WINTER– 17 EXAMINATION

Model Answer

Subject Name: Chemical Process Technology **Subject Code:** 17427

Important Instructions to examiners:

1) The answers should be examined by key words and not as word-to-word as given in the model answer scheme.
2) The model answer and the answer written by candidate may vary but the examiner may try to assess the understanding level of the candidate.
3) The language errors such as grammatical, spelling errors should not be given more Importance (Not applicable for subject English and Communication Skills.
4) While assessing figures, examiner may give credit for principal components indicated in the figure. The figures drawn by candidate and model answer may vary. The examiner may give credit for any equivalent figure drawn.
5) Credits may be given step wise for numerical problems. In some cases, the assumed constant values may vary and there may be some difference in the candidate's answers and model answer.
6) In case of some questions credit may be given by judgement on part of examiner of relevant answer based on candidate's understanding.
7) For programming language papers, credit may be given to any other program based on equivalent concept.

Q. No.	Sub Q. N.	Answer	Marking Scheme
1	**A**	**Attempt any six**	**12**
	a	**Methods for production of pulp** Mechanical Chemical Semi chemical **Chemical Processes** Sulfate (Kraft) Sulfite	1 1
	b	**Rancidity in oil** Oxidation of fats, generally known as rancidity, is caused by a biochemical reaction between fats and oxygen. In this process the long-chain fatty acids are degraded and short-chain compounds are formed. One of the reaction products is butyric acid, which causes the typical rancid taste.	2
	c	**Acetone Properties (any two)** M.P.=-95 ^{o}C	1

		B.P. = 56^{o}C M.W. = 58 It is colorless liquid It is volatile liquid It is flammable liquid **Uses of acetone (any two)** As a solvent in chemical process For the production of bisphenol A As cleansing agent As a drying agent ***If Students attempted to solve the question then Consider and reward appropriate marks.***	1
	d	**Methylated Spirit** Methylated spirits is a mixture of ethyl alcohol and methyl alcohol. The methyl alcohol is poisonous and is added to prevent the methylated spirits being used as cheap drinking alcohol. **Composition** C_2H_5OH(95%) CH_3OH (5%)	1 1
	e	**Conditions of good soap** **Hardness -** This refers to the hardness of the soap bar. Higher is harder. A range of 29 to 54 is satisfactory for this soap quality. **Cleansing -** This refers to the soap's ability to grab on to oils. A soap molecule is a chain of carbon atoms. One end of the chain attracts water, the other end attracts oil. When you wash your skin with soap and water, multiple chains will gather around a droplet of oil (which contains, for lack of a better word, dirt) with their oil-hungry ends attached to the oil droplet. The water hungry ends are surrounded with water. To make this happen you need to mix up (scrub or rub) the soap and water on your skin. **Condition -** Conditioning refers to the soap's emollient content. A soap's emollients are left on the skin. They help the skin retain moisture.	1 mark each for any two

		Bubbly lather - This refers to the soap's ability to lather up and get bubbly. A typical range of values would be 14 to 46. The higher Bubbly numbers will tend to produce a foamy, fluffy lather rather than a creamy lather with littler or no bubbles.	
	f	**Saponification value** It is the no. of milligrams of KOH required to saponify one gram of an oil or fat. **Iodine value** Iodine value is the no. Of grams of iodine absorbed by 100 grams of oil or fat for its complete saturation.	1 1
	g	**Black liquor** Black liquor is the waste product from the kraft process when digesting pulpwood into paper pulp removing lignin, hemicelluloses and other extractives from the wood to free the cellulose fibers.	2
1	**B**	**Attempt any two**	**8**
	a	**Types of plastic** **Thermoplastics** which are softened by heat and can be moulded. (Injection moulded, blow moulded or vacuum formed). Examples are acrylic, polypropylene, polystyrene, polythene and PVC. **Thermosets** which are formed by ha heat process but are then set (like concrete) and cannot change shape by reheating. Examples are melamine (kitchen worktops), Bakelite (black saucepan handles), polyester and epoxy resins.	1 1 1 1
	b	**Constituents of paint** Pigments Drying oil Thinners or solvent	1 mark each for any four.

		Plasticizer Filler	
	c	**Hydrogenation of Oil** The dry pure oil and nickel catalyst is taken in an iron cylinder. The cylinder has two inlets & outlets. One inlet is used for the introduction of oil & the other to introduce dry hydrogen. Unused hydrogen is removed through the upper outlet, while lower outlet is used to take the hydrogenated oil. The cylinder is provided with stirrer inside it. The temp. is regulated between1400C-180oC. From the second inlet, pure hydrogen gas is well mixed with the oil. In the cylinder oil &dry hydrogen gas are well mixed with mechanical stirrer. After certain time a sample of hydrogenated oil is taken through outlet is situated at the bottom of the cylinder. The iodine value of the hydrogenated oil is determined. If it is 60, the process of hydrogenation is stopped. And all the hydrogenated oil is taken out It is passed through cooler then filter pressed to remove nickel particles.	4
2		**Attempt any four**	**16**
	a	**Methods for production of alcohol** **Fermentation** Fermentation is the chemical transformation of of organic substances into simpler compound by the action of enzymes. Alcohol is manufactured from molasses by Fermentation Fermentation has been carried out in the absence of oxygen ,anaerobic fermentation In this fermentation the carbon dioxide is produced pushes out air and automatically creates an anaerobic atmosphere. The fermentation reaction is exothermic temperature control is needed The fermentation is carried out for 50 hours at30- 40 deg C in a fermenter.The production of bread, cheese, butter, beer, wine, vinegar antibiotics and vitamins are the examples of industrial fermentation. **Synthetic (From alkanes)** The manufacture of synthetic alcohol begins with gasification of heavy hydrocarbons such as coal, or lighter carbon resources such as natural gas, biomass and organic landfill waste - using a process that involves high temperature and pressure in an oxygen-controlled	2 2

