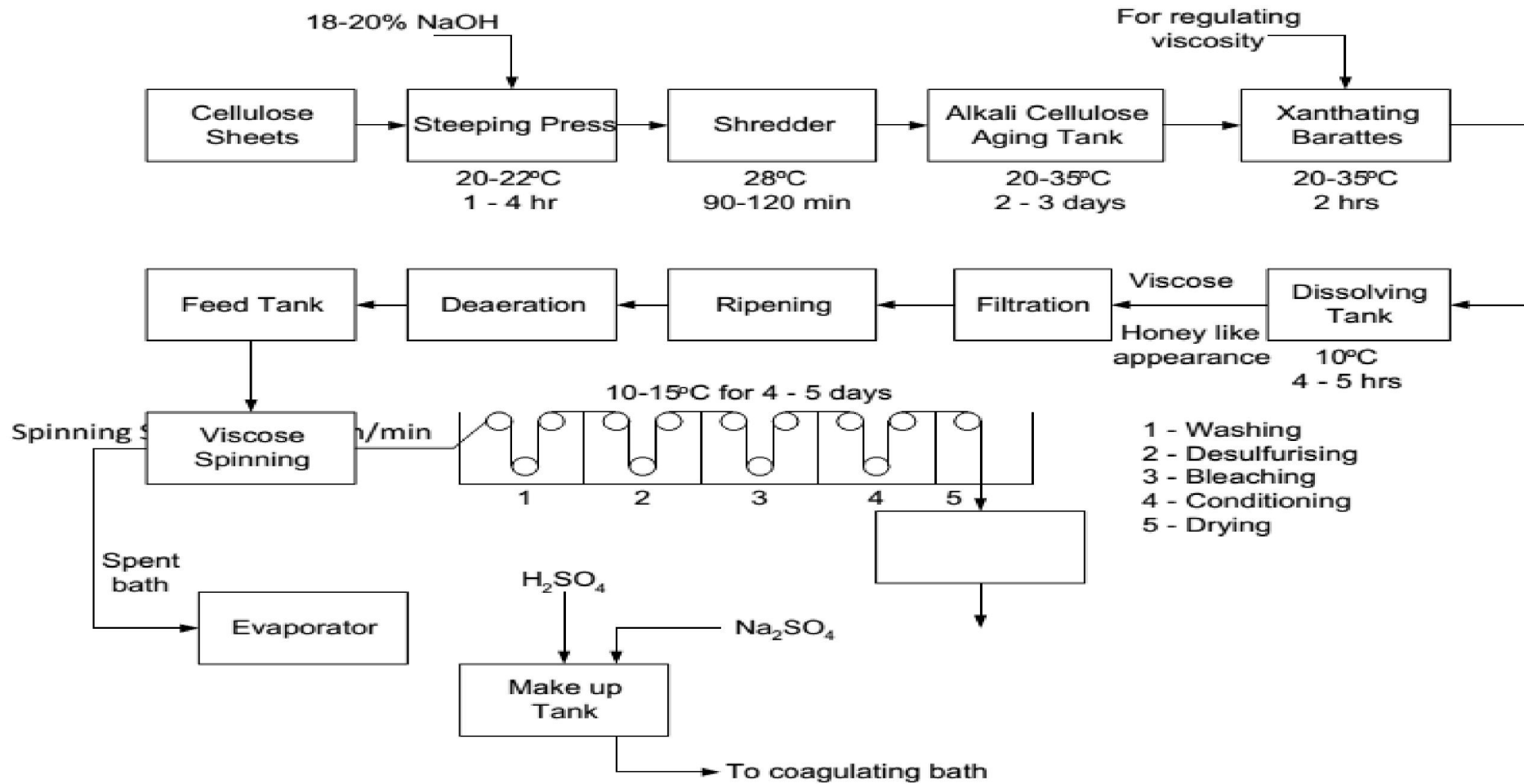
(b) CS₂ solubilization



(c) Acid regeneration

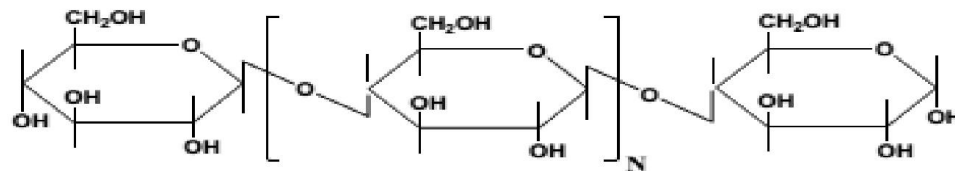


Viscose Rayon Manufacture

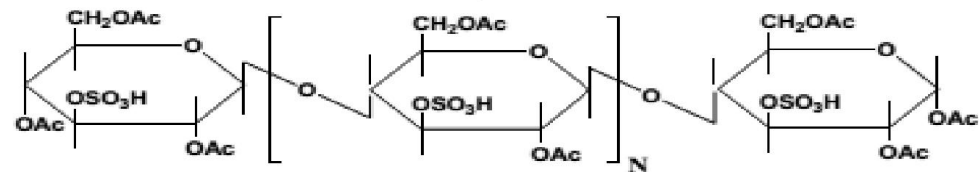


ACETATE RAYON

Cellulose

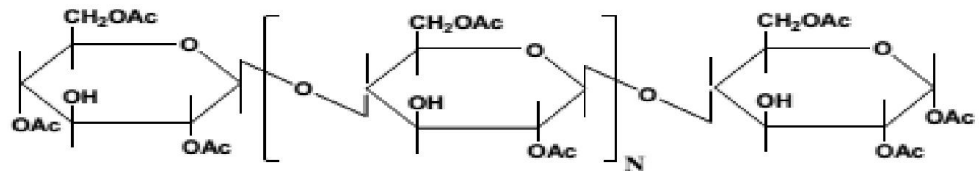


Acetic anhydride/ H_2SO_4



Hydrolysis $\text{CH}_3\text{COOH} + \text{H}_2\text{O}$

