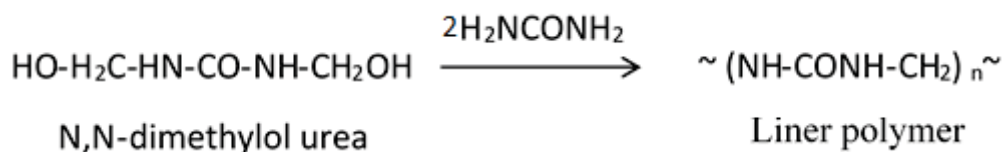# Preparation of Urea-formaldehyde resins

The two important classes of amino resins are the condensation products of urea and melamine with formaldehyde. They are considered together here because of the similarity in their production and applications. In general, the melamine resins have somewhat better properties but are higher in price.
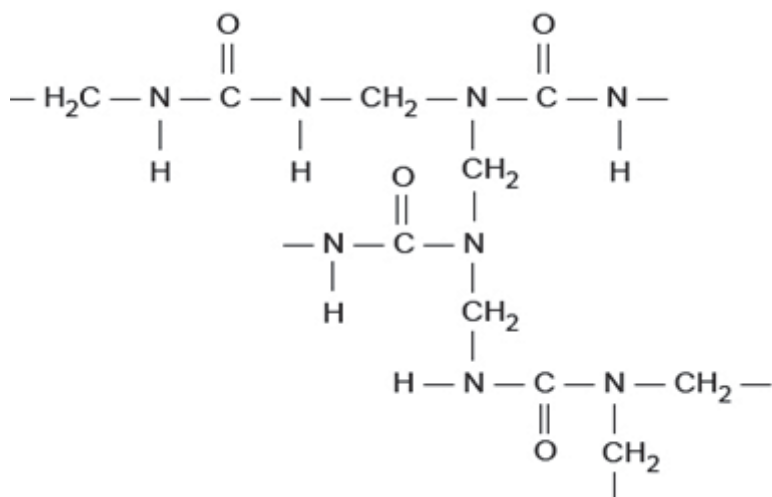
Chemistry and Production:

$$H_2N\text{-}CO\text{-}NH_2 \quad + \quad HCHO \quad \longrightarrow \quad HO\text{-}H_2C\text{-}HN\text{-}CO\text{-}NH\text{-}CH_2OH$$

And which condensed with two more urea molecules to form a liner polymer.

$$HO\text{-}H_2C\text{-}HN\text{-}CO\text{-}NH\text{-}CH_2OH \xrightarrow{2H_2NCONH_2} \sim (NH\text{-}CONH\text{-}CH_2)_n\sim$$

N,N-dimethylol urea $\qquad\qquad\qquad$ Liner polymer

Urea is dissolved in aqueous formaldehyde in a throw-away container . Acidification of this solution initiates condensation polymerization, and a hard, white, thermosetting polymer is formed within a few minutes . After washing, the properties of this substance can be investigated .If a mold is used, the experiment could be extended to show the formation of plastic articles made in a mold by condensation polymerization.The reaction is a condensation polymerisation in which water is eliminated as the hydrogen atoms from the ends of one amino-group from each of two urea molecules combine with the oxygen atom from a formaldehyde molecule .The remaining –CH2– group from the formaldehyde molecule then forms a bridge between two neighboring urea molecules, as shown below .This process, repeated many thousands of times, forms long chains of urea and formaldehyde molecules linked in this way .

Sometimes the second hydrogen atom on an amino-group will also react with a formaldehyde molecule, producing a branch in the chain, and chains may even become cross-linked to each other .Eventually a random three-dimensional network of cross-linked chains is formed, giving a rigid structure and thus a hard, inflexible material .The product has many cross links :Because the tangle of cross-

linked chains is almost impossible to separate, the material does not melt on heating, although it will eventually break down at high temperature, decomposing and giving off small molecules such as steam and nitrogen, leaving a charred mass which is largely carbon.

$$-H_2C-\overset{\displaystyle H}{\underset{\displaystyle |}{N}}-\overset{\displaystyle O \atop ||}{C}-\overset{\displaystyle H}{\underset{\displaystyle |}{N}}-CH_2-\overset{\displaystyle |}{\underset{\displaystyle |}{N}}-\overset{\displaystyle O \atop ||}{C}-\overset{\displaystyle H}{\underset{\displaystyle |}{N}}-$$

Properties and Applications:

A distinct advantage of the amino resins over the phenolics is the fact that they are clear and colorless to milky viscous liquid, with faint (weak) formaldehyde odor, so that objects of light or pastel color can be produced. It is soluble in water and alcohol. The resin is used in the production of an adhesive for bonding particleboard (61% of the urea-formaldehyde used by the industry), largely for plywood and furniture case goods, adhesive, thermosetting resin, safety glass, or coating.

Because of their colorability, solvent and grease resistance, surface hardness, and mar resistance, the urea resins are widely used for container closures, appliance housings, and stove hardware.

Procedure 1;

1- 1- Dissolve 10 g of urea in 20 mL of formaldehyde solution (formalin = 37 − 40)% , in the disposable container .
2- 2- Add about 1 mL of concentrated sulfuric acid H_2SO_4 a drop at a time, using a dropping pipette, and stir steadily .Within a minute the solution

begins to go milky and eventually a hard, white solid is formed which is difficult to remove from the container. A lot of heat is evolved .Show that the polymer is hard by poking the material with a spatula.

3- 3- Wash the polymer thoroughly before passing around the class, as it is likely to be contaminated with unreacted starting materials .Alternatively, pass it round in the container with the lid screwed on.

4- 4- Make a plastic mold from the simple shape and line it with aluminum foil.

5- 5- Make another urea-formaldehyde solution as above, but, immediately after adding the acid, pour some of the solution into the mold and allow it to polymerize, Remove from the mold when solid.

6- 6- Hold a sample of the polymer from the mold with tongs and heat in a Bunsen flame .It will char but not melt, showing that it is a thermosetting polymer.

Procedure 2;

1- Dissolve 12.5 g urea in 25 mL of formaldehyde with agitation until a clear solution is formed

2- Heat the solution in a beaker to boiling and continue heating until a c white resin is formed which solidify with heating.

- **Applications of resin;**

A. Thermosetting materials; this prepared by taking a paste of prepared resin with diluted HCl with addition of filling material (filler) such as glass wool, sawdust, etc., as much as acid was diluted it will take more time to solidify, after that the paste is molded.

B. Plastic plates

- Prepare 4 pieces of carton, paper, or cloth in 5x3 cm
- Paint them with prepared resin, then dry in the little hot oven.
- After drying, increase the ovens temperature to solidify the plates. Now you will have plastic plates

C. Safety glass

- Paint a slide of glass with the resin and diluted HCl, then put another slide of glass on it, Then apply a pressure of about 2Kg until it solidify. After that the glass could be broken without scattering.

# Preparation of phenol formaldehyde resin (Bakelite)

The first completely synthetic organic polymer was Bakelite, named for its discoverer Leo Baekeland. The polymer Baekeland produced is still used for electrical plugs, distributor caps in automobiles, switches, and the black handles and knobs on pots and pans .It has superior electrical insulating properties and very high heat resistance .It is made by the base-catalyzed reaction of excess formaldehyde with phenol .In a low-molecular-weight form it is used to glue together the plies of ply wood or mixed with a filler such as sawdust .When it is heated to a high temperature, crosslinking occurs as the polymer "cures". Most polymers are amorphous, linear macromolecules that are thermoplastic and soften at high temperature .In Bakelite the polymer crosslinks to form a three-dimensional network and the polymer becomes a dark, insoluble, infusible substance.

Since the cross-linked polymer of phenol-formaldehyde reaction is insoluble and infusible, it is necessary for commercial applications to produce first a tractable and fusible low-molecular-weight prepolymer which may, when desired, be transformed into the cross-linked polymer .The initial phenol-formaldehyde products prepolymers may be of two types : resols and novolacs.

Resols:

Resols are produced by reacting a phenol with a molar excess of formaldehyde commonly about 1:1.5–2 by using a basic catalyst ammonia or sodium hydroxide . This procedure corresponds to Baekeland's original technique using reflux. Two classes of resins are generally distinguished .