<table>
<tr><td></td><td></td><td>atmosphere. Gasification produces a synthesis gas, sometimes called syngas (from synthesis gas), which, after cleaned, consists mostly of molecular hydrogen and carbon monoxide. The syngas is then passed over a catalyst, in a controlled environment, creating synthetic molecules, like the ethanol molecule pictured above left. The actual type of molecule depends on the catalyst used in the process.</td><td></td></tr>
<tr><td></td><td>b</td><td>Manufacturing of oil Varnish
Oil Varnishes are produced by dissolving resin in drying oil. The Resin and oil are heated in a kettle to temperature of 250^{o}C to 320^{o}C. The heating is continued till resin is dissolved so the mixture has proper viscosity. The dryers and thinners are added if necessary. The mixture is then allowed to cool and then filtered. The oil thus bind and soften resin to form a varnish and leave more lustrous and durable film.
The varnish prepared by dissolving phenolic resin in oil is tough , hard and water resistant.</td><td>4</td></tr>
<tr><td></td><td>c</td><td>Difference between sulphate and sulphite process
<table>
<tr><th>Sulphate Process</th><th>Sulphite Process</th></tr>
<tr><td>This process is alkaline in nature due to use of caustic and sodium carbonate</td><td>This process is acidic in nature due presence of sulfur dioxide.</td></tr>
<tr><td>Cooking chemicals are recovered from black liquor</td><td>Sulfur dioxide is recovered.</td></tr>
<tr><td>Pulp produced by the kraft process is stronger than that made by other pulping processes</td><td>Acidic sulfite processes degrade cellulose more than the kraft process, which leads to weaker fibers.</td></tr>
<tr><td>Fiber yield is less.</td><td>Fiber yield is more.</td></tr>
<tr><td>Comparatively difficult to</td><td>Can be bleached easily.</td></tr>
</table></td><td>1 mark for each point in both processes. (any four)</td></tr>
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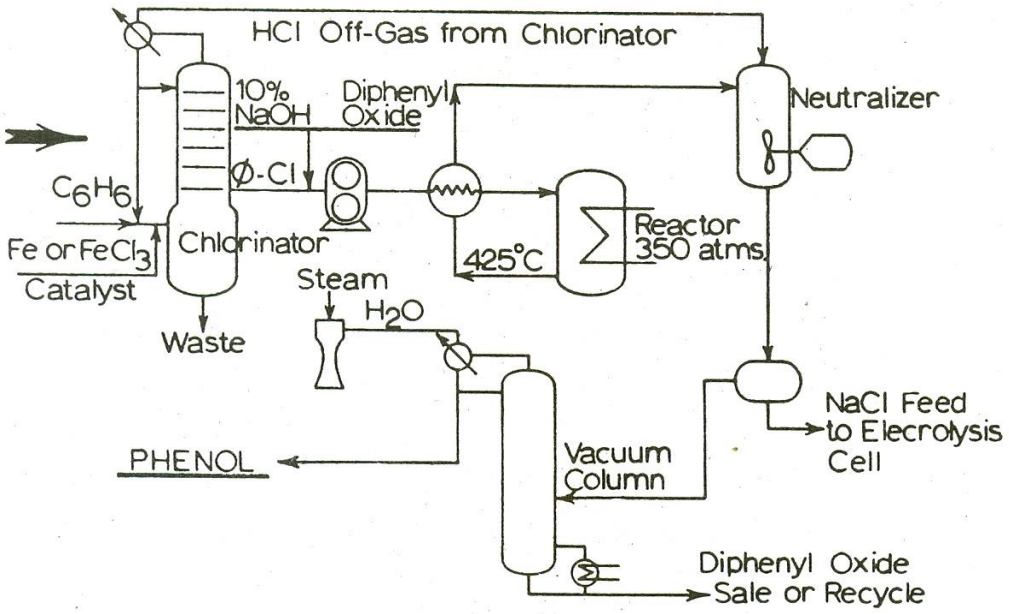
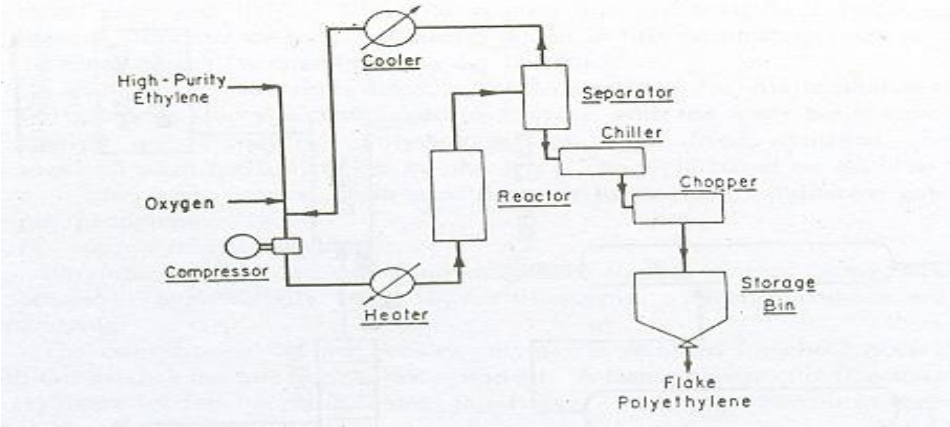
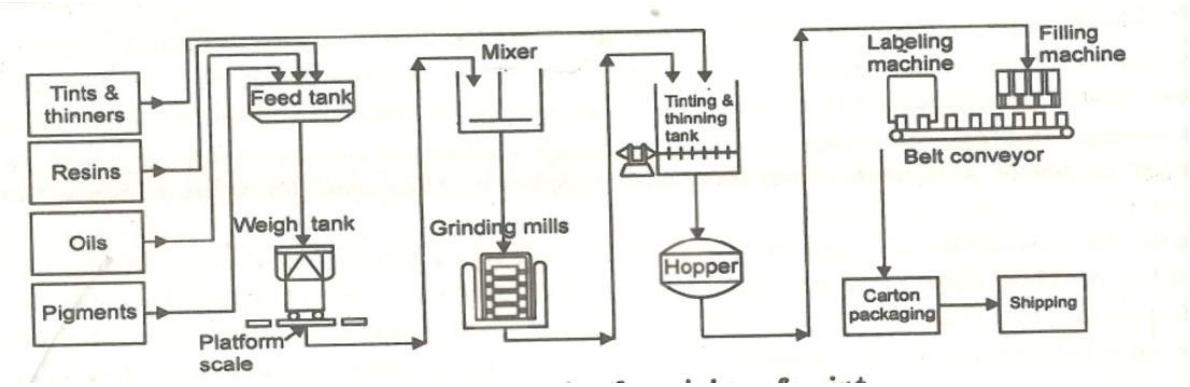
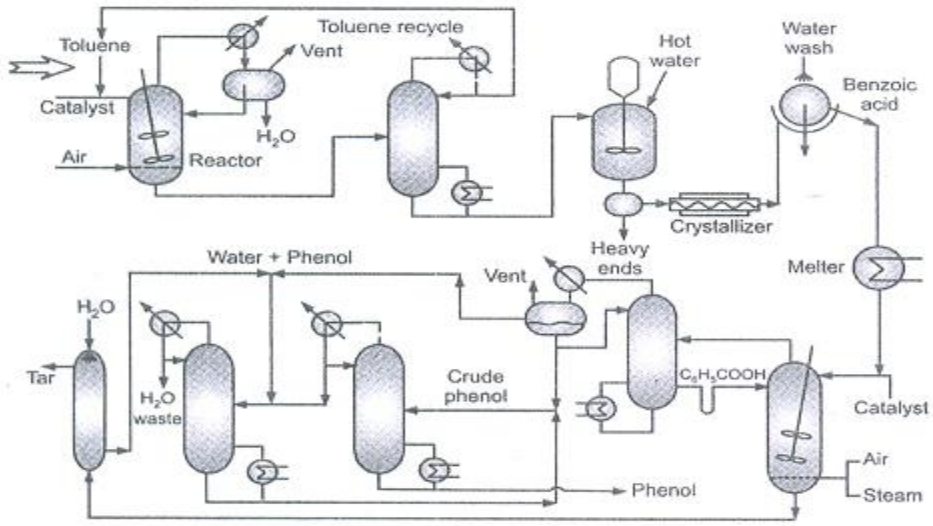
			bleach the pulp.		
	d	**Phenol from chlorobenzene-Caustic process- Process Flow Diagram**  		4
	e	**Polyethylene by High Pressure Process**  			4
	f	**Difference between hot and cold process**			1 mark for each

