| B.Tech Chemical Engineering | | 2019-2020 |
|-------------------------------------|--|--------------|
| | | Semester-II |
| 19BTCE202 | Chemistry-II | 4H-4C |
| Instruction Hours/week: L:3 T:1 P:0 | Marks: Internal:40 External:60 Total:100 | |

End Semester Exam:3 Hours

Course Objective

- To understand the basic chemical reactions and its mechanism
- To understand the mechanism of lubricants
- To study about the nature of oils and fat
- To understand about the dye pigments

Course Outcomes

- 1. To apply the various unit process
- 2. To apply the knowledge on chemical reactions
- 3. To prepare soaps
- 4. To analyses the effect of pigments

UNIT I - UNIT PROCESSES

Nitration, Sulphonation, Halogenation, Esterification, Amination, Saponification and Hydrogenation – Role of the above unit processes in such industries as petroleum, drugs, pharmaceuticals and organic synthesis.

UNIT II - REACTION MECHANISMS

Free radical, substitutions, electrophilic, addition, aromatic electrophilic substitutions, nucleophilic additions, condensation reactions, nucleophilic substitutions in aliphatic and aromatic compounds, cyclo-additions, rearrangements-Beckmann and Fries rearrangement reactions.

UNIT III - OILS, FATS, SOAPS & LUBRICANTS

Chemical constitution, Chemical analysis of oils and fats – acid, saponification and iodine values, Definitions, determinations and significance. Definition, mechanism of lubrication, preparation of petrolubes, desirable characteristics – viscosity, viscosity index, carbon residue, oxidation stability, flash and fire points, cloud and pour points, aniline point. Semisolid lubricant – greases, preparation of sodium, lithium, calcium and axle greases and uses, consistency test and drop point test.Solid lubricants – graphite and molybdenum disulphide.

UNIT IV - CHEMICALS AND AUXILIARIES

Preparation, properties and uses of bleaching powder, sodium hypochlorite, hydrogen peroxide, chlorine dioxide. Estimation of available chlorine in hypochlorite bleach liquor. Determination of strength of hydrogen peroxide.

UNIT V - COLORANTS

Theory of color and constitution: chromophore and auxochrome, classification of dyes based on application. Chemistry and synthesis of azo dye (Methyl red, Methyl orange and Congo red).

SUGGESTED READINGS

1 Dhara S. S (2016), A Text Book of Engineering Chemistry, S. Chand & Co. Ltd., NewDelhi

2 Jain. P.C and Monica Jain (2012), Engineering Chemistry, DhanpetRai& Sons, New Delhi

3 ShikhaAgarwal (2015), Engineering Chemistry-Fundamentals and Applications, CambridgeUniversity Press, Delhi

4 W.L. McCabe, J.C. Smith and P. Harriot (2005), Unit Operations of Chemical Engineering, 7Edition, McGraw Hill Education

5 B.K. Sharma(2011), Industrial chemistry, Krishna Prakashan Media (P) Ltd, Meerut

6 Shore J (2002), Colourants and Auxiliaries: Volume II Auxiliaries, Wood head Publishing Ltd 7 Shenai V. A(1995), Chemistry of Dyes and Principles of Dyeing, Sevak Publications, Mumbai 8 Trotman E. R(1994), Dyeing and Chemical Technology of Textile Fibres, B.I Publishing Pvt. Ltd, New Delhi



KARPAGAM ACADEMY OF HIGHER EDUCATION

(Established under section 3 of the UGC Act 1956) COIMBATORE – 641021

CHEMISTRY –II

19BTCE202

LECTURE PLAN

TOTAL HOURS: 50

UNIT-I

UNIT PROCESSES

| S.No | Topics | | Hours |
|------|---|-------|-------|
| 1. | Introduction to Unit processes | | 1 |
| 2. | Nitration, Sulphonation | | 1 |
| 3. | Halogenation, Esterification | | 1 |
| 4. | Amination, Saponification, Hydrogenation | | 1 |
| 5. | Tutorial | | 1 |
| 6. | Role of the above unit processes in petroleum industry | | 1 |
| 7. | Role of the above unit processes in drug industry | | 1 |
| 8. | Role of the above unit processes in pharmaceutical industry | | 1 |
| 9. | Role of the above unit processes in organic synthesis | | 1 |
| 10. | Tutorial | | 1 |
| | | Total | 8+2 |

UNIT-II

REACTION MECHANISMS

| S.No | Topics | Hours |
|------|--|-------|
| 1. | Free radical, substitutions reactions | 1 |
| 2. | Electrophilic, addition reactions | 1 |
| 3. | Aromatic electrophilic substitutions | 1 |
| 4. | Nucleophilic addition reactions | 1 |
| 5. | Tutorial | 1 |
| 6. | Condensation reactions | 1 |
| 7. | Nucleophilic substitutions in aliphatic and aromatic compounds | 1 |
| 8. | Cyclo-addition reactions | 1 |
| 9. | Beckmann and Fries rearrangement reactions | 1 |
| 10. | Tutorial | 1 |
| | Total | 8+2 |

UNIT-III

OILS, FATS, SOAPS & LUBRICANTS

| S.No | Topics | Hours |
|------|--|-------|
| 1. | Chemical constitution of oils and fats | 1 |
| 2. | Chemical analysis - acid value- definition, determination and significance | 1 |
| 3. | Chemical analysis - saponification value- definition, determination and significance | 1 |
| 4. | Chemical analysis - iodine value- definition, determination and significance | 1 |
| 5. | Tutorial | 1 |
| 6. | Definition, mechanism of lubrication- preparation of petrolubes | 1 |
| 7. | Desirable characteristics | 1 |
| 8. | Semisolid lubricant- greases | 1 |
| 9. | Solid lubricants – graphite and molybdenum disulphide | 1 |
| 10. | Tutorial | 1 |
| | Total | 8+2 |

UNIT-IV

CHEMICALS AND AUXILIARIES

| S.No | Topics | Hours |
|------|--|-------|
| 1. | Introduction to chemicals and auxiliaries | 2 |
| 2. | Preparation, properties and uses of bleaching powder | 1 |
| 3. | Preparation, properties and uses of sodium hypochlorite | 1 |
| 4. | Preparation, properties and uses of hydrogen peroxide | 1 |
| 5. | Tutorial | 1 |
| 6. | Preparation, properties and uses of chlorine dioxide | 1 |
| 7. | Estimation of available chlorine in hypochlorite bleach liquor | 1 |
| 8. | Determination of strength of hydrogen peroxide | 1 |
| 9. | Tutorial | 1 |
| | Total | 8+2 |

UNIT-V

COLORANTS

| S.No | Topics | Hours |
|------|---|-------|
| | | |
| 1. | Introduction to colorants | 1 |
| 2. | Theory of color and constitution -chromophore | 1 |
| 3. | Theory of color and constitution- auxochrome | 1 |
| 4. | Classification of dyes based on application | 1 |
| 5. | Tutorial | 1 |
| 6. | Azo dyes | 1 |
| 7. | Chemistry and synthesis of Methyl red dye | 1 |
| 8. | Chemistry and synthesis of Methyl orange dye | 1 |
| 9. | Chemistry and synthesis of Congo red dye | 1 |
| 10 | Tutorial | 1 |
| | Total | 8+2 |