Resols prepared with ammonia as catalysts are spirit soluble resins having good electrical insulation properties. Water-soluble resols are prepared with caustic soda as catalyst .In aqueous solutions with a solids content of about 70 %these are used mainly for mechanical grade paper and cloth laminates and in decorative laminates. The reaction of phenol and formaldehyde in alkaline conditions results in the formation of o -and p-methylol phenols .These are more reactive towards formaldehyde than the original phenol and undergo rapid substitution with the formation of di -and trimethylol derivatives .The methylol phenols obtained are relatively stable in an alkaline medium but can undergo self-condensation to form dinuclear and polynuclear phenols of low molecular weight in which the phenolic nuclei are bridged by methylene groups, shown below .Thus, in the base-catalyzed condensation of phenol and formaldehyde, there is a tendency for polynuclear phenols, as well as mono-, di-, and trimethylol phenols to be formed.
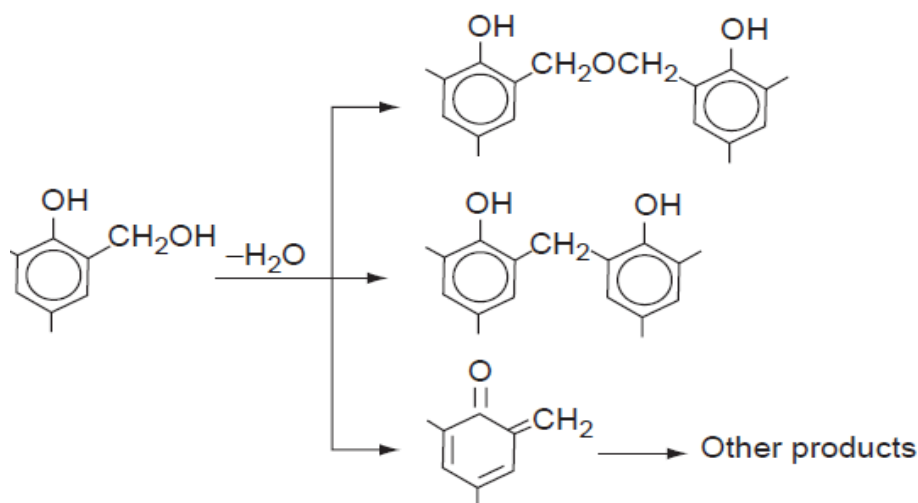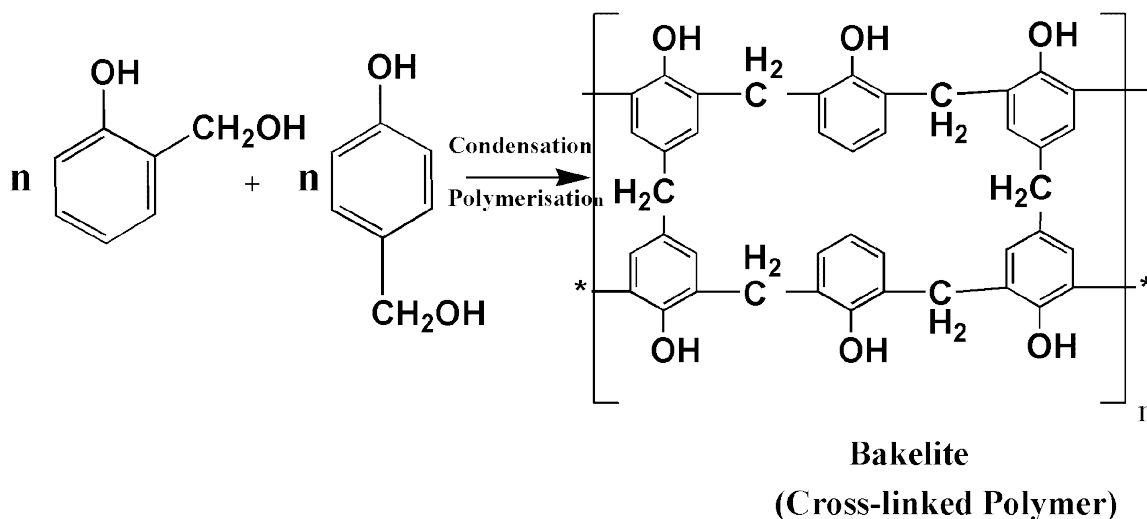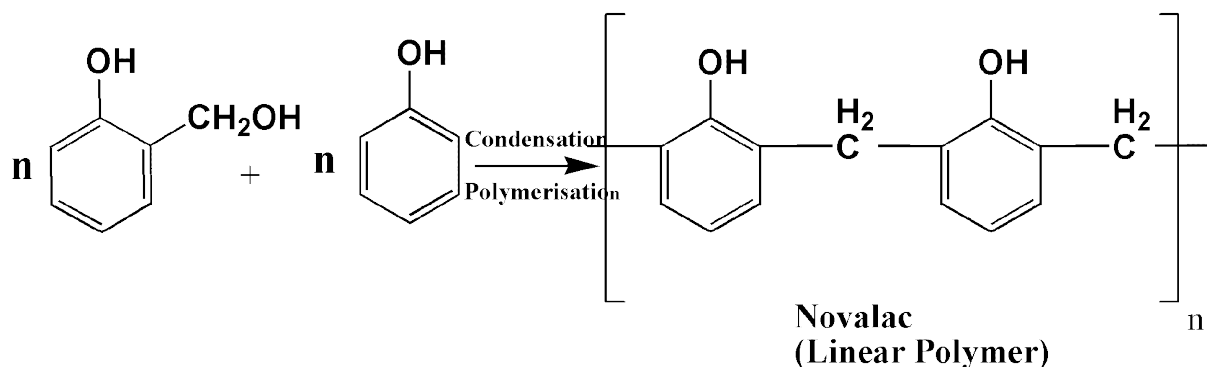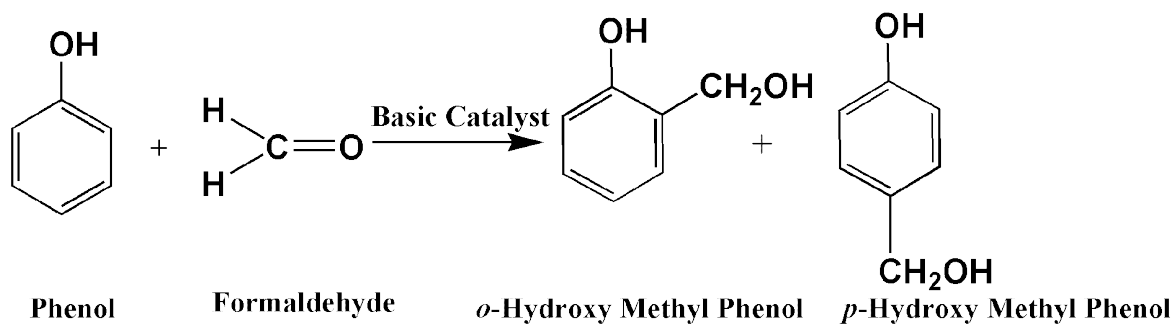
Novolac:

Novolac resins are normally prepared by the reaction of a molar excess of phenol with formaldehyde commonly about 1.25:1under acidic conditions .The reaction is commonly carried out batchwise in a resin kettle of the type used for resol manufacture .Typically, a mixture of phenol, formalin, and acid is heated under reflux at about 100°C .The acid is usually either hydrochloric acid 0.1–0.3 %on the weight of phenol or oxalic acid 0.5–2%. Under acidic conditions the formation of methylol phenols is rather slow, and the condensation reaction thus takes approximately 2–4 h .When the resin reaches the requisite degree of condensation, it become hydrophobic, and the mixture appears turbid. Water is then distilled off until a cooled sample of the residual resin shows a melting point of 65–758C .The resin is then discharged and cooled to give a hard, brittle solid Novolac.