Hot process	Cold process
High purity of soap is obtained.	Low purity of soap is obtained.

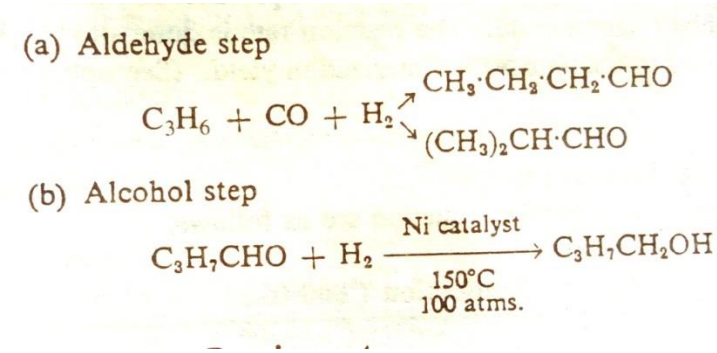
			Byproduct glycerol is separated.	Glycerol is mixed in soap	
			Reaction temperature is high	Reaction temperature is low	
			Maximum yield is possible.	Lesser yield is obtained.	
3		**Attempt any four**			**16**
	a	**Principle of production of Ethyl Acetate** Manufacturing of ethyl acetate**:-** Ethyl acetate is produced by action of ethanol on acetic acid in the presence of concentrated H_2SO_4 catalyst . *Chemical reaction* $CH_3CH_2OH + CH_3COOH \xrightarrow{H_2SO_4} CH_3COOCH_2C\ H_3 + H_2O$ Esterification reaction The reaction is reversible. It is removed by removal of water, using one reactant in excess and a catalyst			2 2
	b	**PFD of paint manufacturing**  			4
	c	**Bleaching of pulp** Bleaching of wood pulp is the chemical processing carried out on various types of wood pulp to decrease the color of the pulp, so that it becomes whiter. The main use of wood pulp is to make paper where whiteness (similar to but not exactly the same as "brightness") is an			4