SUGGESTED READINGS

1. Dhara S. S (2016), A Text Book of Engineering Chemistry, S. Chand & Co. Ltd., NewDelhi

2. Jain. P.C and Monica Jain (2012), Engineering Chemistry, Dhanpet Rai & Sons, New Delhi

3. Shikha Agarwal (2015), Engineering Chemistry-Fundamentals and Applications, CambridgeUniversity Press, Delhi

4. W.L. McCabe, J.C. Smith and P. Harriot (2005), Unit Operations of Chemical Engineering,7Edition, McGraw Hill Education

5 .B.K. Sharma(2011), Industrial chemistry, Krishna Prakashan Media (P) Ltd, Meerut

6.Shore J (2002), Colourants and Auxiliaries: Volume II Auxiliaries, Wood head Publishing Ltd

7. Shenai V. A(1995), Chemistry of Dyes and Principles of Dyeing, Sevak Publications, Mumbai

8. Trotman E. R(1994), Dyeing and Chemical Technology of Textile Fibres, B.I Publishing Pvt. Ltd, New Delhi

STAFF

MENTOR

HoD

BASIC PRINCIPLES CHEMICALPROCESSES, UNIT PROCESSES AND UNIT OPERATIONS IN ORGANIC CHEMICAL INDUSTRIES

Chemical processes usually have three interrelated elementary processes

- Transfer of reactants to the reaction zone
- Chemical reactions involving various unit processes
- Separation of the products from the reaction zone using various unit operations

Processes may involve homogeneous system or heterogeneous systems. In homogeneous system, reactants are in same phase-liquid, gases or solids while heterogeneous system include two or more phases; gas liquid, gas–solid, gas-gas, liquid–liquid, liquid solid etc. Various type reactions involve maybe reversible or irreversible, endothermic or exothermic, catalytic or non-catalytic. Various variables affecting chemical reactions are temperature pressure, composition, catalyst activity, catalyst selectivity, catalyst stability, catalyst life, the rate of heat and mass transfer. The reaction may be carried out in batch, semi batch or continuous. Reactors may be batch, plug flow, CSTR. It may be isothermal or adiabatic. Catalytic reactors may be packed bed, moving bed or fluidised bed

Along with knowledge of various unit processes and unit operation following information are very important for the development of a process and its commercialization [Austin,1984] Basic Chemical data: Yield conversion, kinetics

- Material and energy balance, raw material and energy consumption per tone of product, energy changes
- Batch vs Continuous, process flow diagram
- Chemical process selection: design and operation, pilot plant data, Equipment required, material of construction
- Chemical Process Control and Instrumentation
- Chemical Process Economics: Competing processes, Material and, Energy cost, Labour, Overall Cost of production
- Market evaluation: Purity of product and uniformity of product for further processing

- Plant Location
- Environment, Health, Safety and Hazard
- Construction, Erection and Commissioning
- Management for Productivity and creativity: Training of plant personals and motivation at all levels
- Research, Development and patent
- Process Intensification

Inorder to improve productivity and make the process cost effective and for improving overall economy, compact, safe, energy efficient and environmentally sustainable plant, process intensification has become very important and industry is looking beyond the traditional chemical engineering.

UNIT PROCESSES AND UNIT OPERATIONS IN CHEMICAL PROCESS INDUSTRIES

Chemical process is combination of unit processes and Unit operation. Unit process involves principle chemical conversions leading to synthesis of various useful product and provide basic information regarding the reaction temperature and pressure, extent of chemical conversions and yield of product of reaction nature of reaction whether endothermic or exothermic, type of catalyst used. Unit operations involve the physical separation of the products obtained during various unit processes. Various unit processes in chemical industries are given in Table M-I 3.1. Various chemical reactions and its application in process industries are given in Table M-I 3.2.

NITRATION

Nitration involves the introduction of one or more nitro groups into reacting molecules using various nitrating agents like fuming, concentrated, aqueous nitric acid mixture of nitric acid and sulphuric acid in batch or continuous process. Nitration products find wide application in chemical industry as solvent, dyestuff, pharmaceuticals, explosive, chemical intermediates. Typical products: TNT, Nitrobenzene, m-dinitrobenzene, nitroacetanilide, alpha nitronaphthalene, nitroparaffins

| Alkylation and Hydro delkylation | Decomposition |
|--|--|
| Acylation | Fermentation |
| Ammonoxidation | Halogenation |
| Amination by reduction | Hydsogenation |
| Amination | Hydrohenatlysis |
| Aromatisation | Hydroformylation |
| Amination by ammonalysis | Hydro lysis |
| Calcination | Hydration |
| Carbonation | Hydroammonalysis |
| Causticisation | Isomerisation |
| Chlorination and Oxy chlorination | Neutralistion |
| Condensation | Nitration |
| Biomethhanation | Methanation |
| Carbinisation | |
| Disproportination | Oxidation and partial oxidation |
| Cracking; Thermal, steam cracking, catalytic | Pyrolysis |
| cracking | |
| Dehydration | Polymeristion: Addition and condensation |
| | Chain growth and step growth, Bulk, |
| | Emulsion, suspension, solution, Radical |
| | and coordination polymeristion |
| Dehydrogenation | Reduction |
| Ditozitation and coupling | Reforming: Steam reforming |
| | Catalytic reforming |
| Gasification of coal and biomass | Sulphidation |
| Desulphurisation and hydro desulphurisation | Sulphonatiomn |
| Electrolysis | Sulphation |
| Etherification | Xanthation |
| Estertification and Trans Estrerificartion | |

Table M-I 3.1: Unit Processes in Chemical Process Industries

Table M-I 3.2: Important Chemical Reaction and their Application in Chemical Process Industries

| Reaction | Description |
|-----------------|---|
| Fisher-Tropsch | The Fisher-Tropsch process produce a variety of hydrocarbons (alkanes: |
| (FT) Process | $C_nH_{(2n+2)}$) by involves a series of chemical reaction. |
| | $(2n+1) H_2 + nCO \rightarrow C_n H_{(2n+2)} + nH_2O$ |
| | FT process is used for synthesis of alkanes. |
| Friedel-Crafts | In this reaction attach substituent's to an aromatic ring. Two main types |
| reactions | of Friedel-Crafts reaction are acylations reaction and alkylation reactions, |
| | both proceeding by electrophilic aromatic substitution. |
| | |
| | AlCI3 catalyst, |
| | reflux annyarous conditions |
| | Friedel-Crafts process used in alkelation reactions. |
| Oxosynthesis | In this process Isomeric mixture of normal- and iso-aldehydes get |
| Reactions | produces by utilizing syngas (CO and H_2) and olefinic hydrocarbons as |
| | reactants. It is exothermic process, this process thermodynamically |
| | tavorable at ambient pressure and temperatures. This reaction also called |
| | as hydroiormylation reaction. PCH = CH + CO + H = PCH = CH + P(CH) + CHCHO |
| | $ACH = CH_2 + CO + H_2 \rightarrow RCH_2 CHO + R(CH_3) CHCHOOxosynthesis used for production of alcohols$ |
| Hofman Process | In this process, organic reaction of primary amide converts into a primary |
| Horman 1 100055 | amine with one fewer carbon atom |
| | 0 B_{π} 0 $H_{2}O$ |
| | $= \overset{\text{BI}_2}{\longrightarrow} [R _{\text{C}}] \overset{\text{H}_2\text{O}}{\longrightarrow} R-\text{NH}_2$ |
| | R NH_2 $NaOH$ N^{-1} $-CO_2$ |
| | Hofman process typical examples are conversion of aliphatic amides to |
| | aliphatic amines and aromatic amides to aromatic amines. |
| Free-Radical | Any chemical reaction involving free radicals, generally radical generated |
| Reaction | from radical initiators such as peroxide or azo bis compounds. Radical |
| | reactions are chain reactions with chain initiation, propagation and |
| | termination steps. Free radical reactions are used many organic synthesis |
| | and polymerization reactions |
| Beckmann | Beckmann rearrangement is acid catalyzed rearrangement of an oxime to |
| rearrangement | an amide, which developed by German chemist Ernst Otto. A typical |
| | example of Beckmann rearrangement is synthesis of capiolacian from cyclobeyapone. Caprolactam is monomer for pylon 6 |
| | |
| | |
| | H_2SO_4 |
| | |
| | |
| | |
| | |