Cellulose acetate

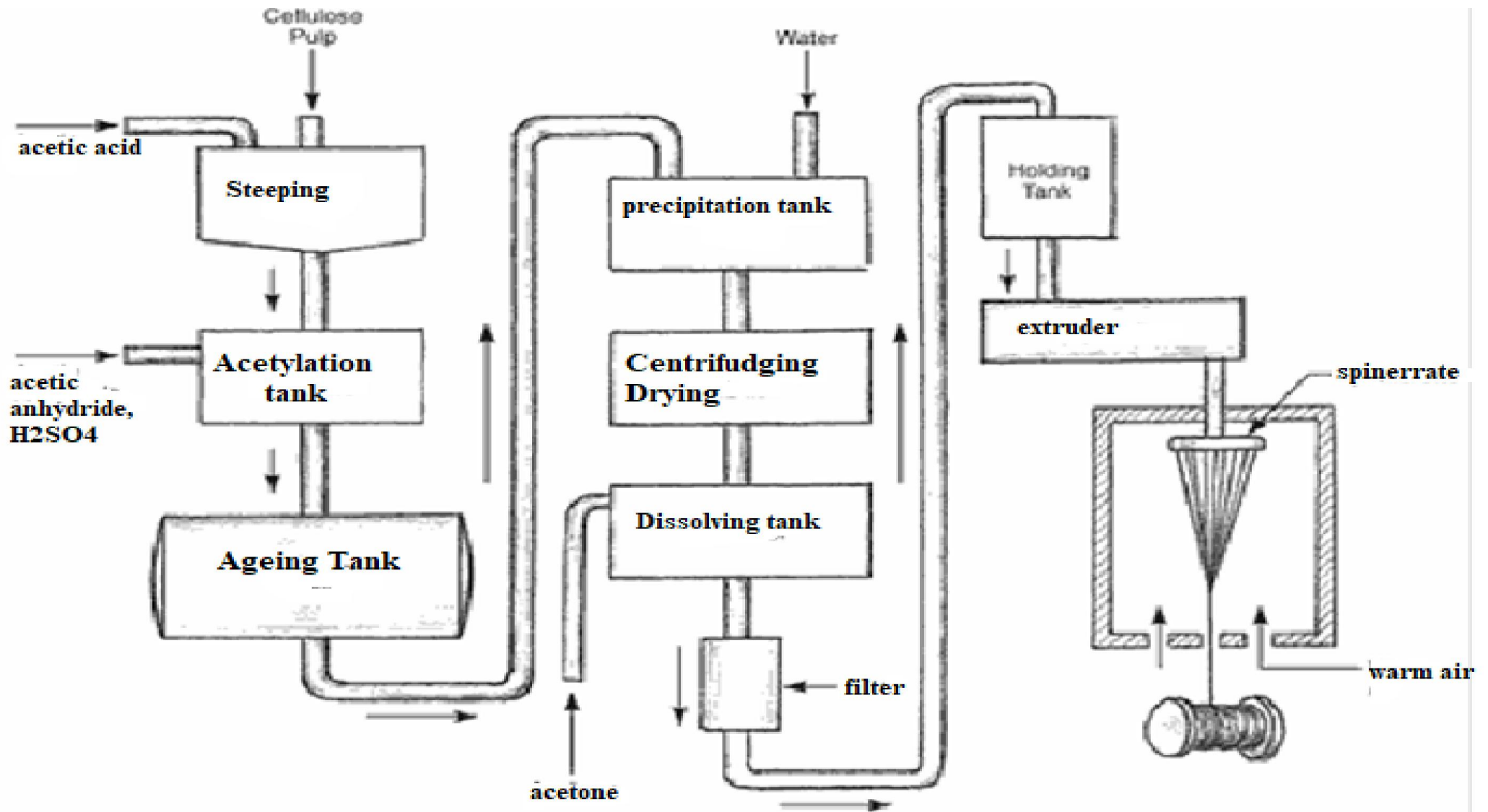


Manufacturing of Acetate Rayon:

Takes place in four stages;

- Acetylation process
- Hydrolysis
- Preparation of Dope solution
- Spinning

Manufacture of Acetate rayon



NYLON

Nylon is a thermoplastic silky material that can be melt-processed into fibers, films, or shapes.

It is made of repeating units linked by amide links

Common nylons (i.e. nylon 6, nylon 66) are polyamides with structural units derived predominantly from aliphatic monomers.

Although many reactions are known that are suitable for polyamide formation, but commercially important nylons have been obtained by either (a) polycondensation or (b) ring opening.