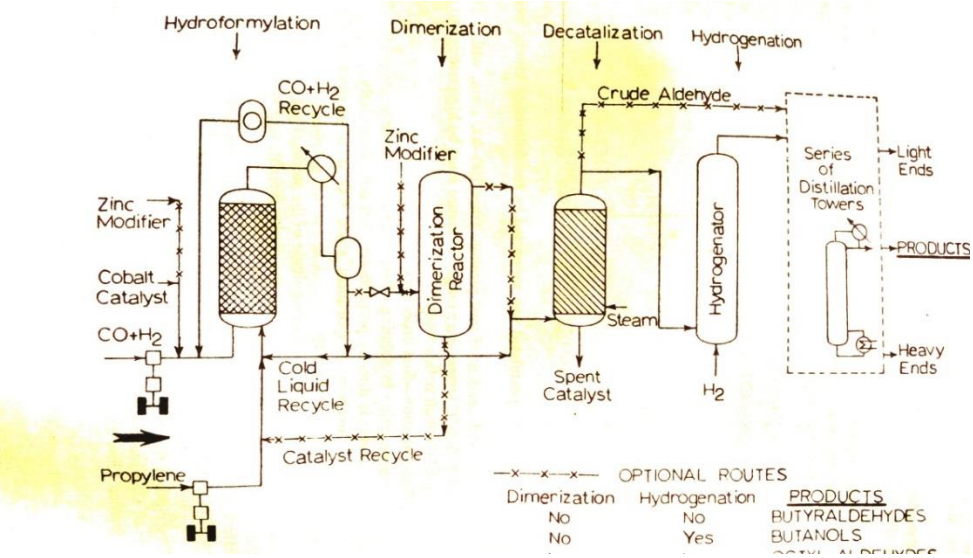
		important characteristic. The processes of bleaching consists of solubilizing and removal of coloring material namely lignin. Bleaching can be done either in stage or in multi-stages where the pulp is not easily bleachable. Bamboo pulp needs multi-stage bleaching. The following stages of bleaching are used 1. Chlorination 2. Washing 3. Alkali Extraction 4. Washing 5. Hypochloride	
	d	**PFD- Phenol manufacturing by toluene oxidation**  **Flow sheet for manufacturing of Phenol from Toluene oxidation**	4
	e	**Raw material for mfg. of rayon-** The wood cellulose, caustic soda, carbon di-sulphide aqueous solution of H_2SO_4 **Uses-:**It is used for making fibres, For manufacturing cellophane(film),tire cord, artificial hair and astrakhan and bottle plugs.	2 2
	f	**1) Classification Based on Source** (i) **Natural polymers**: *Ex:- Proteins, Cellulose, Starch, Rubber etc.*	2 marks each for any

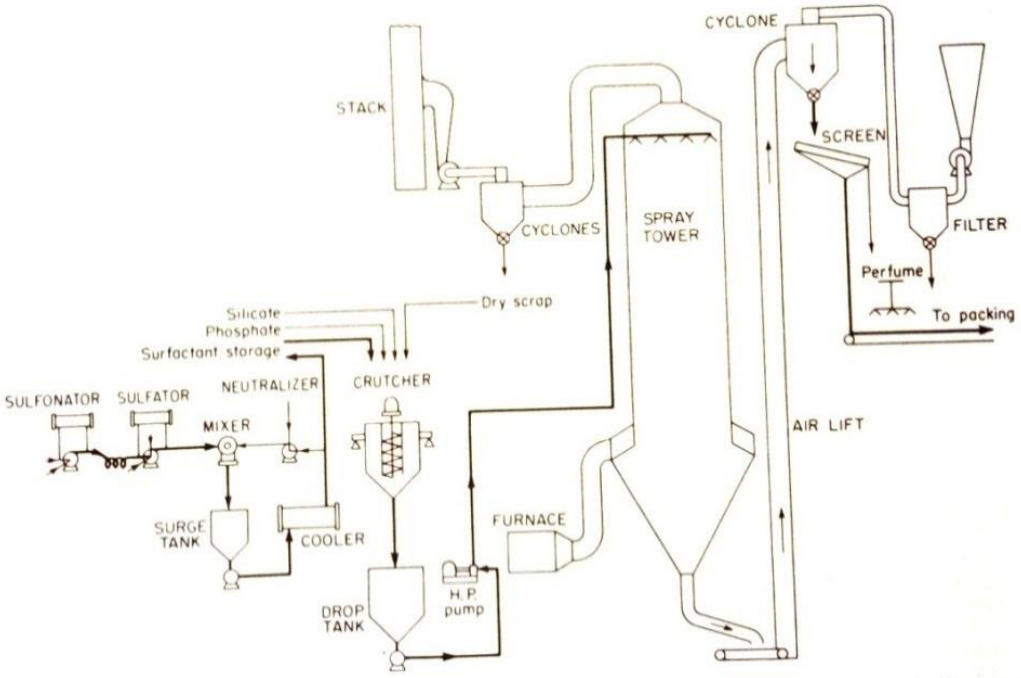
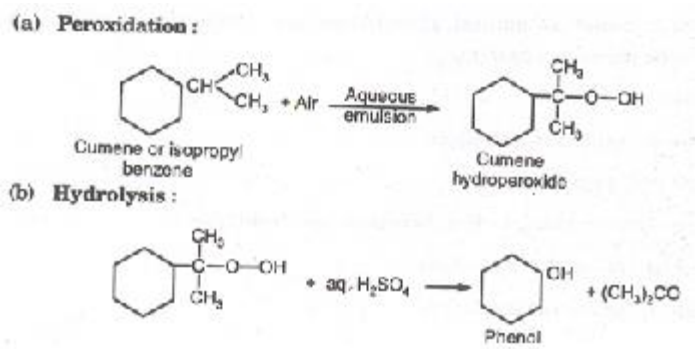
		(ii) **Synthetic polymers**: *Polythene, Fibers, Buna–s etc.* (iii) **Semi Synthetic polymers**: *Cellulose acetate (rayon) etc.* **2) Classification Based on Structure of Polymers** Based on structure polymers have three types. (i) **Linear polymers:** *Ex:- Polythene, Polyvinyl chloride, High density polythene (HDPE) etc.* (ii) **Branch chain polymers:** *Ex:- Low density polythene (LDPE) etc.* (iii) **Cross linked or Network polymers**: *Ex:- Bakelite, Melamine etc.* **3) Based on Mode of Polymerisation** Based on polymerization polymers have two types. (i) Addition polymers (ii)Condensation polymers (i) **Addition polymers**: *Ex: – Vinyl chloride to Poly vinyl chloride.* 2) **Condensation polymers:** *Ex:- Nylone – 66 is formed by condensation of Hexamethelene diamine and adipic acid.* **4) Classification Based on Molecular Forces** (i) **Elastomers:** *Ex:- Vulcanised rubber* (ii) **Thermoplastics:** *Ex:- Polyetene, Polystyrene, PVC etc.* (iii) **Thermosetting:** *Ex:- Bakelit, Melamine formaldehyde, Resin etc.* (iv) **Fibers:** *Ex:- nylone 66, Dacron, silk etc.*	two classification
4		**Attempt any four**	**12**
	a	**Various Methods for phenol manufacturing** 1. Cumene peroxidation – hydrolysis 2. Toluene two – stage oxidation. 3. Rasching : vapour phase hydrochlorination & hydrolysis. 4. Chlorobenzene - caustic hydrolysis.	4