| Wackers Process | Wacker process is similar to hydroformylation and used for aldehyde |
|-----------------|---|
| | compounds. A typical example of wacker process is oxidation of ethylene |
| | to acetaldehyde in the presence of Pd catalyst. |
| | $[PdCl_4]^-+C_2H_4+H_2O\rightarrow CH_3CHO+Pd+2HCl+2Cl^-$ |
| | $Pd^{++}CuCl_2+2Cl^{-} \rightarrow [PdCl4]^{-+}+2CuCl$ |
| | $2CuCl+0.5 O_2+2HCl\rightarrow 2CuCl_2+H_2O$ |

Example Preparation of TNT (trinitrotoluene)

TNT is produce in a three-step process: First, toluene is nitrated with a mixture of sulfuric acid and nitric acid to produce mono-nitrotoluene or MNT. The MNT is separated and then renitrated to dinitrotoluene or DNT. In the final step, the DNT is nitrated to trinitrotoluene or TNT using an anhydrous mixture of nitric acid and oleum.



HALOGENATION

Halogens involve introduction of one or more halogen groups into a organic compound for making various chlorine, bromine, iodine, fluorine organic derivatives. All though chlorine derivatives find larger application, however some of the bromine and fluorine derivatives are also important. Various chlorinating agents are chlorine, HCl, phosgene sulfuric chloride, hypochlorite, bromination, bromine, hydrobromic acid, bromide, bromated, alkaline hypobromites. In iodination iodine, hydroiodic acid and alkali hypoiodites

Example

Typical important chemicals are chlorinated products: Ethylene dichloride, chlorinated methanes Chloroform, Carbon tetra chloride etc) Chlorinate ethane, Chloro propane, chloro butanes, chloroparaffins, chlorination of acetaldehyde (Chloral), alkyl halhides, Chlorobenzene, Ethylene diiodide, Chloroflurocarbon (CFCs).

Preparation of chloroform and chloroflurocarbon (CFCs)

1. $CH_{4} + Cl_{2} \xrightarrow{\text{photochemically}}_{-HCl} - HCl \xrightarrow{CH}_{3} \xrightarrow{Cl_{2}}_{-HCl} \xrightarrow{CH}_{2} Cl_{2} \xrightarrow{Cl_{2}}_{-HCl} \xrightarrow{CHCl}_{3}$ Methane Choloroform 2. $CHCl_{3} + 2HF \xrightarrow{HF}_{Choloroform} HCF_{2}Cl + HCl$ Choloroform (CFCs)

SULPHONATION AND SULPHATION

Sulphonation involves the introduction of sulphonic acid group or corresponding salt like sulphonyl halide into a organic compound while sulphationinvolves introduction of -OSO₂OH or -SO₄-. Various sulphonating agents are sulphur trioxide and compounds, sulphurdixide, sulphoalkylating agents. Some of the sulphaming agents are sulphamic acid. Apart from sulfonation and sulphamate sulpho chlorinated, sulfoxidation is also used.

Typical application of sulphonation and sulphation are production of lingo sulphonates, linear alkyl benzene sulphonate, Toluene sulphonates, phenolic sulphonates, chlorosulphonicacd, sulphamates for production of herbicide, sweetening agent (sidiumcyclohexysulphamate). Oil soluble sulphonate, saccharin

Preparation of Saccharin

The industrial synthesis entails the reaction of hydrogen chloride with a solution of sulfur trioxide in sulfuric acid. Sulfonation by chlorosulfonic acid gives the ortho and para substituted chlorosulfones. The ortho isomer is separated and converted to the sulfonamide with ammonia. Oxidation of the methyl substituent gives the carboxylic acid, which cyclicizes to give saccharin.

 $HCl + SO_3 \rightarrow ClSO_3H$



OXIDATION

Oxidation used extensively in the organic chemical industry for the manufacture of a large number of chemicals. Oxidation using oxygen, are combinations of various reactions like oxidation via dehydrogenation using oxygen, dehydrogenation and the introduction of oxygen and destruction of carbon, partial oxidation, peroxidation, oxidation in presence of strong oxidizing agent like KMnO₄, chlorate, dichromate, peroxides H₂O₂, PbO₂, MnO₂; nitric acid and nitrogen tertra oxide, oleum, ozone. Some of the important product of oxidation are aldehyde, ketone, benzyl alcohol, phthalic anhydride, ethylene oxide, vanillin, bezaldehyde, acetic acid, cumene, synthesis gas from hydrocarbon, propylene oxide, benzoic acid, maleic acid, benzaldehyde, phtathalic anhydride. Oxidation maybe carried out either in liquid phase or vapour phase.

Preparation of synthesis gas from hydrocarbon

By using the Fischer–Tropsch process, or Fischer–Tropsch synthesis, is a collection of chemical reactions that converts a mixture of carbon monoxide and hydrogen into liquid hydrocarbons.



HYDROGENATION

Hydrogenation involves the reaction of a substance with hydrogen in the presence of a catalyst. Some of the other reaction involving hydrogen are, hydrodesulphurisation, hydroracking, hydro formylation, oxosynthesis, hydroammonylsis, synthesis of ammonia.

Preparation of aldehyde (Hydro-formylation):

 $H_2 + CO + CH_3CH = CH_2$ \longrightarrow $HCo(CO)PBu_3$ $CH_3CH_2CH_2CHO$

ESTERIFICATION

Esterification is an important unit process in the manufacture of polyethylene terephathalate, methyl metha acrylate, cellulose ester in viscose rayon manufacture (xanthation of alkali cellulose with carbon disulphide), nitroglycerine.



HYDROLYSIS

Hydrolysis is used both in inorganic and organic chemical industry. Typical application is in oil and fats industry during soap manufacture where hydrolysis of fats are carried out to obtain fatty acid and glycerol followed by addition of sodium hydroxide to form soap. Other application is in the manufacture of amyl alcohols. Some of the major product using hydrogen is ethylene from acetylene, methanol, propanol, butanol, production of alcohol from olefins (eg. Ethanol from ethylene).

Various types of hydrolysis reaction may be pure hydrolysis, hydrolysis with aqueous acid or alkali, dilute or concentrated, alkali fusion, hydrolysis with enzyme and catalyst.