Preparation: -

PFs are prepared by reaction of phenol with formaldehyde in the presence of acidic or basic catalyst. The process may be carried out as follows;
A mixture of phenol and formaldehyde are allowed to react in the presence of a catalyst. The process involves formation of methylene bridges in ortho, para or both ortho and para positions. This results first in the formation of linear polymer (Called NOVALAC) and then in to cross-linked polymer called phenol-formaldehyde resin or Bakelite.

Phenol + **Formaldehyde** →(Basic Catalyst)→ **o-Hydroxy Methyl Phenol** + **p-Hydroxy Methyl Phenol**

n (o-Hydroxy Methyl Phenol) + n (Phenol) →(Condensation Polymerisation)→ **Novalac (Linear Polymer)** $_n$

n (o-Hydroxy Methyl Phenol) + n (p-Hydroxy Methyl Phenol) →(Condensation Polymerisation)→ **Bakelite (Cross-linked Polymer)** $_n$

ROCEDURE: -

1. Place 5ml of glacial acetic acid and 2.5ml of 40% formaldehyde solution in a 500ml beaker and add 2 grams of phenol.
2. Add few ml of conc. Sulphuric acid into the mixture carefully. Within 5 min. a large mass of plastic is formed.
3. The residue obtained is washed several times with distilled water, and filtered product is dried and yield is calculated.
4. For the purpose of making a handle, heat the polymer in a handle mould (such as disposable test tube) on a water bath at 60-65°C for 30 min .Then, after placing a wood stick in the polymer to use as a handle, leave the mould, with your name attached, in an 85°C oven overnight or until the next laboratory period. To free the polymer the mould may need to be broken.

PRECAUTIONS: -

1. The reaction is sometimes vigorous and it is better to be a few feet away from the beaker while adding the H_2SO_4 and until the reaction is complete.

2. The experiment should be preferably carried out in fume cupboard.

Safety Instructions

1. Phenol:- Most phenols are harmful if inhaled, ingested or absorbed through skin. They cause severe irritation or damage to skin and eyes. Some phenols are suspected carcinogen, should not inhale its dust or vapor, wear gloves and avoid contact.

2. H_2SO_4:- It is poisonous and corrosive. Contact or inhalation can cause severe damage to the eyes, skin and respiratory tract. Wear gloves and dispense under a hood, avoid contact and do not breathe the vapor

QUESTIONS BANK:

1. Phenol formaldehyde is also called as.

2. What do you understand by resin?

3. Give main uses of the phenol formaldehyde resin.

4. What type of co-polymer is phenol formaldehyde resin?

5. Briefly describe the properties of phenolic resins.

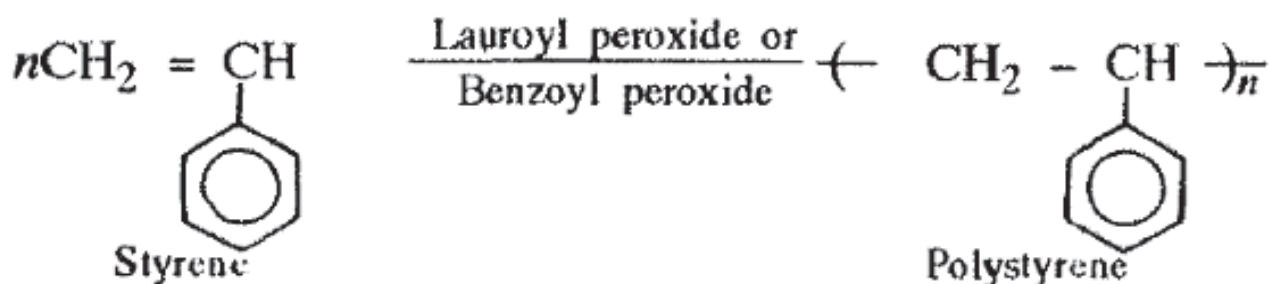6. Write chemical equations for preparation of phenolic resins.

Preparation of Polystyrene by Bulk polymerization

Theory:

Bulk polymerization consists of heating the monomer without solvent with initiator in a vessel .The monomer-initiator mixture polymerizes to a solid shape fixed by the shape of the polymerization vessel .A free radical catalyst or initiator is dissolved in the monomer which is then heated and stirred in a suitable vessel .The polymerization is exothermic and dissipation of heat through cooling may be required. In the use of polystyrene, the polymerization reaction is exothermic to the extent of 17 Kcal/mol or 200 BTU/lb .As the reaction progresses, the system becomes viscous making stirring difficult .The method is economical and the product is of high purity . The main practical disadvantages of this method are the difficulty in the removal of polymer from a reactor or flask and the dissipation of the heat evolved by the polymerization.

The technique is used for preparing polyvinyl chloride [PVC], polystyrene [PS] and po!ymethymethacrylale [PMMA]

Polystyrene is a brilliantly clear, high-refractive-index polymer familiar in the form of disposable drinking glasses .It is brittle and produces sharp, jagged edges when fractured. It softens in boiling water and it burns readily with a very smoky flame .But it foams readily and makes a very good insulator; witness the disposable, white, hot-drink cup .It is used extensively for insulation when properly protected from ignition .The addition of a small quantity of butadiene to the styrene makes a polymer that is no longer

transparent but that has high impact resistance .Blends of acrylonitrile, butadiene, and styrene [ABS] have excellent molding properties and are used to make car bodies .One formulation can be chrome-plated for automobile grills and bumpers .

$$nCH_2 = CH \underset{\text{Benzoyl peroxide}}{\overset{\text{Lauroyl peroxide or}}{\longrightarrow}} \left(CH_2 - CH \right)_{\!\!n}$$

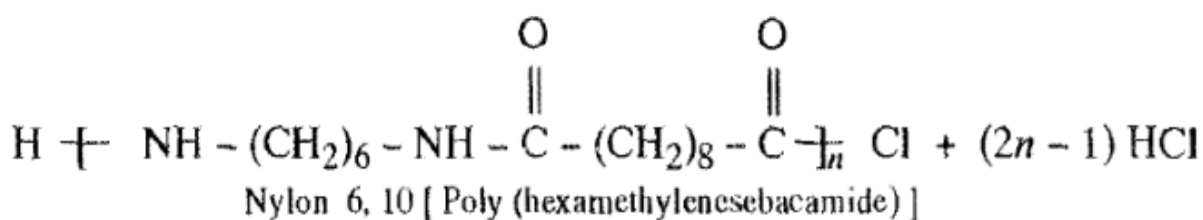Styrene   Polystyrene
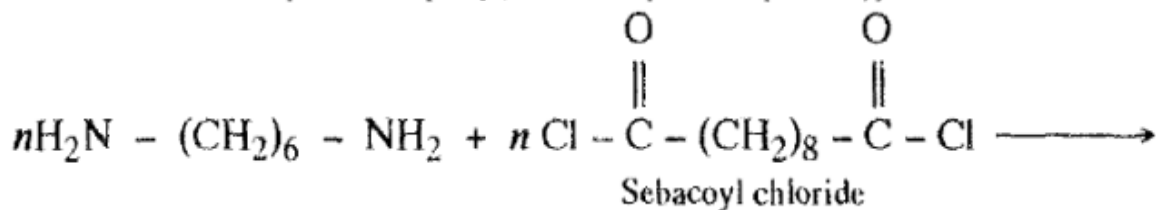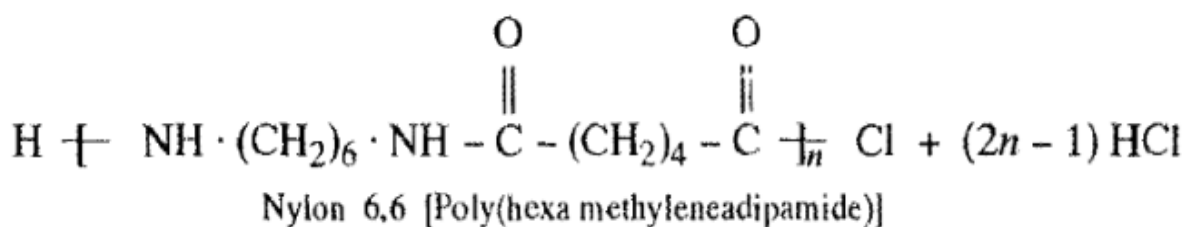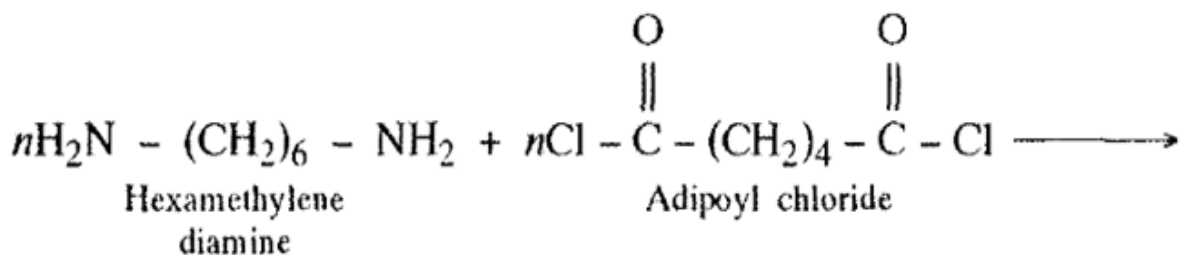
Procedure:

A :Polymerisation of styrene:

1 .Add 50 g of inhibitor-free dry styrene [Wash the styrene monomer twice with 25-ml portions of 25 %aqueous sodium hydroxide in order to remove the inhibitor .Then wash twice with 25 ml of distilled water to remove any residual caustic reagent.], to a test tube.

2 .Flush the tube with nitrogen and add 1.0 g of benzoyl peroxide .Gently shake, stopper, and place the tube in a oil bath at 80°C for 1-2 hr.

3 .When the styrene becomes syrupy and viscous and before it stops flowing, dissolve the contents in 50 ml of toluene and then pour into 500 ml of methanol or propanol in order to precipitate the polystyrene that is formed.

4 .Isolate the polymer by filtration and dry in order to calculate the percentage conversion after this time of reaction.

Preparation of Nylon 6,6 and Nylon 6,10 by interfacial Polycondensation

Background:

In interfacial polycondensation the reaction takes place at the interface between solutions of the reactants in immiscible solvents. Increasing the interface by thorough agitation of the two solutions substantially increase the rate of polymerization. Exact stoichiometry is not necessary and a high molecular weight product can be easily formed .Being very simple, the method is widely used for the production of polyamides, polyesters, polyurethanes and polysulphonamides. Difference in the reactivity of materials can be utilized to prepare ordered copolymers which otherwise are very difficult to produce. The technique is however limited to reactants having highly reactive functional groups that can readily react at the ambient temperatures . When an aqueous solution of the diamine is carefully brought in contact with the solution of the diacid or diacid chloride in an organic solvent [immiscible with water], the reactants diffuse to the interface where the polycondensation reaction takes place: The polymer film, which is insoluble in both the solvents, is formed at the Interface and, using a pair of forceps, can be drawn out in the form of a thread or a rope.

$$n H_2N - (CH_2)_6 - NH_2 + nCl - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} - Cl \longrightarrow$$

Hexamethylene diamine   Adipoyl chloride

$$H -\!\!\left[NH \cdot (CH_2)_6 \cdot NH - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} \right]_n\!\!- Cl + (2n - 1) HCl$$

Nylon 6,6 [Poly(hexa methyleneadipamide)]

$$n H_2N - (CH_2)_6 - NH_2 + n Cl - \overset{O}{\overset{\|}{C}} - (CH_2)_8 - \overset{O}{\overset{\|}{C}} - Cl \longrightarrow$$

Sebacoyl chloride

$$H -\!\!\left[NH - (CH_2)_6 - NH - \overset{O}{\overset{\|}{C}} - (CH_2)_8 - \overset{O}{\overset{\|}{C}} \right]_n\!\!- Cl + (2n - 1) HCl$$

Nylon 6, 10 [Poly (hexamethylenesebacamide)]

Nylon could be prepared either by reacting diamine with diacid or even easier reacting diamine with diacid chloride instead of diacid. This is because acid chlorides are much more reactive than acids. The reaction of diamines with diacid chlorides have equilibrium constants that are about two orders of magnitude higher than those of diamines with diacids.

Procedure:

Reagents Required

1 .Hexamethylene diamine solution [~ 1 %]

2 .Adipoyl chloride solution [~2 %]

3 .Sebacoyl chloride solution[~ 3 %]

Place about 50 ml of the solution of the appropriate diacid chloride [in CCl_4] in a 100-ml beaker .Carefully pour about 25 ml of the aqueous solution of hexamethyiene diamine along the sides of the beaker so that it forms a separate layer over the heavier CCl4 solution layer .When the polymer film appears at the interface, hold it gently at its Centre with a pair of forceps and lift out of the beaker .As it comes out in the form of a thread or rope, wrap it around a thick glass rod or a test tube .

For continuous and automatic wrapping of the thread, a mechanical or an electrical wind-up device may be placed up the beaker.
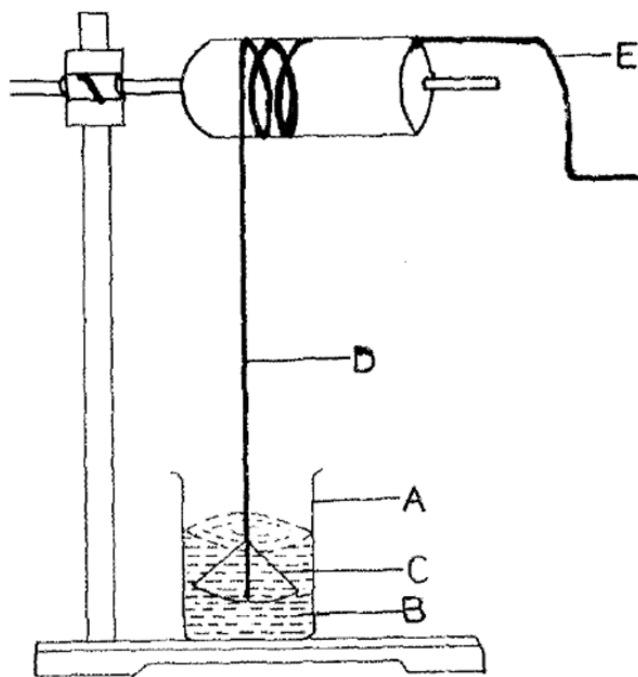
Preparation of Nylon 'Thread

Preparation of phthalic alkyde resin

Alkyd resins are a class of polyesters synthesized by condensation between an alcohol and an acid or anhydride. The term alk-yd derived from "alcohol and acid or anhydride]". Alkyd resins are based on polymeric resins developed in the 1920s. The network polymer formed by glycerol and phthalic anhydride (PA) was described by Smith as early as 1901, but was not a useful product, because it resembled glass and was far too brittle. The first alkyd resins sold commercially under the name Glyptal were made by the General Electric Company. In the mid1920s, Kienle, working for the company, made an important discovery. These network polyesters could be modified significantly by so-called drying oils. The presence of drying oils, usually natural products, made the initial resin soluble in aliphatic solvents. Upon drying and exposure to oxygen, these modified resins rapidly cross-linked and the resultant films were flexible and durable. Oil-modified polyesters, or alkyd resins, were born and still account for a significant fraction of the polymeric resins used in the surface coating industry.

Actually, the anhydride is modified with a monofunctional acid, most commonly C18 fatty acid, which can be obtained from vegetable oil (rubber seed oil (RSO) or palm oil). The major advantage of the alkyd resins is their components (fatty acids and triglyceride derivatives) are obtained from low cost renewable resources. The synthesis of alkyd resins using vegetable oils proceeds in two stages. For example, pentaerythritol, the tetraol of choice and mainly responsible for the degree of branching of the alkyd, and a vegetable oil are reacted to form an ester by transesterification. Then, a slight excess of phthalic anhydride is added to obtain a cross-linked alkyd resin. Both reactions are monitored by acidity and viscosity measurements.