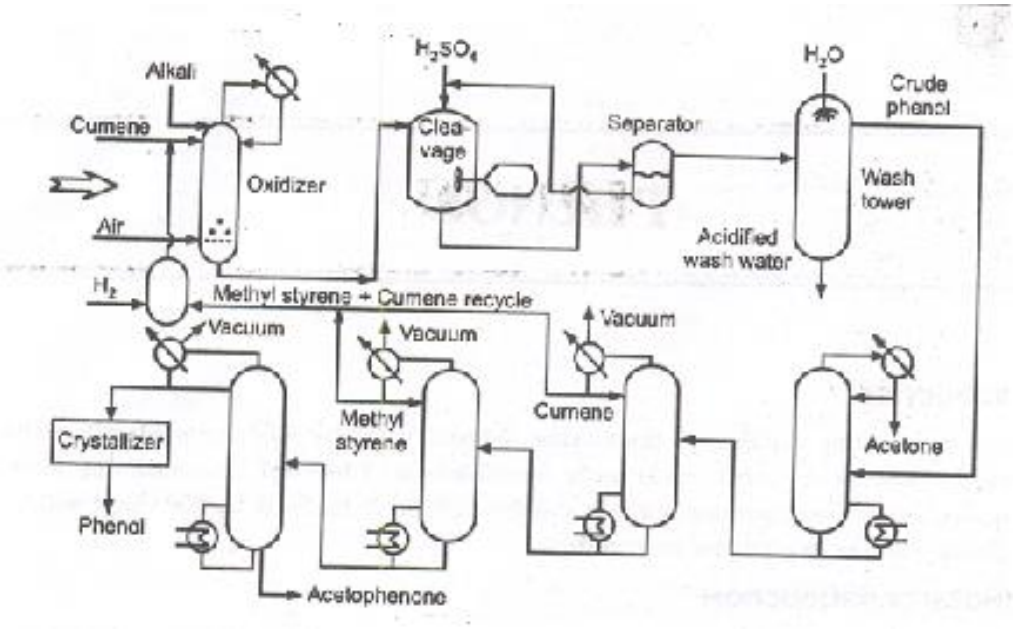
		5. Benzene sulfonate – caustic fusion. 6. Benzene – direct oxidation.	
	b	**Uses of Varnishes** • For the protection of articles against corrosion • As a brightening code to the painted surface • Improving the appearance I • Intensifying the ornamental grains of wood surfaces.	4
	c	**Short note on Fermentation** Origanally the word fermentation referred to the bubbling observed when sugar and starchy materials underwent transformation to yield alcoholic beverags. Fermentation is the chemical transformation of of organic substances into simpler compound by the action of enzymes. Alcohol is manufactured from molasses by Fermentation $C_{12}H_{22}O_{11}$----------→$C_6H_{12}O_6$+$C_6H_{12}O_6$ $C_6H_{12}O_6$ ---------→$2C_2H_5OH+CO_2$ Fermentation has been carried out in the absence of oxygen,anaerobic fermentation In this fermentation the carbon dioxide is produced pushes out air and automatically creates an aneorobic atmosphere. The fermentation reaction is exothermic temperature control is needed The fermentation is carried out for 50 hours at30- 40 deg C in a fermenter. The production of bread, cheese, butter, beer, wine, vinegar antibiotics and vitamins are the examples of industrial fermentation.	4
	d	**Comparison between soap and detergents.** **Soaps** | **Detergents** Soap is sodium salt of fatty acid | Are sodium salts of long chain benzene sulphonic acids or alkyl sulfate It is made from fats and oils | It is made from petrochemical compound	1 mark each for any four