Preparation of ethanol from ethylene:

 $CH_2 = CH_{2(g)} + H_2O_{(g)}$ catalyst $CH_3CH_2OH_{(g)}$ $H = -45 \text{ kJ mol}^{-1}$

ALKYLATION

Alkylation involves the introduction of an alkyl radical into an organic compound by substitution or reduction. Products from alkylation find application in detergent, lubricants, high octane gasoline, photographic chemicals, plasticizers, synthetic rubber, chemicals etc. Some of the alkylating agents are olefins, alcohols, alkyl halides. Although sulphuric acid and phosphoric acid were commonly used as catalyst in alkylation process, however due to the corrosive nature of these acid now solid acid catalyst is finding wide application in new alkylation processes.

Preparation of toluene

Alkylation is the transfer of an alkyl group from one molecule to another.



POLYMERIZATION

Polymerization is one of the very important unit processes which find application in manufacture of polymer, synthetic fibre, synthetic rubber, polyurethane, paint and petroleum industry for high octane gasoline. Polymerisation maybe carried out either with single monomer or with comonomer. Polymerisation reaction can be addition or condensation reaction. Various Polymerisation methods may be bulk, emulsion, solution, suspension. Typical important product from polymerization are, Polyethyelene, PVC, poly styrene, nylon, polyester, acryicfibre, poly butadiene, poly styrene, phenylic, urea, melamine and alkyd resins epoxy resin, silicon polymers, poly vinyl alcohol etc.

Preparation of Polyethylene or polythene

It is the most common plastic.

$$n CH_2 = CH_2 \longrightarrow (CH_2 - CH_2)_n$$



polyethylene terethalate (polyester)

Definition of Saponication

Saponication is an organic chemical reaction that utilizes an alkali to cleave an ester into a carboxylic acid and alcohol. As we will see shortly, the primary use for this reaction is during the production of soap products. The terms ester, carboxylic acid, and alcohol are functional groups. A functional group is simply a group of molecules or atoms that we can easily identify in a compound.



Mechanics: Reaction and Mechanism

The general saponication reaction is shown on screen here. As you can see, saponication involves two major players: ester and alkali. Note that one of the products is a carboxylate ion. This is simply a carboxylic acid that carries a negative charge once its proton is removed. Use this ion as an ID marker to help you decide whether or not you are dealing with a saponication reaction.



General Equation for Saponication

If we look at the mechanism, or instruction guide for this reaction, we will see there is a series of steps that must be followed. Those steps, provided with illustrations, are shown here:

Step 1: The hydroxide ion from the alkali molecule swoops in and performs a nucleophilic attack on the ester or fatty molecule. Don't be alarmed by the word nucleophile. It simply refers to a molecule that will form a chemical bond due to its attraction to electrons in a dierent atom or molecule.



Step 1 of the Saponication Reaction

Step 2: The OR group becomes a leaving group, following Step 1. OR refers to the oxygen atom bonded to R, which is simply a placeholder for any molecule or atom. Desperately wanting to leave, the OR group departs, causing a double bond to form. This creates a carbonyl group. This new product may look familiar, as it is a carboxylic acid functional group.



Step 2 of the Saponication Reaction

Step 3: Not able to leave alone, the OR group plucks the proton (H) from carboxylic acid. This process of removing a proton from a molecule is called deprotonation. Once deprotonated, the nal products, carboxylate and alcohol, are formed.



Application: Soap Making

Although there are different uses for the saponication reaction, production of soap is by far the most popular application. If we use a saponication reaction to make soap, we need two substances: a fat and an alkali. The type of fat and alkali greatly influences the end product. Sources of fat can range from your common oils, such as coconut oil or olive oil, to animal fat. The two most common alkalis used are potassium hydroxide (KOH) and sodium hydroxide (NaOH).

UNIT PROCESSES IN PHARMA AND DRUG INDUSTRY

Paracetamol, or **acetaminophen**, is a widely used over-the-counteranalgesic (pain reliever) and antipyretic (fever reducer). It is commonly used for the relief of headaches and other minor aches and pains and is a major ingredient in numerous cold and flu remedies. In combination with opioid analgesics, paracetamol can also be used in the management of more severe pain such as post-surgical pain and providing palliative care in advanced cancer patients. The onset of analgesia is approximately 11 minutes after oral administration of paracetamol, and its half-life is 1–4 hours.

Synthesis of Paracetamol

In the laboratory, paracetamol is easily prepared by nitrating phenol with sodium nitrate, separating the desired *p*-nitrophenol from the *ortho*- byproduct, and reducing the nitro group with sodium borohydride. The resultant *p*-aminophenol is then acetylated with acetic anhydride. In this reaction, phenol is strongly activating, thus the reaction requires only mild conditions (cf. the nitration of benzene). The industrial process is analogous, but hydrogenation is used instead of the sodium borohydride reduction.



A simpler synthesis by Hoechst-Celanese involves direct acylation of phenol with acetic anhydride catalyzed by HF, conversion of the ketone to a ketoxime with hydroxylamine, followed by the acid-catalyzed Beckmann rearrangement to give the amide



SYNTHESIS OF IBUPROFEN

- Ibuprofen is available over-the-counter to relieve the pain, stiffness and inflammation that may accompany a number of disorders.
- it is similar in aspirin the way it works and in the way it can be used, because it acts as an analgesic as well as anti-inflammatory
 12
- > it is an effective treatment for rheumatoid arthritis, ostheoarthitis, and gout.

- \triangleright it also relieves mild to moderate headache, menstrual pains, pain from soft tissue, injuries and following operations.
- > sometimes Ibuprofen is prescribed along with slower acting drugs in the treatment of Rheumatoid arthritis.

The making of Ibuprofen begins with the compound Isobutyl benzene.

Step1: a Friedel-Crafts acylation that uses the catalyst aluminum-chloride that generates aluminum trichloride hydrate as waste by-product.

Step 2: a Darzens reaction with ethyl-chloroacetate that results in an epoxy ester compound.

Step 3: involves **decarboxylation** and **hydrolyzation** forming an aldehyde.

Step 4: a reaction with hydroxylamine giving an oxime.

Step 5: the oxime is converted to a nitrile.

Step 6: hydrolyzation of the nitrile resulting in the final product 2,4-isobutylphenyl-propanoic acid. This process has a 40% atom economy which translates into 60% waste products. This means that if 30 million pounds of Ibuprofen is produced each year, then more than 35 million pounds of waste is generated

> The green synthesis of Ibuprofen also begins with the compound isobutyl benzene

Step 1: a Friedel-Crafts acylation using hydrogen fluoride as the catalyst that can be recovered and reused.

Step 2: involves **hydrogenation** with Raney nickel, which is recovered and reused, to produce an alcohol.

Step 3: the alcohol undergoes **carbonylation** with the catalyst, palladium, also recovered and reused, to produce Ibuprofen or 2,4-isobutyl-phenylpropanoic acid.

This process has a 99% atom economy, includes the recovered acetic acid that was generated in Step 1. This means that only 1% is waste by-products which Translated to less than 500,000 pounds of waste for the production of 30 million pounds of Ibuprofen.

ASPIRIN (acetyl salicylic acid) is a widely used drug in modern society.