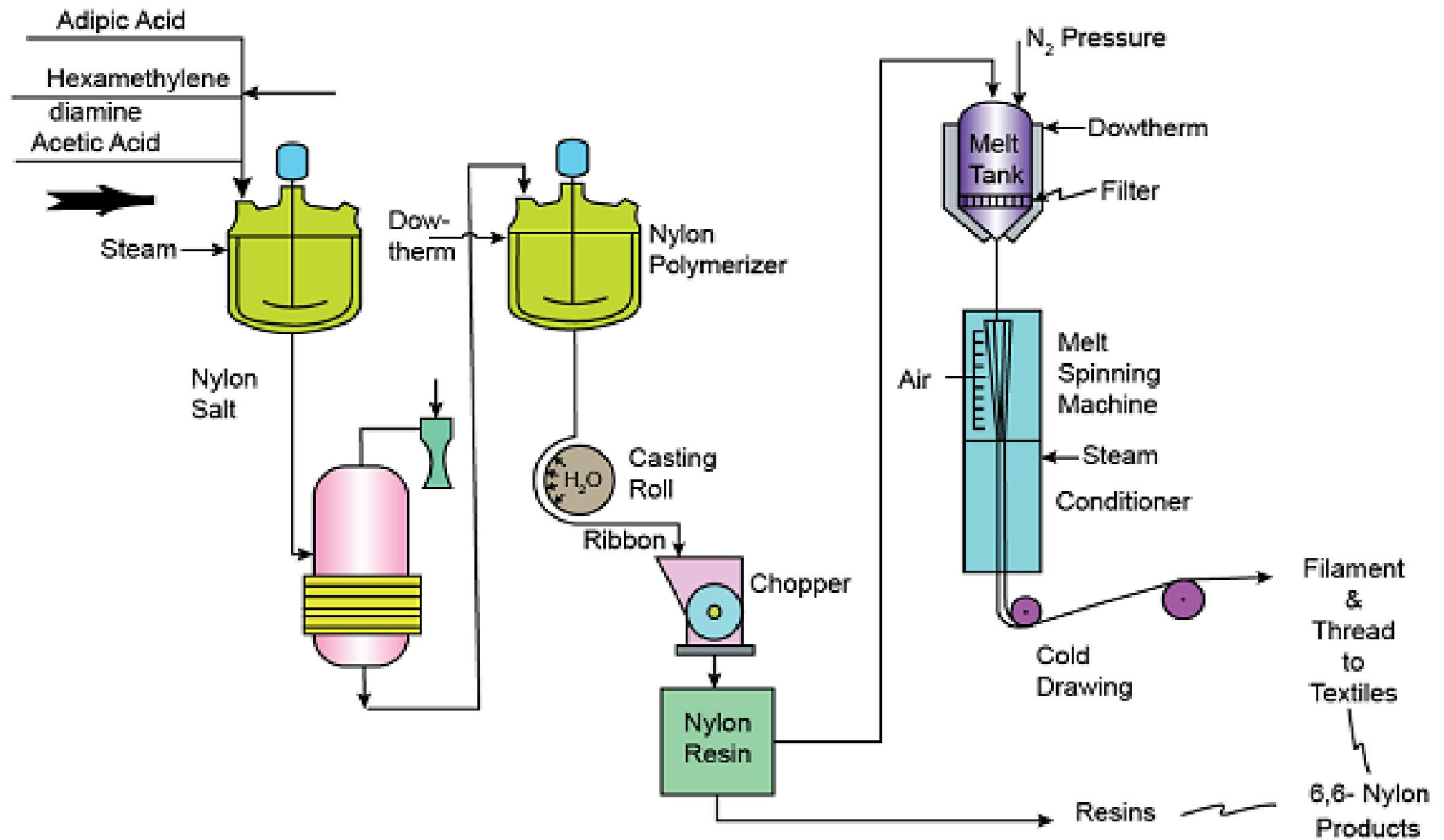
Nylon polymers can be mixed with a wide variety of additives to achieve many different property variations.

Nylon polymers have found significant commercial applications in fabric and fibers (apparel, flooring and rubber reinforcement), in shapes (molded parts, gears, electrical equipment, etc.), and in films (mostly for food packaging).

Uses

- **Textiles:** Apparel, tooth brushes, Tyre cord
- **Automotive:** Bearings, slides, door handles, door & window stops.
- **Furniture:** Locks, hangers, chairs etc.,
- **Packaging:** Film sheet
- **Mech. Engg.:** Drive gears, bearings, fish plates for railways lines tubing.