			It form scum in hard water	It form lather in hard water
			Soaps are more biodegradable	Detergents are less biodegradable.
			Soaps have lesser cleansing action or quality as compared to detergents.	Detergents have better cleansing action as compared to soaps.
	e	**Refining of Oil** The colour and flavor to fats of edible and non-edible oils is mainly due to presence of non-glyceride components. Free fatty acids, waves, coloured bodies, mucilaginous materials, gossypol compounds (found only in cottonseed oil) and phosphatides are responsible for the undesirable properties of fat or oil used for edible purposes and industrial applications. Most of those compounds are removed by treatment with aqueous solution of caustic soda at 40^{o} -85^{o}C . It reduces fatty acid contents to 0.01%. This process of refining is carried out in a tank called batch. The aquous emulsion of soaps formed from fatty acids along with the other impurities (soap-stock) settles to the bottom and is taken out. Then refined oil is washed with water to remove traces of alkali and soap stock. Oils which are refined with soda ash or ammonia generally require a treatment with caustic soda. After water-washing., the oil is dried by heating in a vaccum or by filtering through dry filter and material. This refined oil is used for industrial purposes or may be processed further to achieve food value	4
	f	**Polymer:** A substance which has a molecular structure built up chiefly or completely from a large number of similar units bonded together, e.g. many synthetic organic materials used as plastics and resins. Mechanism of polymerisation*1) Addition polymerization:* i) In this the monomer molecules simply add together to form chains und suitable conditions of temperature and pressure and initiation ii) This type of polymerization can only occur when monomer molecule unsaturated. Polymers formed by addition polymerization are thermoplastic Ex. Polyethylene is produces by the addition polymerization of ethylene monomers. *2) Condensation polymerization:* i) In this a new bond is formed between the monomers by elimination of small molecules	1 1.5

		like water under suitable conditions of temperature and pressure ii) The reaction by which this polymerization takes place is condensation reaction. condensation polymerization is used to form simple hydrocarbons ex. Production of phenol formaldehyde from phenol and formaldehyde monomers with condensation of water	1.5
5		**Attempt any two**	**16**
	a	**Raw materials for butanol** Propylene , Hydrogen, Synthesis gas **Reaction**  **Process description:** Propylene is compressed at 150 atm and cobalt napthanate added to give 0.5 to 1 % CO in sol. This stream is passed concurrently with $CO+H_2$ stream through a packed bed tower The tower contains a porous carrier with 2 % metallic cobalt deposited The reaction is highly exothermic and temperature of 170 deg C is controlled by recycle of a portion of prod stream after cooling The product liquid fraction is mixed with steam at 180 deg C and a relatively low pressure of 20 atm. To decompose cobalt carbonyl and napthanate depositing cobalt on porous carrier as oxides This cobalt is dissolved periodically in an acid wash and converted in napthanate for reuse Crude butaraldehyde from demerisation reactor is continuously hydrogenated using a fixed bed nickel catalyst at 100 atm and 150 degC The resulting butanol are fed to a distillation column comprising of several fractionating column in series Light and heavy ends are	1 1 2

		obtained in addition to the product alcohol.  *If Students attempted to solve the question then Consider and reward appropriate marks.*	4
	b	**Manufacturing of detergents**. The alkyl benzene is introduced continuously into sulfonator with the requisite amount of oleum, using the dominant batch principle. To control the heat of sulphonation conversion and maintain the temperature at about 55^{o}C. Into the sulfonation mixture is fed the fatty alcohol and more of the oleum. All are pumped through the sulfater , also operating on the dominant bath principle to maintain the temperature at 50-55^{o}C, thus manufacturing a mixture of surfactants. The sulfonated –sufated product is neutralized with caustic solution under controlled temperature to maintain fluidity of the surfactant slurry. The surfactant slurry , the sodium triphosphate, and most of the miscellaneous additives are introduced into the crutcher. A considerable amount of water is removed , and the paste is thickened by the tripolyposphate hydration reaction. This mixture is pumped into an upper story, where it is sprayed under high pressure into 24 meter high spray tower , counter to hot air from furnace. Dried granules are transferred to an upper story again by an air lift which cools them from 115^{o}C and stabilizes the granules. The granules are separated in cyclone separator, screened,	4

		perfumed and packed.  	4
	c	**Manufacturing of Phenol from Cumene**  Process description: Cumene is mixed with recycle cumene & send to the hydrogenerator. Unsaturated compounds are converted to saturated materials to avoid undesirable decomposition of the peroxide during the oxidation step.H2 over nickel catalyst at 1000c in a batch reactor is used for purification. Oxidation is carried out in the presence of air in an aqueous emulsion stabilized by an alkali such as sodium carbonate in the 8.5-10.5 pH range. Vent gases are passed through a condenser to recover hydrocarbon.	2