- > Salicylic acid which is a constituent of certain plant is itself an analysic & was originally administered as sodium salicylate, since salicylic acid has an irritating effect on the stomach, chemists thought of a modification which would retain its properties while decreasing the adverse side effects.
- Conversion to the ester satisfied this requirement& aspirin proved to be as effective as sodium salicylate without the irritation of phenolic compound.
- > Aspirin however hydrolyzed to salicylic acid in the alkaline media of the intestine by esterase enzyme.



Aspirin - acetylsalicylic acid

UNIT II

FREE RADICAL SUBSTITUTION

Free-Radical Chain Reaction

Initiation generates a reactive intermediate.

Propagation: the intermediate reacts with a stable molecule to produce another reactive intermediate (and a product molecule).

Termination: side reactions that destroy the reactive intermediate

Chlorination of Methane

$CH_4 \ + \ Cl_2 \rightarrow CH_3Cl \ + \ HCl$

• Requires heat or light for initiation. The most effective wavelength is blue, which is absorbed by chlorine gas. High quantum yield. Lots of product formed from absorption of only one photon of light (chain reaction). Some ethane is formed. These factors are characteristics of free-radical reactions

Initiation

Ultraviolet light causes splitting of chlorine molecules into chlorine atoms

| Cl - Cl | $\rightarrow Cl^{\bullet} + Cl^{\bullet}$ |
|----------|---|
| Chlorine | Chlorine atoms |

molecule (free radicals)

Propagation

 $\begin{array}{ccc} CH_4 & + & Cl^{\bullet} & \rightarrow CH_3^{\bullet} & + & HCl \\ & & Methyl \ radical & & Hydrogen \ chloride \end{array}$

 $CH_3^{\bullet} + Cl_2 \rightarrow CH_3Cl + Cl^{\bullet}$ *Chloromethane*

Chlorine atom free to react with another methane molecule

Termination

 $\begin{array}{rcl} Cl^{\bullet} &+ & Cl^{\bullet} & \rightarrow & Cl_2 \\ CH_3^{\bullet} &+ & Cl^{\bullet} &= & CH_3Cl \\ CH_3^{\bullet} &+ & CH_3^{\bullet} &= & C_2H_6 \end{array}$

Initiation Step

A chlorine molecule splits homolytically into chlorine atoms (free radicals)

$$\ddot{\mathbf{Cl}}: \ddot{\mathbf{Cl}}: + \text{ photon } (h \nu) \longrightarrow \ddot{\mathbf{Cl}}: + \ddot{\mathbf{Cl}}$$

The chlorine atom is electrophilic - lewis acid

Seeks an electron to regain octet of electrons

Usually abstracts a hydrogen atom

Propagation Step (1)

The chlorine atom collides with a methane molecule and abstracts (removes) a H, forming another free radical and one of the products (HCl).



Methyl radicals is also electrophilic -seeks e.

Methyl radical is a member of the highly reactive intermediates gang

Propagation Step (2)

The methyl free radical collides with another chlorine molecule, producing the other product (methyl chloride) and regenerating the chlorine radical



chlorine atom then attacks another methyl step 1 and 2 repeat over and over again. Overall Reaction



Termination Steps

- Collision of any two free radicals
- Combination of free radical with contaminant or collision with wall.



Evidence for this mechanism

- Use of ultraviolet light even for a very short period causes a chain reaction
- Formation of trace quantities of butane
- Reaction speeded up by sources of free radicals such as tetraethyl lead

ADDITION REACTIONS

In **addition** reactions the substrate gains atoms (or groups) from the reactant but doesn't lose any.

- Substrate is unsaturated
- Occur easily & quickly because σ -bonds are more stable than the π bonds they replace



Nucleophilic addition: *a Nu:- attacks the electrophilic carbonyl carbon of the substrate and adds to the substrate.*



Electrophilic addition: *an alkene or alkyne serves as the Nu: and donates : to the electropositive atom of a molecule, typically an acid*

- Substrate is unsaturated
- Reactant is often an acid
- The two halves (electropositive & electronegative) are both added "across" the double bond



In electrophilic addition, the reactant is '<u>added across</u>' the double bond. The first step of electrophilic addition forms a carbocation, and **formation favors the more stable carbocation**.

To stabilize the carbocation, maximize the amount of charge delocalization

So, adding the H+(E+) to the less substituted C places the + on the more substituted carbon, creates the most stable carbocation.

Sometimes the substituted carbocation is also stabilized by resonance.

ELECTROPHILIC AROMATIC SUBSTITUTION

The characteristic reaction of benzene is electrophilic aromatic substitution—a hydrogen atom is replaced by an electrophile.

- Benzene has six π electrons delocalized in six p orbitals that overlap above and below the plane of the ring. These loosely held π electrons make the benzene ring electron rich, and so it reacts with electrophiles.
- Because benzene's six π electrons satisfy Hückel's rule, benzene is especially stable. Reactions that keep the aromatic ring intact are therefore favored.



substitution of H by E

- Benzene does not undergo addition reactions like other unsaturated hydrocarbons, because addition would yield a product that is not aromatic.
- Substitution of hydrogen keeps the aromatic ring intact.
- There are five main examples of electrophilic aromatic substitution.
- Regardless of the electrophile used, all electrophilic aromatic substitution reactions occur by the same two-step mechanism—addition of the electrophile E⁺ to form a resonance-stabilized carbocation, followed by deprotonation with base, as shown below:
- Regardless of the electrophile used, all electrophilic aromatic substitution reactions occur by the same two-step mechanism—addition of the electrophile E⁺ to form a resonance-stabilized carbocation, followed by deprotonation with base, as shown below:



Regardless of the electrophile used, all electrophilic aromatic substitution reactions occur by the same two-step mechanism—addition of the electrophile E^+ to form a resonance-stabilized carbocation, followed by deprotonation with base, as shown below



The first step in electrophilic aromatic substitution forms a carbocation, for which three resonance structures can be drawn. To help keep track of the location of the positive charge

- Always draw in the H atom on the carbon bonded to E. This serves as a reminder that it is the only sp³ hybridized carbon in the carbocation intermediate.
- Notice that the positive charge in a given resonance structure is always located ortho or para to the new C – E bond. In the hybrid, therefore, the charge is delocalized over three atoms of the ring.



CONDENSATION REACTIONS

A condensation reaction is a reaction in which two molecules combine to form a single molecule. A small molecule, often water, is usually removed during a condensation reaction.

ALDOL CONDENSATION:

An aldol condensation is an organic reaction in which an enol or an enolate ion reacts with a carbonyl compound to form a β - hydroxyaldehyde or β -hydroxyketone, followed by a dehydration to give a conjugated enone. **Aldol** condensations are important in organic synthesis, providing a good way to form carbon–carbon bonds.

• The Aldol Reaction of Aldehydes



• The Aldol Reaction of Ketones



MECHANISM OF THE ALDOL REACTION

Step 1:

First, an acid-base reaction. Hydroxide functions as a base and removes the acidic α -hydrogen giving the reactive enolate.

Step 2:

The nucleophilic enolate attacks the aldehyde at the electrophilic carbonyl **C** in a <u>nucleophilic addition type process</u> giving an intermediate alkoxide.

Step 3:

An acid-base reaction. The alkoxide deprotonates a water molecule creating hydroxide and the β -hydroxyaldehydes or **aldol** product.



Step 1:

First, an acid-base reaction. Hydroxide functions as a base and removes an acidic α -hydrogen giving the reactive enolate.