Alkyd resins are either branched or cross-linked polyesters obtained, for example, by polycondensation of a dicarboxylic acid with a polyfunctional alcohol. Branching and crosslinking occur consecutively in a controllable manner. Thus, in the polycondensation

of glycerol with phthalic acid anhydride, there is first formed a branched polyester that remains soluble and fusible as long as the polycondensation is interrupted before more than about 75 mol% of the hydroxy or carboxyl groups have reacted. If this degree of condensation is exceeded the branched polyester transforms by further polycondensation (self-crosslinking) into completely insoluble products. Since one is dealing with crosslinking by polycondensation here, a temperature of about 200 ºC is generally required [baking varnishes]. Of course, if carboxylic acids containing double bonds are incorporated into the alkyd resins they can be cross-linked by the action of atmospheric oxygen at lower temperatures. However, the crosslinking then proceeds by a different mechanism. The dicarboxylic acids normally employed are phthalic acid or its anhydride, or mixtures of them with for example, adipic acid or unsaturated acids. The polyhydroxy compounds generally used are glycerol, trimethylolpropane, or pentaerythritol. In the preparation and cross-linking of alkyd resins [with the exception of some unsaturated alkyd resins] the reaction is practically always carried out in the melt.

For many years, resins resulting from the polycondensation of polyacids and polyols have been used in the paint industry. They have been named in many different ways which have led to uncertainties, as to the composition and utilisation of these products. Alkyds, Polyesters, Glycerols, Glycerophthalics, oil-free Polyesters".

The term "Glycerophthalic" arises from the fact that the first resins were based on glycerol and phthalic anhydride. Alkyd resins today are typically manufactured from acid anhydrides such as phthalic anhydride or maleic anhydride and polyols such as glycerine [which is the first polyol used in production of alkyd resins] or pentaerythritol and are modified with unsaturated fatty acids [from plant and vegetable oils] to give them air drying properties. The reaction between phthalic anhydride and glycerol, is a multistage reaction, if it stopped in its earlier stages, it will give a viscous solution used in manufacturing of some types of paints, and if the reaction continued for higher

temperature, the product will solidify and more interlaced, which is used in varnish production and some types of paints after the addition of the unsaturated fatty acids to give which is known as alkyde paints.

Phthalic anhydride

+ Glycerol

Linear polymer

Excess of phthalic anhydride

Glyptal
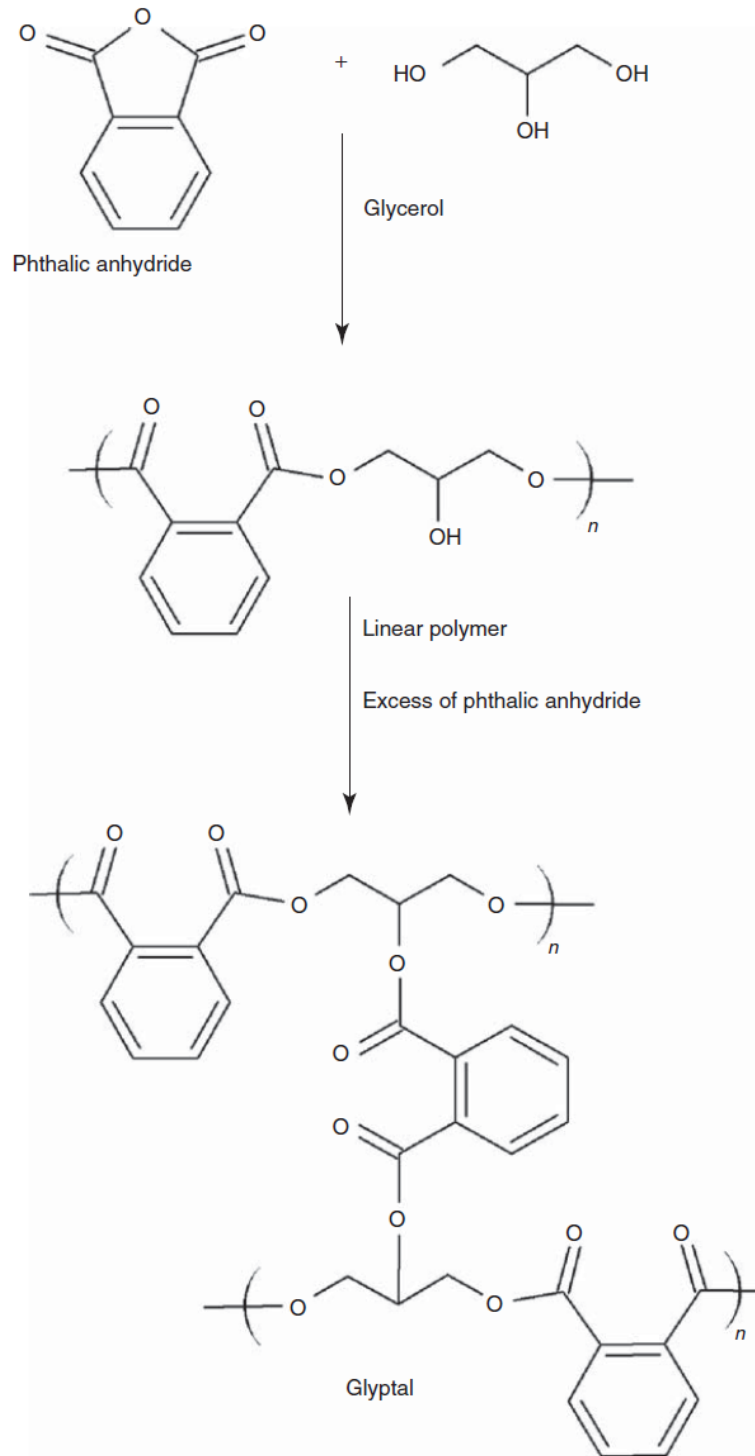
Major applications of alkyd resins are in paints, brushing enamels, and clear varnish. industrial coatings (spraying, dipping, flow coating, roller coating). industrial baking finishes.

Properties; rapid drying, good adhesion, flexibility, mar resistance and durability, ester groups can be hydrolyzed under alkaline conditions.

Procedure:

1. Put 6g of phthalic anhydride after fine grinding, with 4g of glycerol in a large test tube and mix them.

2. Heat with mixing for one hour using an oil bath maintained at temperature 150-180 ^{o}C.

3. One group of students will stop the reaction and take a part of the solution on a filter paper which become viscous not solid.

4. The second group will continue the reaction by increasing the temperature to 200-230 ^{o}C, where the mixture agglomerate, and the completion of the reaction can be noticed by taking a drop from the solution on a filter paper, if it solidified after cooling, it indicates the completion of the reaction, and the alkyd resin is formed

5. After the reaction is completed, pour the solution on a filter paper and let it to cool and solidify, then grind it.

Preparation of cellulose nitrate

Cellulose nitrate (CN) was first made around 1833, when cellulose-containing linen, paper, or sawdust was reacted with concentrated nitric acid. It was the first recognized "synthetic" cellulose product. Initially, CN was used as a military explosive, and improvements allowed the manufacture of smokeless powder.

This remarkable substance was discovered by Christian Friedrich Schönbein. During one set of experiments in 1846, Schönbein accidentally dropped a mixture of sulfuric and nitric acids on the kitchen floor. He quickly cleaned up the spill with his wife's cotton apron and hung it over the oven to dry. Upon drying, the apron spontaneously burst into flame.

The utility of CN produced by Schonbein was limited until Parkes added castor oil to CN in 1865 and Hyatt added camphor to plasticize CN in 1870. Another plasticizer, tricresyl phosphate (TCP), was used to replace part of the camphor and reduce the flammability of celluloid in 1910.

CN is the product obtained by the reaction of cellulose with nitric acid and sulfuric acid; erroneously called nitrocellulose shown below.