		The cumene peroxide thus formed is cleaved in an acidifier containing 10-25% H_2SO_4 . This is an agitated vessel at 55-650C . The reaction products are separated into an aqueous acid layer for recycle to the cleavage vessel and an oil layer containing 76 wt % cumene,14% phenol,8% acetone % 1-2% α- methyl styrene & acetophenone. This mix is separated in a series of four distillation steps, that last three of which are under vacuum. Phenol is the overhead of the last vacuum fractionator.	2
			4
6		**Attempt any two**	**16**
	a	**Manufacturing of Viscos Rayon** **Reaction** $[C_6H_7O_2(OH)_3]_n + nNaOH \rightarrow [C_6H_7O_2(OH)_3NaOH]_n$ Cellulose alkali Alkali cellulose $[C_6H_7O_2(OH)_3NaOH]_n + nCS_2 \rightarrow \left(\begin{matrix} OC_6H_9O_4 \\ C=S \\ SNa \end{matrix}\right)_n + nH_2O$ $\left(\begin{matrix} OC_6H_9O_4 \\ C=S+ \quad nH_2O \\ SNa \quad n \end{matrix}\right) + nH_2SO_4 \rightarrow [C_6H_{10}O_5]_n + nCS_2 + nNaHSO_4$ Viscose fibre	2

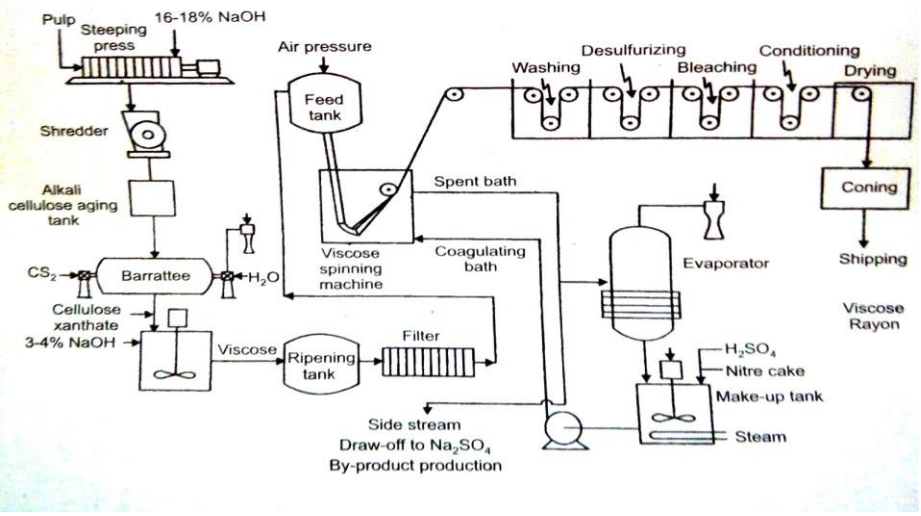
Process

Viscose rayon is a fiber of regenerated cellulose; it is structurally similar to cotton but may be produced from a variety of plants such as soy, bamboo, and sugar cane. To prepare viscose, dissolving pulp is treated with aqueous sodium hydroxide (typically 16-19% w/w) to form "alkali cellulose," which has the approximate formula [C6H9O4-ONa]n. The alkali cellulose is then treated with carbon disulfide to form sodium cellulose xanthate. 2

The higher the ratio of cellulose to combined sulfur, the lower the solubility of the cellulose xanthate. The xanthate is dissolved in aqueous sodium hydroxide (typically 2-5% w/w) and allowed to depolymerize to a desired extent, indicated by the solution's viscosity. The rate of depolymerization (ripening or maturing) depends on temperature and is affected by the presence of various inorganic and organic additives, such as metal oxides and hydroxides. Air also affects the ripening process since oxygen causes depolymerization.

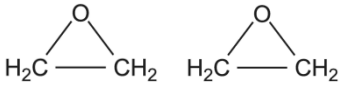
Rayon fiber is produced from the ripened solutions by treatment with a mineral acid, such as sulfuric acid. In this step, the xanthate groups are hydrolyzed to regenerate cellulose and release dithiocarbonic acid that later decomposes to carbon disulfide and water:

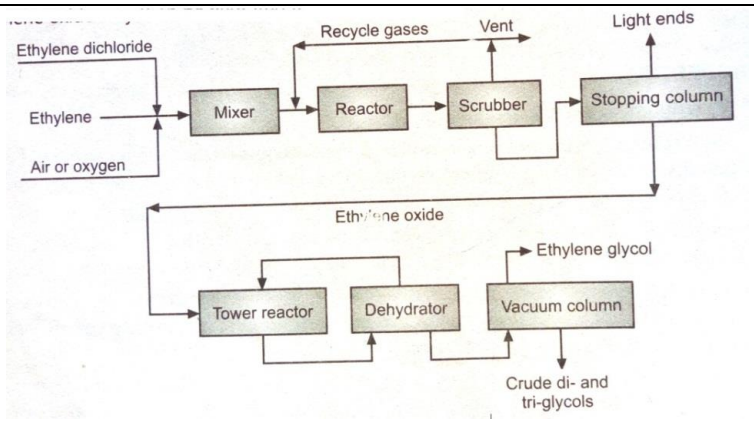
Aside from regenerated cellulose, acidification gives hydrogen sulfide, sulfur, and carbon disulfide. The thread made from the regenerated cellulose is washed to remove residual acid. The sulfur is then removed by the addition of sodium sulfide solution and impurities are oxidized by bleaching with sodium hypochlorite solution.