Step 2:

The electrons associated with the negative charge of the enolate are used to form the C=C and displace the leaving group, regenerating hydroxide giving the conjugated aldehyde.



BENZOIN CONDENSATION

Benzoin Condensation is an important reaction in which carbon-carbon bond is formed when two molecules of aldehydes (particularly benzaldehyde) reacts with each other to form a condensed product called Benzoin. - This reaction is catalyzed by cyanide ion.

 When 2 moles of aromatic aldehydes react in the presence of KCN, an alpha hydroxyl ketone is obtained



NUCLEOPHILIC AROMATIC SUBSTITUTION

- Aryl halides with electron-withdrawing substituents ortho and para react with nucleophiles.
- Form addition intermediate (Meisenheimer complex) that is stabilized by electron withdrawal.
- Halide ion is lost to give aromatic ring.



A nucleophile replaces a leaving group on the aromatic ring. This is an addition– elimination reaction. Electron-withdrawing substituents activate the ring for nucleophilic substitution.



Mechanism

Step 1: Attack by hydroxide gives a resonance-stabilized complex



Copyright © 2010 Pearson Prentice Hall, Inc.

Step 2: Loss of chloride gives the product



Step 3: Excess base deprotonates the product



Activated Positions





Nitro groups ortho and para to the halogen stabilize the intermediate (and the transition state leading to it).

Electron-withdrawing groups are essential for the reaction to occur

Benzyne Reaction: Elimination-Addition



- Reactant is halobenzene with no electron-withdrawing groups on the ring.
- Use a very strong base like NaNH₂.

Benzyne Mechanism

- Sodium amide abstracts a proton.
- The benzyne intermediate forms when the bromide is expelled and the electrons on the sp^2 orbital adjacent to it overlap with the empty sp^2 orbital of the carbon that lost the bromide.
- Benzynes are very reactive species due to the high strain of the triple bond.



Copyright © 2010 Pearson Prentice Hall, Inc.

CYCLOADDITION REACTION

Cycloaddition describes the union of two independent π -systems through a concerted process involving a cyclic movement of electrons and resulting in the formation of a new ring.

Cycloaddition reactions are considered among the most powerful bond-forming reactions in organic synthesis because of their ability to form many bonds in one step and also for their potential in generating several stereogenic centres at the same time with predictable stereochemical outcomes.

A cycloaddition reaction is categorized as a [m + n]-cycloaddition when a system of m conjugated atoms combines with a system of n conjugated atoms.

Cycloaddition reaction: A reaction in which two reactants add together in a single step to form a cyclic product.

Diels-Alder reaction: A cycloaddition reaction of a conjugated diene and certain types of double and triple bonds.

dienophile: Diene-loving.

Diels-Alder adduct: The product of a Diels-Alder reaction.



- The special value of D-A reactions are that they:
 - 1. form six-membered rings.
 - 2. form two new C-C bonds at the same time.
 - 3. are stereospecific and regioselective.

Reaction is facilitated by a combination of electron-withdrawing substituents on one reactant and electron-releasing substituents on the other



- Mechanism
 - No evidence for the participation of either radical of ionic intermediates.
 - Chemists propose that the Diels-Alder reaction is a concerted pericyclic reaction.

REARRANGEMENT REACTION

The reactions which proceed by a rearrangement or reshuffling of the atoms groups in the molecule to produce a structural isomer of the original substance are called Rearrangement reactions.

Most are migrations from an atom to an adjacent one (called 1,2-shifts), but some are over longer distances.

Classification :

Intermolecular rearrangement

- Reactions which involve migration of group between two molecules.
- In which the migration group gets completely detached and is later on reattached are called intermolecular rearrangements.
- Eg :Aromatic rearrangements

Intra molecular rearrangement :

- Reactions which involve rearrangement with in the same molecule. Those rearrangements in which the migration group is never fully detached from the system
- Eg: Nucleophillic rearrangement, Electrophillic rearrangement, Free radical rearrangement



INTRAMOLECULAR

BECKMANN REARRANGEMENT

An acid-induced rearrangement of oximes to give amides.

This reaction is related to the Hofmann and Schmidt Reactions and the Curtius Rearrangement, in that electropositive nitrogen is formed that initiates an alkyl migration.



The R group trans to the leaving group migrates to the nitrogen



- Applications:
- Some of the uses of this reaction are as below-

- It is used in the industries for the synthesis of paracetamol. This integration is achieved by the process of conversion of a ketone to ketoxime with the help of hydroxylamine.
- It is mainly used in the synthesis of various steroids and drugs

The Beckmann Rearrangement synthesis is helpful in the production of some of the chloro bicyclic lactams

Fries rearrangement

The Fries rearrangement is an organic reaction used to convert a phenyl ester to an ortho- and para-hydroxy aryl ketone using a Lewis acid catalyst and Brønsted acid work-up.

- The mechanism begins with coordination of the ester to the Lewis acid, followed by a rearrangement which generates an electrophilic acylium cation.
- The aromatic compound then attacks the alkyl cation (both the ortho and para attack are allowed) via an electrophilic aromatic substitution (S_EAr).

Deprotonation to regenerate aromaticity and Brønsted acid work-up to regenerate the Lewis acid catalyst provide the two hydroxy aryl ketone products.



The Fries rearrangement proceeds through ionic intermediates. The reaction depends on the structure of the substrates and the reaction conditions



LUBRICATION

Lubrication is the process, or technique employed to reduce wear of one or both surfaces in close proximity, and moving relative to each other, by interposing a substance called lubricant between the surfaces to carry or to help carry the load (pressure generated) between the opposing surfaces.
Lubricants and Lubrication

Fluid which is introduced in between moving parts in order to reduce the friction, generated heat & wear and tear of machine parts are called Lubricants.

This process of introducing lubricant is called Lubrication.

Functions of lubricants :

a) Reduces the frictional resistance.

b) Reduces wear & tear, surface deformation

c) Acts as a coolant

d) Provides protection against corrosion

e) Acts as a seal in some cases

f) Improves the efficiency of the machine

Characteristics

- A good lubricating oil should have:
- High boiling point
- Adequate Viscosity
- Low freezing point
- High oxidation resist
- Non Corrosive properties
- Good thermal stability



Types of Lubricants

- Solid lubricants possess lamellar structure preventing direct contact between the sliding surfaces even at high loads.
- Graphite and molybdenum disulfide particles are common Solid lubricants. Boron nitride, tungsten disulfide and polytetrafluorethylene (PTFE) are other solid lubricants.
- Solid lubricants are mainly used as additives to oils and greases. Solid lubricants are also used in form of dry powder or as constituents of coatings.

Types of Lubricants

- Semi-fluid lubricants (greases) are produced by emulsifying oils or fats with metallic soap and water at 400-600°F (204- 316°C).
- Typical mineral oil base grease is vaseline.
- Grease properties are determined by a type of oil (mineral, synthetic, vegetable, animal fat), type of soap (lithium, sodium, calcium, etc. salts of long-chained fatty acids) and additives (extra pressure, corrosion protection, anti-oxidation, etc.).
- Semi-fluid lubricants (greases) are used in variety applications where fluid oil is not applicable and where thick lubrication film is required: lubrication of roller bearings in railway car wheels, rolling mill bearings, steam turbines, spindles, jet engine bearings and other various machinery bearings.