Cellulose

HNO_3 / H_2SO_4

Cellulose nitrate

$$H_2SO_4 + HNO_3 \longrightarrow NO_2^+ + H_2O + HSO_4^-$$
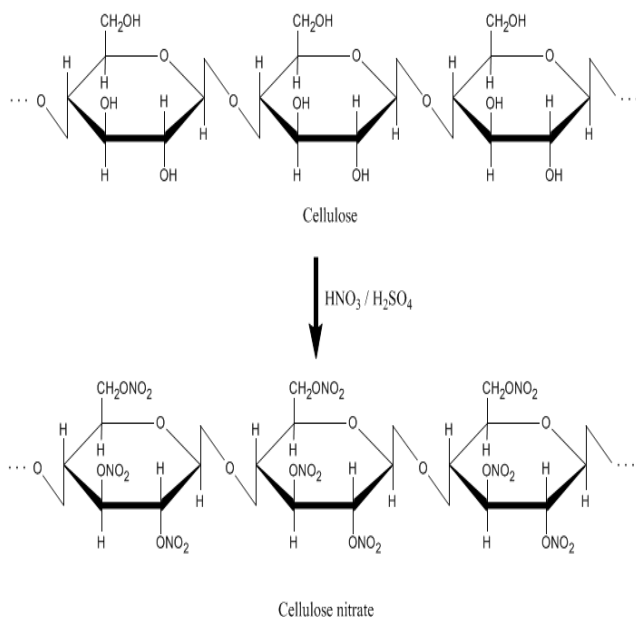
The product is classified as primary, secondary, or tertiary according to how many groups in each repeating anhydro-glucose unit in cellulose are nitrated. The degree of substitution (DS) of this inorganic ester may be controlled by the concentration of the esterifying acids. The OH groups on cellulose repeating units can form strong hydrogen bonds between cellulose molecules, therefore cellulose cannot be softened by heat or dissolved by solvents without causing chemical decomposition. However, upon treatment with nitric acid in the presence of a sulfuric acid as a catalyst and water, as shown above, for each repeating unit, three hydroxyl H are replaced by NO_2.

In theory, all three (H) groups can be replaced, resulting in cellulose trinitrate, which contains more than 14 percent nitrogen. In practice, however, most nitrocellulose compounds are dinitrates, average 1.8 to 2.8 nitro groups per molecule. The degree of nitration determines the solubility and flammability of the final product.

CN is a highly flammable polymer, Burning small quantities of it makes a very entertaining flash. It is also known as flash paper, flash cotton or guncotton. The commercial CN product has a DS of about 2.0, corresponding to a nitrogen content of about 11%. Despite its flammability, plasticized CN by camphor is still used for personal accessories, toiletries, and industrial items. However, the principal use of CN is for coatings, in which the CN has a DP of 200 and a DS of about 2.0. Highly nitrated cellulose—i.e., cellulose nitrate containing more than approximately 12.5 percent nitrogen—will dry to a fluffy white substance known variously guncotton. Guncotton is unstable to heat, and even carefully prepared samples will ignite on a brief heating.

It is very important to note that the nitration should be done at 30-40 °C with little amount of water for decreasing the chain polymer eruption by hydrolysis. The products of nitration, trintrocellulose, dinitrocellulose and nitrocellulose are dissolved in acetone and ethyl acetate.

In 1903 Edouard Benedictus, a French chemist experimented with placing some of the cellulose nitrate between sheets of glass, using pressure to help adhere the glass with the

cellulose nitrate. This was the first safety glass and it was called Triplex since it consisted of outer layers of glass and an inner layer of polymer. By 1909, Benedictus had patented the material and it came into use in automobiles.

Procedure:

Nitric and sulfuric acid are strong oxidizing agents, which can cause severe burns. Sulfuric acid is also a powerful dehydrating agent. Mixing conc. nitric and sulfuric acids produces considerable heat.

When working with these agents, you must:

- You must wear, lab coat, safety goggles and gloves. It is recommended that you wear an apron. All spills must be neutralized with Sodium Bicarbonate. If any should get on your skin, initially flush the area with Ice- Water followed by plenty of tap-water. The area should then be treated with Baking Soda.
  1. Prepare 3-4 water baths and a 250 mL bath of 1M $NaHCO_3$. This must be done before proceeding to the next part of the lab.
  2. A mixture of 70 mL conc. sulfuric acid and 30 ml conc. nitric acid is prepared and place in an ice-bath in the fume hood.
  3. Under the supervision of a laboratory instructor, use tongs to immerse a standard cotton ball in the acid mixture for a few minutes. Then leave the whole mixture for 1 h (cotton + nitration + acid).
  4. Once the nitration is complete, rinse the cotton ball in three successive water baths 500 mL each. Allow the cotton ball to stand in each bath for few minutes.
  5. Then immerse the cotton ball in 250 mL of 1M $NaHCO_3$; sodium bicarbonate. This will react with any excess acid to produce gaseous

carbon dioxide:

$$H^+(aq) + HCO_3^-(aq) \longrightarrow H_2CO_3(aq)$$

$$H_2CO_3(aq) \longrightarrow CO_2(g) + H_2O$$
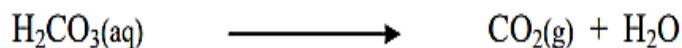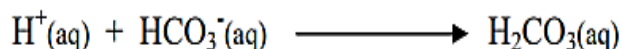
If excess bubbling occurs, repeat the process of rinsing the cotton ball. Otherwise, continue rinsing in the bicarbonate solution until the bubbling ceases.
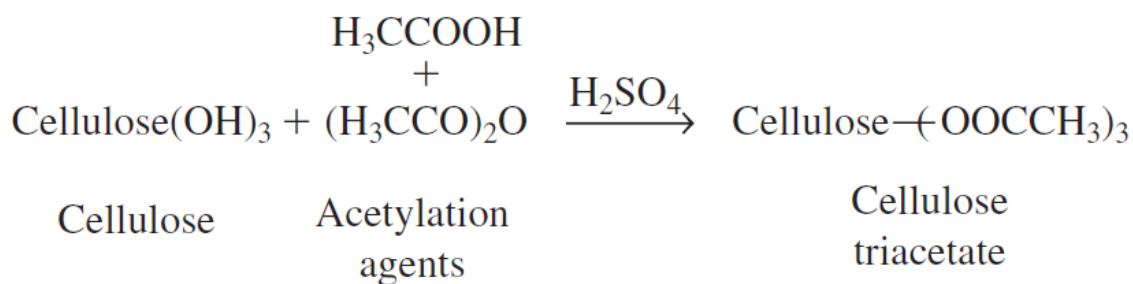
6. Squeeze dries the cotton ball and spread it out to dry or put it in furnace at 40- 50°C until next week.

7. Using a long match to burn small fraction of nitrocellulose in the fume hood and see the flame color. Also burn the original cotton and compare with the nitrated cotton ball.

Notes:

1- When not properly neutralized, Nitrocellulose doesn't burn as beautifully and leaves residues. To be sure, take a small sample and burn it. If it burns quickly, without residue, it is done. If it takes some time and leaves black residue, it hasn't dried fully yet.

2- When you burn the original cotton and the Nitrated Cotton Ball separately. What is the difference between them as you see it?

3- How to make nitrocellulose?

Preparation of poly cellulose acetate

Amongst the important chemical conversions of macromolecular substances are the various reactions of cellulose. Cellulose triacetate (degree ofnsubstitution (DS)= 2.8) was originally prepared by Schutzenberger and Naudine in 1865 by the reaction of cellulose with acetic acid and acetic anhydride in the presence of sulfuric acid.

$$\text{Cellulose(OH)}_3 + (\text{H}_3\text{CCO})_2\text{O} \xrightarrow[\text{+}]{\substack{\text{H}_3\text{CCOOH} \\ \text{H}_2\text{SO}_4}} \text{Cellulose} (\text{OOCCH}_3)_3$$

Cellulose   Acetylation agents   Cellulose triacetate

This ester, which has an acetyl content of 43%, is soluble in chloroform or in mixtures of methylene chloride and ethanol. The three hydroxy groups per repeating units can be partially or completely esterified or etherified. The number of hydroxy groups acetylated per repeating units are indicated by the names, i.e., <u>cellulose triacetate</u>, <u>cellulose diacetate</u>, etc.

Cellulose acetate used as osmatic-cell membrane, cigarette filters, magnetic tapes, photographic film, protective coating solutions, and acetate fibers. When plasticized by ethyl phthaloyl ethyl glycolate, it is used as a film, a molding, and an extrusion.