Manufacture of Nylon 6,6



NYLON 6

The production of Nylon-6 is similar to that of Nylon-66, the only difference being the nature of polymerization. Nylon - 6 is manufactured by the step-wise condensation of caprolactam with no net water removal

Polymerization at 240-270°C in presence of water

Nylon 6 is produced from polymerisation of caprolactam. Process steps involved in production of Nylon 6 involve the following steps:

Caprolactam melting and addition of additives

Polymerisation: Batch/continuous and chips production

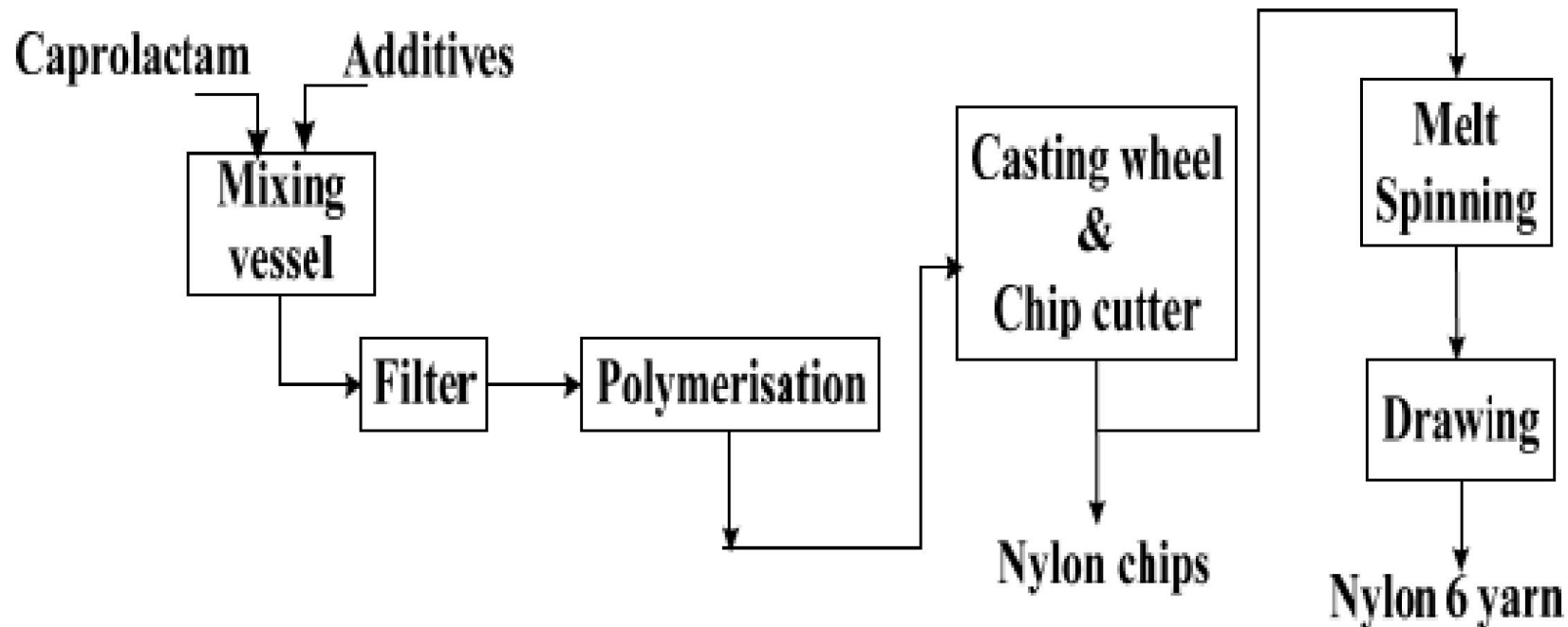
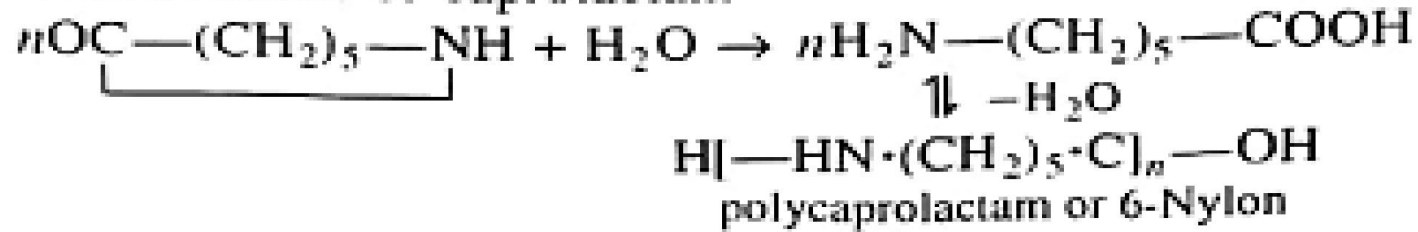
Chips washing and drying