Types of Lubricants

- Fluid lubricants (Oils) Mineral fluid lubricants are based on mineral oils. Mineral oils (petroleum oils) are products of refining crude oil. There are three types of mineral oil: paraffinic, naphtenic and aromatic.
- Paraffinic oils are produced either by hydrocracking or solvent extraction process.
- Naphtenic oils are produced from crude oil distillates.
- Aromatic oils are products of refining process in manufacture of paraffinic oils.

Properties of Lubricants Viscosity

It's a measure of a fluid's resistance to flow.

- Viscosity of the lubricating oil determines its performance under operating conditions.
- A low viscosity oil is thin and flows easily .
- A high viscosity oil is thick and flows slowly.
- As oil heats up it becomes lessviscous (Becomes thin)
- Too low viscosity of the liquid > Lubricant film cannot be maintained between the moving surfaces > Excessive wear.
- Too high viscosity of the liquid > Excessive friction.
- Selected Lubricant must be proper viscous.
- Viscosity is usually expressed in centipoise or centistoke.

Viscosity Index

- It is "Avg. decrease in viscosity of oil per degree rise in temp between 1000F & 2100F."
- Viscosity of liquids decreases with increasing temperature.
- The rate at which viscosity of a lubricant changes with temperature is measured by a scale called Viscosity Index.
- Silicones, polyglycol ethers, Diesters or triesters have high Viscosity Index.

Viscosity Index :

- It is "Avg. decrease in viscosity of oil per degree rise in temp between 1000F & 2100F."
- Viscosity of liquids decreases with increasing temperature.
- The rate at which viscosity of a lubricant changes with temperature is measured by a scale called <u>Viscosity Index</u>.
- Silicones, polyglycol ethers, Diesters or triesters have high Viscosity Index.

Determination of Viscosity Index :

- First the viscosity of the oil under test is determined at 100°F & 210°F. Let it be U and V respectively.
- Then viscosity of Pennsylvanian oil is determined. Let it be V_{H.}
- Then viscosity of Gulf oil is determined. Let it be V_L viscosity Index = $\frac{V_L - U}{V_L - V_H}$ x 100 Viscosity

V.I. = 100 (Pennsylvanian oils.)

V.I. = Zero (Naphthanic-base gulf oils)

Higher the V.I, lesser is the variation of viscosity with change in temperature. Thus, a good lubricating oil should possess high V.I.

100O

200

lemp

2. Iodine Number

- Iodine number is the number of Gms equivalent of iodine to amount of ICl absorbed by 100gm of oil.
- Each oil has its specific Iodine Number.
- So Iodine Number determines the extent of contamination of oil.
- Low Iodine Number is desirable in oils.

Some oils and their Iodine Numbers are given below :

| Iodine Number | Oil | Example |
|---------------|----------------|---------------------------|
| >150 | Drying oil | Linseed oil, tung oil |
| 100-150 | Semidrying oil | Castor oil , Soyabean oil |
| <100 | Non-Drying oil | Coconut oil, Olive oil |

3. Aniline Point

- Aniline point is the Min temp at which oil is miscible with equal amt of aniline
- Aniline Point is a measure of aromatic content of the lubricating oil.
- Low Aniline Point oil have high aromatic content which attacks rubber seals.
- Higher Aniline point means low %age of hydrocarbons (desirable).
- Thus Aniline Point is used as an indication of possible deterioration of rubber sealing etc.

Determination of Aniline Point :



The temperature at which separation of the two phases (Aniline + oil) takes place is the Aniline Point.

4. Emulsion Number

- Emulsification is the property of water to get mixed with water easily.
- Emulsions can be oil in water emulsion or water in oil emulsion.
- A good lubricating oil should form such an emulsion with water which breaks easily. This property is called demulsification.
- The time in seconds in which a given volume of oil and water separates out in distinct layers is called steam demulsification number.
- A good lubricating oil should have lower demulsification number.
- Quicker the oil separates out from the emulsion formed, better is the lubricating oil.
- In cutting oils the higher the emulsification number, better the oil is. This is because the emulsion acts as a coolant as well as a lubricant.

5. Flash point and Fire point

- Flash Point is the min temp at which the lubricant vaporizes that ignite for a momwhen tiny flame is brought near.
- Fire Point is the Min temp at which the lubricant's vapours burn constantly for 5 seconds when tiny flame is brought near.
- Fire point = flashpoint+5 to 400C.
- Both should be higher than the max temp of country (for transportation)
- If flash point < 140°F = Flammable liquids

And if flash point > $140^{\circ}F$ =Combustible liquids.



The flash and fire points are generally determined by using Pensky-Marten's apparatus.

Oil under examination is filled in the oil cup up to the mark and heated by the air bath by a burner.
Stirrer is worked b/n tests at a rate of about 1 – 2 rev/sec.
Heat is applied so as to raise the oil temp by about 5c/min.

•The temp at which distinct flash appeared in side the oil cup is recorded as flashpoint.

•The heating is continued to record the fire point.

6. Drop Point

 Drop Point is the Temperature at which grease passes from the semisolid to the liquid state. So, it determines the upper temp limit for the applicability of grease.

Determination :

- Beaker is heated.
- Temperature is raised.
- Grease sample passes from a semisolid to a fluid state.
- Temp at which its first drop falls from the opening is recorded as drop-point.



7. Cloud point and Pour Point

- Cloud Point is the temp at which the lubricant becomes cloudy or hazy when cooled.
- Pour Point is the temp at which the lubricant just ceases to flow when cooled.
- Both indicates suitability of lubricant in cold conditions and thus must be low.
- Pour point of wax can be lowered by dewaxing or adding suitable pour point depressant.
- Pour point of an oil can be lowered by lowering the viscosity of the oil which is achieved by removing the viscous constituent of the oil.
- Lubricating oils used in capillary feed systems should have low cloud points, otherwise impurities will clog the capillary.
- A high pour point leads to the solidification of the lubricant that may cause jamming of the machine.

8. Neutralization Point

- Neutralization Point determines Acidity or Alkalinity of oil.
- Acidity/Acid value/Acid number is mgs of KOH required to neutralize acid in 1 gm of oil.
- Alkalinity/Base value/Base number is mgs of acid required to neutralize all bases in 1 gm oil.
- As Neutralization Point of oil increases, age of oil decreases.

9. Soaponification Number

- It's the mgs of KOH required to saponify 1 gm of oil.
- Saponification is hydrolysis of an Easter with KOH to give alcohol and Na/K salt of acid.
- Mineral oils do not react with KOH and are not saponifiable.
- Vegetable and animal oils have very high saponification values.

Significance

- Saponification value helps us to ascertain whether the oil under reference is mineral or vegetable oil or a compounded oil.
- Each oil has its specific Soaponification Number.
 Deviation from it indicates the extent of adulteration of oil.