During World War I, a cellulose acetate coating replaced the highly flammable cellulose nitrate coating on airplane wings and fuselage fabrics. Varying properties of cellulose acetate are achieved by varying the amount of substitution. The melting point generally decreases with decreasing acetylation. Lower acetylations give products with greater solubility in polar liquids and corresponding decreased moisture resistance.

Chain length and of chain lengths distribution are also important factors in determining the specific behavior and uses for cellulose acetates.

Acetylation reaction occurs beginning with the surface or outermost layer and continues on layer by layr as new areas are exposed. When more homogeneous modification is

desired, pre-swelling of the cellulose in water, aqueous acetic acid solutions, or glacial acetic acid is carried out.

(A)

(B)
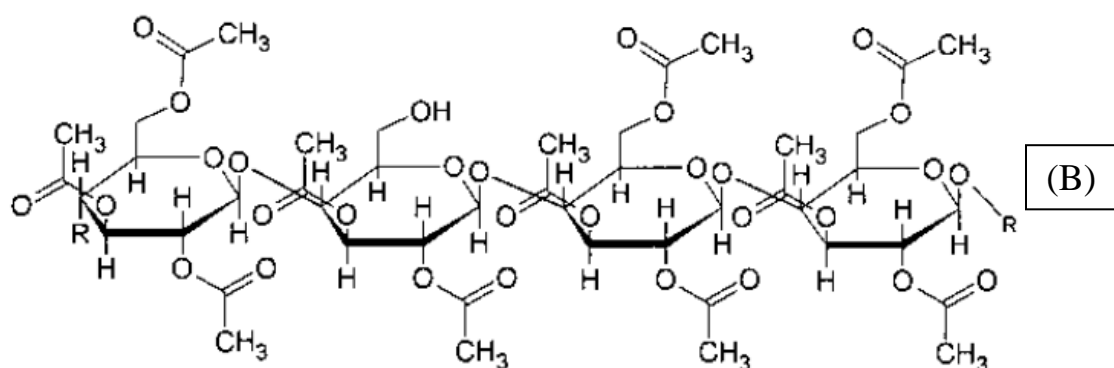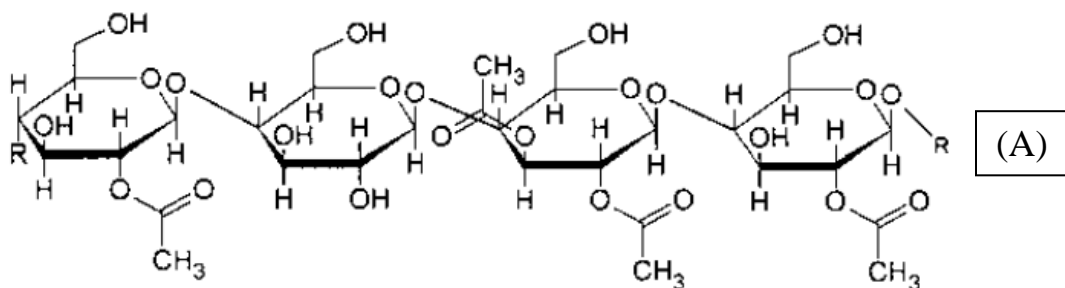
Reaction occurs differently since there are two "types" of hydroxyl groups, the two ring hydroxyls and the methylene hydroxyl. In the typical formation of esters, such as cellulose acetate, the ring hydroxyl groups are acetylated initially Figure (A) prior to the C-6 exocyclic hydroxyl. Under the appropriate reaction conditions reaction continues to almost completion with all three of the hydroxyl groups esterified Figure (B). In triacetate products, only small amounts (on the order of 1%) of the hydroxyls remain free and of these generally about 80% are the C-6 hydroxyl.

The most common commercial products are the triacetate (DS approaching 3) and the secondary acetate (DS about 2.45). While cellulose acetates are the most important cellulose esters, they suffer by their relatively poor moisture sensitivity, limited compatibility with other synthetic resins, and a relatively high processing temperature. While other organic esters are commercially available, namely, cellulose butyrate

and cellulose propionate, by far the most widely used is cellulose acetate. Cellulose acetate is available as plastics, in films, sheets, fibers, and in lacquers. Cellulose acetate is used in the manufacture of display packaging and as extruded film for decorative signs, and to coat a variety of fibers. Injected molded products include toothbrush handles, combs, and brushes. It is also used in lacquers and protective coatings for metal, glass, and paper.

Cellulose acetate films are used in reverse osmosis to purify blood, fruit juices, and brackish water. Some eyeglass frames are made of cellulose acetate. Biodegradable film, sponges, and microencapsulation of drugs for control release also utilize cellulose acetate.

Procedure:

1-In a conical flask add 10 ml of acetic anhydride to 10 ml of acetic acid ,then add 2 drops of Conc. H_2SO_4 .

2-Add about 1.5 g shredded cellulose [small parts of paper] to the acedic solution , warm it with stirring in a water bath until the cellulose parts just dissolves completely.

3-After completely dissolving the cellulose, cool the solution in ice /water with continuous stirring.

4-Filter the product [cellulose acetate] by Büchner funnel, then wash with water.

5-Dry the product in oven at 100°C .

6-Make powder of the product and test the solubility in Acetone, Acetic acid.

7-Calculate the pecentage of product

Preparation of Rayon a regenarated cellulose

Cellulose is not found in a pure form but rather is associated with other materials such as lignin and the so-called hemicelluloses. Cotton contains the purest form of cellulose. Wood, in its dry state, contains 40–55% cellulose, 15–35% lignin, and 25–40% hemicellulose. The extraction of cellulose from plants is called pulping. Pulping is generally achieved using thermo-mechanical, chemical, or mechanical approaches. Pulp is dissolved when removal of the hemicelluloses and lignin are required. After pulping, the pulp is bleached to achieve the desired whiteness.

While the celluloses are often largely linear polymers, they are not soluble in water because of the presence of strong intermolecular hydrogen bonds and sometimes the presence of a small amount of crosslinking. Cellulose is sometimes used in its original or native form as fibers for textile and paper, but is often modified through dissolving and re-precipitation or through chemical reaction.

High molecular weight native cellulose, which is insoluble in 17.5% aqueous sodium hydroxide solution, is called α–cellulose. The fraction that is soluble in 17.5% sodium hydroxide solution but insoluble in 8% solution is called β-cellulose, and that which is soluble in 8% sodium hydroxide solution is called γ–cellulose. Strong caustic solutions penetrate the crystal lattice of -cellulose and produce an alkoxide called alkali or soda cellulose.

The xanthate viscose process, which is used for the production of rayon and cellophane, is the most widely used regeneration process. The cellulose obtained by the removal of lignin from wood pulp is converted to alkali cellulose. The addition of carbon disulfide to the latter produces cellulose xanthate. Water-soluble sodium cellulose xanthate, is produced by the room temperature reaction of carbon disulfide and soda cellulose. Since xanthic acids are unstable, the cellulose is readily regenerated by passing extrudates into an acid bath.

In the cellulose-regenerating process, sodium hydroxide is initially added such that approximately one hydrogen, believed to be predominately a mixture of the hydroxyl groups on carbons 2 and 3, is replaced by the sodium ion. This is followed by treatment with carbon disulfide forming cellulose xanthate, which is eventually re-changed back again (regenerated) to cellulose. This sequence is depicted in the following structure.