Spinning of nylon

Recovery section

Manufacturing process of Nylon 6

Stage condensation of caprolactam



Elastomers

- Elastomer is an elastic polymer which returns to original dimensions when stretched considerably from its original shape.
- Rubber is a collective term for macromolecular substances of natural (natural rubber, NR) or synthetic (synthetic rubber, SR) origin. Natural rubber is prepared by material produced from the milk of rubber trees, which has been treated with more or less amounts of sulfur and vulcanized.
- Synthetic rubbers are complex chemical compounds built by means of polymerization of monomers. The synthetic rubber industry provides a high number of different synthetic rubbers which are produced in chemical plants world wide to reflect the different applications and the wide range of requirements from the market.

Examples are

- Styrene-Butadiene Rubber (SBR),
- Polybutadiene Rubber (BR)
- Polyisoprene Rubber (IR)
- Butyl Rubber (IIR)
- Nitrile Rubber (NBR)
- Halobutyl Rubber (HIIR)
- Ethylene Propylene Diene Monomer (EPDM)

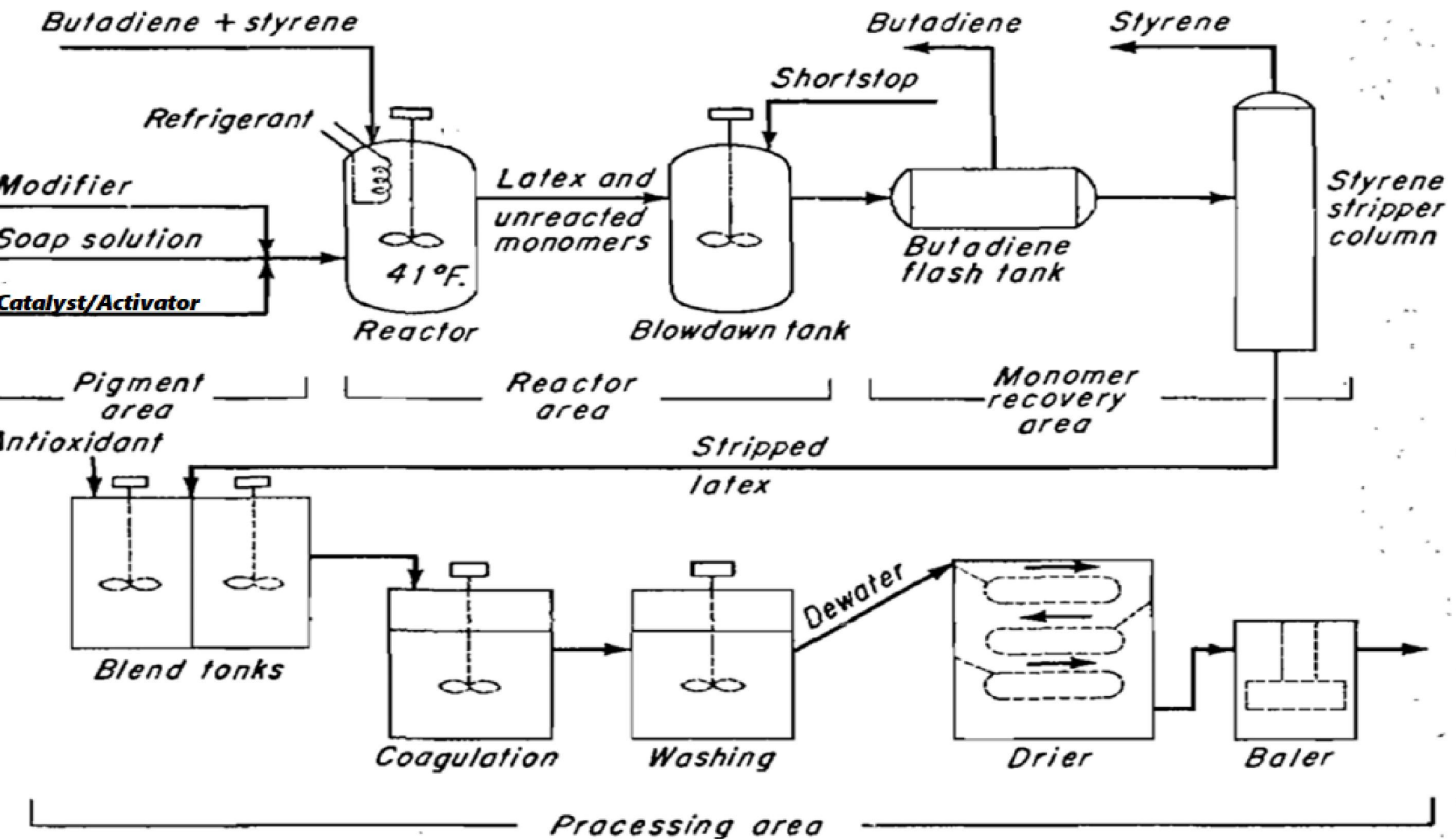
Styrene-Butadiene Rubber (SBR),

Styrene-butadiene rubber (SBR) is the most commonly produced synthetic rubber obtained from styrene and butadiene

About 70 % of SBR is used for the manufacture of car tyres, SBR is also used to manufacture conveyor belts, flooring and carpet underlay, hoses, seals, sheeting, footwear and a large number of other rubber goods.