4

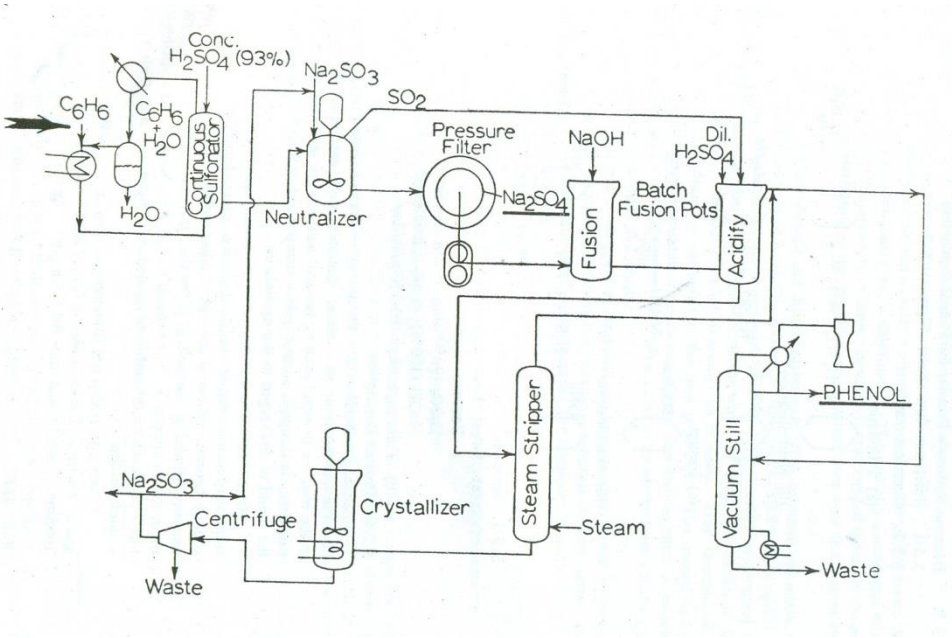
b **Ethylene glycol: Process is carried out at different steps**

		Ethylene oxide production. Ethylene and oxygen are fed to a multi-tubular reactor, forming EO. This exothermic reaction, conducted in fixed beds in the reactor tubes, occurs in the gaseous phase with the use of a silver catalyst supported on alumina. Steam is generated by the heat of reaction.	**2**
		Ethylene oxide recovery. The reactor product stream is fed to the EO absorber for lights removal by water quenching. Part of this gaseous overhead stream is recycled to the reactor, while the other part is sent to a carbon-dioxide-removal unit composed of an absorber and a stripper. In this unit, CO2 is separated to be used in ethylene carbonate production. A diluted EO stream removed from the absorber is fed to the EO stripper, where it is concentrated and recovered in the overheads. The crude EO stream is condensed. Residual light gases are recovered from it and recycled to the reactor. The resulting EO stream is directed to the next section.	
		Ethylene glycol production and purification. Ethylene oxide is reacted with CO2, forming ethylene carbonate, which is then hydrolyzed to form MEG and CO2. Both reactions are carried out in the liquid phase using homogeneous catalysts. CO2 streams from the reaction steps are recycled to the ethylene carbonate reactor. MEG is purified in two distillation columns where water is removed, leading to the final MEG product. The catalyst is separated and recycled to the ethylene carbonate reactors.	**2**
		Reaction $H_2C = CH_2 + ½\ O_2 \rightarrow$  + H2O → HO-CH_2-CH_2-HO	**2**

		 ***If Students attempted to solve the question then Consider and reward appropriate marks.***	**2**
	c	**Phenol by benzene sulphonate process** **Reactions :** a) Sulphonation : $C_6H_6 + H_2SO_4 \rightarrow C_6H_5\text{-}SO_3H + H_2O$ b) Neutralization : $2C_6H_5\text{-}SO_3H + Na_2SO_3 \rightarrow 2C_6H_5\text{-}SO_3Na + SO_2 + Na_2SO_4$ c) Fusion : $C_6H_5\text{-}SO_3Na + NaOH \rightarrow C_6H_5\text{-}ONa + SO_2$ d) Acidification : $C_6H_5\text{-}ONa + H_2SO_4 + SO_2 \rightarrow C_6H_5\text{-}OH + Na_2SO_3 + Na_2SO_4$ **Process description :** Benzene sulphonic acid is formed by contact of benzene vap. With H_2SO_4 liquid in a counter current reactor. Excess benzene carries off the water form in the reaction to avoid the diluting the acid and slowing down the sulphonation. The sulphonator is designed so that only a few percent of free H_2SO_4 remains before the liquid is discharged to the neutralizer .	2 2

Neutralisation is accomplished by rapidely adding the reactor liquor to a solution of sodium sulfite . Sulphur dioxide is released and the pot residue contains sodium benzene sulphonate in a solution and precipitated Na_2SO_4 . This mixture is pressure filtered at the B.P with the clear solution moving onto the batch fusion operation. In a process modification some plant centrifuge the hot liquor concentrate the sulfonate liquor further by evaporation then removed more sodium sulfate .

A cast iron fusion pot containing molten caustic is kept at 300^0c by the direct gas or oil fire. The sulfonate is slowly added at the bottom of the pot and the reaction allowed to continue for 5-6 hrs. The melt is then diluted with water ,acidified with SO_2 from the neutralization step and the final PH adjusted with H_2SO_4 . The released crude phenol floats on an aq. Solution containing sodium sulphate, sodium sulfite and small percentage of phenol.



4

If Students attempted to solve the question then Consider and reward appropriate marks.