Cellulose -------> Sodium salt ------> Cellulose xanthate ------> Regenerated cellulose–rayon or cellophane
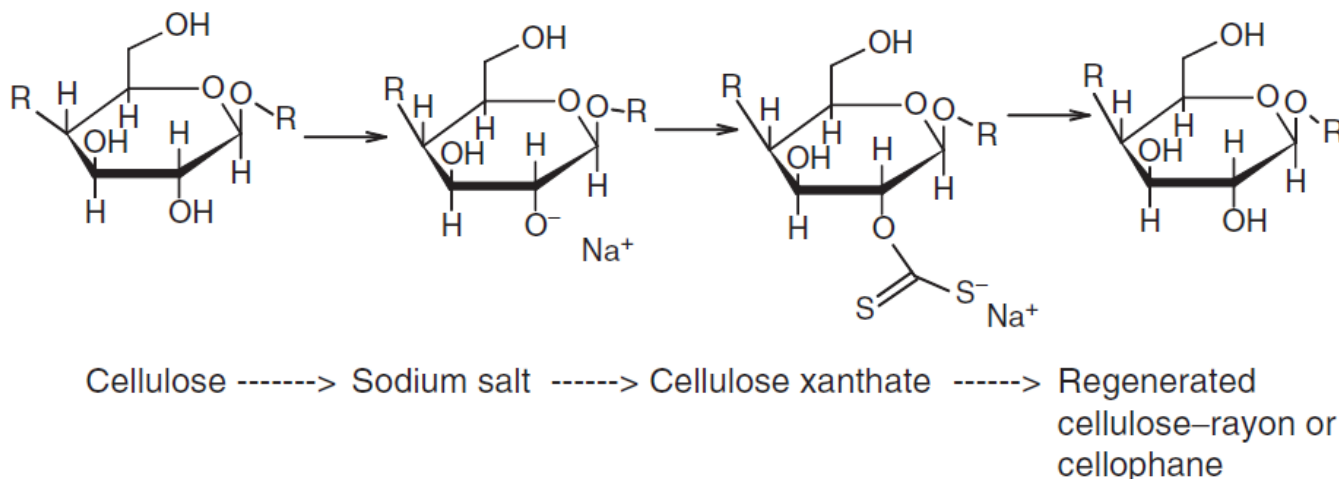
The orange-colored xanthate solution, or viscose, is allowed to age and then extruded as a filament through holes in a spinneret. The filament is converted to cellulose when it is immersed in a solution of sodium bisulfite, zinc II sulfate, and dilute sulfuric acid. The tenacity, or tensile strength, of this regenerated cellulose is increased by a stretching process that reorients the molecules so that the amorphous polymer becomes more crystalline. Cellophane is produced by passing the viscos e solution through a slit into an acid bath.

Since an average of only one hydroxyl group in each repeating glucose unit in cellulose reacts with carbon disulfide, the xanthate product is said to have a degree of substitution (DS) of one out of a potential DS of three.
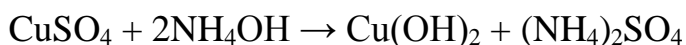
Control of the regeneration conditions, together with a wide variety of modification, allows the production of a wide variety of products including high-wet modulus fibers, hollow fibers, crimped fibers, and flame-resistant fibers. While almost all rayon is produced using the viscose process, some fibers are still produced using the

cuprammionium process whereby an alternate procedure used in a few specialty applications.

This process involves stabilization of cellulose in an ammonia solution of cupric oxide. Solubilization occurs by complex formation of cupric ion with ammonia and the hydroxyl groups of cellulose. Regeneration of cellulose, after formation of the desired products, is accomplished by treatment with acid. The main application of the cuprammonium process is for the synthesis of films and hollow fibers for use in artificial kidney dialysis machines. The cuprammonium process yields products with superior permeability and biocompatibility properties compared to the xanthation process. Less than 1% of all regenerated cellulose is produced by the cuprammonium process.

Cuprammonium rayon is obtained by dissolving cotton or pieces of filter paper in a deep blue solution containing tetra-ammine cupric hydroxide $[Cu(NH_3)_4](OH)_2$. The latter is obtained from a solution of copper sulphate. To it, NH_4OH solution is added to precipitate cupric hydroxide, which is then dissolved in excess of ammonium hydroxide.

Reactions:
$$CuSO_4 + 2NH_4OH \rightarrow Cu(OH)_2 + (NH_4)_2SO_4$$

Pale blue ppt

$$Cu(OH)_2 + 4NH_4OH \rightarrow [Cu(NH_3)_4](OH)_2 + 4H_2O$$

$[Cu(NH_3)_4](OH)_2$ + pieces of filter paper or cotton left for 8-15 days give a viscous solution called viscose, which is referred as Schweitzer's reagent.

Procedure for xanthate rayon:
- **Steeping process**
1. Put in a beaker 1g of cotton or filter paper (the paper must be divided into very small pieces) and add 25 ml of 18% NaOH then mix the content thoroughly with the aid of glass rod and leave the beaker for one hour.
2. Decant the extra NaOH solution from the beaker, then dry the cellulose (cotton or pieces of filter paper) very well by squeezing it between two glass plates and leave it in a sealed (closed) conical flask for the next week.
- **Xanthation process**

1. Inside a hood add 2-3 ml of carbon disulfide (CS_2) carefully to the conical flask that leaved last week, (avoid any working fires close to the process) and mix the content thoroughly every 5 minutes for one hour which results in yellow-red solution.
2. Decant extra CS_2 from the flask then squeeze the cellulose xanthate between two glass plates to remove most of the remained CS_2, dissolve cellulose xanthate with small amount of 5% NaOH to form a yellow viscous solution.
3. Leave the solution in a fridge for the next week.

- **Formation of rayon thread**

- The viscose solution is extruded by pressure in a precipitation bath. This bath contains an aqueous solution of sulphuric acid, sodium sulphate, zinc sulphate and glucose. The acid in the coagulating and regenerating bath precipitates the cellulose xanthate and further breaks down the xanthate, releasing cellulose. This cellulose is known as the 'regenerated cellulose'

1. In a beaker prepare the regeneration bath by mixing 5ml of conc. H_2SO_4, 6.2g of sodium sulphate, 1gm of glucose, 0.5g of zinc sulphate and 20 ml of distilled water.
2. Fill a syringe with viscose solution prepared before and immerse the tip of the syringe in the regeneration bath then press gently. Notice the fibers getting formed in a bath. Continue to move your hand and keep pressing the syringe to extrude more fibers into the bath. (Use a thick needle otherwise the fibers won't come out).
3. Leave the fibers in a solution for 5 minutes till they decolorize and become strong enough then remove the rayon from the bath by the aid of tong and dry it in air.
4. Examine solubility test in ethanol, acetone, ethylacetate and record your observation (soluble, insoluble or swell)
5. Burn the rayon and observe the colour of fire, smoke and ash.

Procedure for cuprammonium rayon:
  I. **Schweitzer's reagent**
1- Dissolve 20g of $CuSO_4.5H_2O$ in l00 of D.W. , and add 15ml of H_2SO_4 to avoid hydrolysis of $CuSO_4$.
2- Stir the solution with the aid of glass rod until a clear solution is obtained, then add 11 ml of ammonium hydroxide drop by drop with slow stirring, this results in the formation of $Cu(OH)_2$ precipitate.
3- Filter the product to remove (SO_4^{2-}) ions as clear filtrate.

4- Wash the ppt. several times with D.W. in order to remove the traces of sulfate ions (SO_4^{2-}) until the filtrate fails to give positive test with barium chloride solution.
5- Transfer the precipitate to a beaker containing 50 ml of ammonium hydroxide. The precipitate when dissolved in ammonia solution gives a dark blue solution of tetra-amine cupric hydroxide which is referred as Schweitzer's reagent [$Cu(NH_3)_4(OH)_2$].

II. Preparation of cellulose material

1- After weighing 1.5g of cotton or filter paper and divide it into very small pieces and transfer them to the tetra-ammine cupric hydroxide solution prepared in step 5 in a conical flask.
2- Seal the flask and keep it for next week, during this period the filter paper is dissolved completely. Instead of filter paper, the cotton could be used as well.

III. Formation of rayon thread

1- In a big glass container add 20 mL of conc. H_2SO_4 drop by drop to 50 mL of distilled water and cool the solution under tap water.
2- Place the big glass container containing H_2SO_4 solution in an ice (the reaction being spontaneous results in excess release of energy in the form of heat which makes the fibers weak and breaks them)
3- Fill a syringe with cellulose solution prepared before and immerse the tip of the syringe in an acidic solution and press gently. Notice the fibers getting formed in the acid bath. Continue to move your hand and keep pressing the syringe to extrude more fibers into the bath.
4- Leave the fibers in a solution for 5 minutes till they decolorize and become strong enough then remove the rayon from the bath by the aid of tong and dry it in air.
5- Examine solubility test in ethanol, acetone, ethylacetate and record your observation (soluble, insoluble or swell)
6- Burn the rayon and observe the colour of fire, smoke and ash.