There are two different process types utilized for SBR production: emulsion polymerization and solution polymerization. In emulsion polymerization, the monomers polymerize in the presence of an emulsifier (fatty acid or rosin soap) while in solution polymerization a solvent (n-hexane or cyclopentane) is utilized.

Manufacturing process of SBR



| Product type | ESBR |
|----------------------------------|--|
| Reactor type | Continuously stirred tank reactors in series |
| Reactor size | 10 - 40 m ³ |
| Number of reactors in use | up to 15 |
| Polymerisation pressure | up to 0.5 MPa |
| Polymerisation temperature | 5 – 10 °C (50 °C is used to produce the so-called 'hot SBR') |
| Emulsifying agent | Various anionic surfactants, usually fatty or rosin acid soaps. Nonylphenols are used at some sites (see footnote) |
| Modifier | Tertiary dodecyl mercaptan |
| Shortstops | Sodium polysulphide |
| Catalyst/initiators | Isopropyl hydroxylamine, diethyl hydroxylamine Hydroperoxides/iron peroxide salts for hot SBR |
| % solids at end of reaction | 15 - 30 % |
| Conversion of monomer to polymer | 50 – 70 % |
| Antioxidant | p-phenylenediamine derivatives, phenolic types, phosphite types |
| Extender oil | Highly aromatic, naphthenic, treated distillate aromatic extract (TDAE), mild extract solvate (MES) |
| Capacity per reactor line | Typically 30000 - 60000 t/yr. |

Note: Nonylphenol is harmful for aquatic ecosystems, and it has been declared as a 'hazardous priority substance' under the Water Framework Directive, meaning that discharge to all water bodies should be stopped by 2015.