SEMI-SOLID LUBRICANTS OR GREASES: -

- Greases are semi-solid lubricants which consist of metallic soap in lubricating oil.
- Conditions for using semi-solid lubricants:
- When it is necessary to seal the bearing or joint against the dirty & dust particles.
- When the machine is worked at low speed under high load.
- When the contamination of lubricating oil is unacceptable and harmful for products.
- When the lubricating oil is not suitable for machines

Preparation

<u>Greases</u> are semi-solid lubricants obtained by thickening of lubricating oil by the addition of metallic soaps. Soaps are prepared by saponification of vegetable oils (or) fats with alkali (like as thickness (or) gelling agents)

- Consistency of grease is governed by amount of oil added.
- A grease is made up of the three following components:
- Thickening agent 5% to 20%
- Base oils 80% to 95%
- Additives 0% to 10%

- On the basis of soap used in manufacture of semi solid are classified as:-
- CALCIUM BASED GREASE: These greases are prepared by mixing of calcium soap with petroleum oil. They are insoluble in water. These can be used upto 80°C. These are also called 'Cup grease'.
- SODA-BASED GREASE: These grease are prepared by mixing of sodium soap with petroleum oil. They are soluble in water. These can be used upto 175°C. These greases are used in ball bearings.
- LITHIUM-BASED GREASE: These greases are prepared by mixing of lithium soap with petroleum oil. They are water resistant. They have high stability and suitable for use at high temperature.
- AXLE GREASE:-These are prepared by adding lime or any metal hydroxide to fatty acids. They are water resisting and suitable for high temp and low speed. These are used in tractor rollers and machines bearings.

- Advantages Of Greases : •
- Remains at application point & adhere to surface.
 - Less-frequent application needed.
 - Good for inclined/vertical shafts.
 - Seal out contaminants & less expensive seals needed.
 - Water resistant & reduce oil vapor problems.
 - Prolong the life of worn parts by filing irregularities

• Provide better mechanical lubrication cushion for extreme conditions such as shock loading, reversing operations, low speeds & high loads.

• Reduce noise and vibration.

Consistency and Drop point

The consistency of grease is defined as the distance in tenths of millimetres that a standard cone travels through a sample of grease (, a cone of a specific weight is allowed to sink into a grease)under test at standard condition of load (150g) temperature $(25^{\circ}C)$ and time (5 seconds). Drop point of grease is defined as the temperature at which grease passes from semi-solid to a liquid state.

Solid lubricant

- SOLID LUBRICANTS:-"The lubricants that exist in solid form are called solid lubricants". E.g.: graphite,molybdenum disulphide etc.
- They are used in heavy machines under high load and low speed.
- Conditions for using Solid Lubricants:-
- Machines that are under high load and low speed.
- When liquid and semi-solid lubricants are highly combustible.
- In machines where liquid and semi-solid lubricants can't work.
- When contamination of oil and grease with dust particles is noticed

| Advantages | Disadvantages |
|--|---|
| More effective than fluid lubricants at high loads (high pressure). | Poor self-healing properties. A broken solid film tends to shorten the useful life of the lubricant. |
| High resistance to deterioration in storage. | |
| Highly <u>stable</u> in extreme temperature, radiation, and reactive environments. | Poor heat dissipation. This condition is especially true with polymers due to their low thermal conductivities. |
| Permit equipment to be <u>lighter and</u> <u>simpler.</u> Superior cleanliness | Higher coefficient of friction and wear than liquid lubricated bearings. |

Molybdenum disulphide as solid lubricant:-

- It has sand-witch like structure. The layer of molybdenum atoms lie between two layers of sulphur atom. These layers are held together by very weak vander Waals forces. Due to these forces, it is soft & smooth in nature.
- It possesses very low coefficient of friction
- It is stable in air up to 400° C.
- It has high specific gravity than graphite.
- It is used as either in powdered form or in additives

• Strengths of MoS_2 :

1. High Load Carrying (> 700 MPa)

2. Low Friction

3. High temperature lubricant particularly in space.

Weaknesses of MoS₂ :

1. Moisture detrimental to performance

2. Film thickness $\sim 15 \ \mu m$.



Molybdenum disulphide starts to oxidize significantly above 350°C in oxygen and 450°C in air, but the main oxidation product is molybdic oxide, which is itself a fair high temp lubricant. In high vacuum, the disulphide is said to be stable to 1000°C and it evaporates very slowly, so that it has been widely used in space.

The thickness of the film when applied is generally 15 microns, which provides the longest life. Thicker films apparently do not last as long, apparently because it becomes easier for wear particles consisting of the MoS₂-resin material to come off in lose form.

- Graphite as solid lubricant:-
- It is soapy in touch.
- It is non inflammable.
- It is not oxidized in air up to 3750C
- It is used either in powdered form or in suspension form.
- When graphite is dispersed in oil, it is called 'oil dag' and when it is dispersed in water; it is called 'aquadag'. Oil dag is useful in internal combustion engine and aquadag is useful in food stuffs industry.

• <u>Strengths of graphite :</u>

Moderate loads (< 275 MPa).
 Low friction.
 High temp. stability.

• <u>Weaknesses of graphite :</u>

 Corrosion.
 Vacuum detrimental to performance.



Mechanical distortion of graphite is shown in Fig, which limits its usage to moderate load(< 275 MPa). It is interesting to note that presence of water helps graphite in lubrication, while presence of water detrimental to MoS_2 . On other hand vacuum is detrimental to graphite, but favorable for MoS_2 .



Bleaching powder

Bleaching powder is also called calcium chloro hypochlorite because it is considered as a mixed salt of hydrochloric acid and hypochlorous acid.

It is also called as Calcium oxychloride and chloride of lime.

It is represented as:



- Preparation
- It is manufactured by the action of chlorine on dry slaked lime, Ca(OH), at 40°C.

• There is another view proposed by Clifford according to which bleaching powder is a mixture of calcium hypochlorite and basic calcium chloride.

- The manufacture of bleaching powder is carried out in Backmann's plant as follows:
- It consists of a vertical cast-iron tower.
- The tower is provided with a hopper at the top, two inlets near the base (one for chlorine and other for hot air) and an exit for waste gases near the top.
- The tower is fitted with eight shelves at different heights each equipped with rotating rakes.
- The slaked lime is introduced through the hopper and it comes in contact with chlorine, which slowly moves upwards.
- Bleaching powder is collected in a barrel at the base.
- The chlorine used in the manufacture of bleaching powder should be dilute and the temperature should be maintained below 40°C.

- Properties
- 1. It is a pale yellow powder. It has strong smell of chlorine. It is soluble in water but a clear solution is never formed due to the presence of impurities.
- 2. On long standing it undergoes auto-oxidation into calcium chlorate and calcium chloride.

 $6 \operatorname{CaOCl}_2 \longrightarrow 6 \operatorname{Ca}(\operatorname{ClO}_3)_2 + 5 \operatorname{CaCl}_2$

3. In the presence of cobalt chloride it looses its oxygen.

$$2CaOCl_2 \xrightarrow{CoCl_2} 5 CaCl_2 + O_2$$

4. On account of the formation of nascent oxygen, it shows oxidising and bleaching properties.

$$CaOCl_2 + H_2SO_4 \longrightarrow CaCl_2 + CaSO_4 + 2HClO$$

5. It loses its chlorine by the action of dilute acids (in excess).

$$CaOCl_2 + HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$

 The amount of chlorine obtained from a sample of bleaching powder by treatment with excess of dilute acids or carbon dioxide is called available chlorine. A good sample of bleaching powder contains 35 38% available chlorine.

Uses of Bleaching Powder

It is used

- (i) as a disinfectant and germicide especially in the sterilization of drinking water.
- (ii) for manufacture of chloroform.
- (iii) for making wool unshrinkable.
- (iv) as an oxidising agent in industry.
- (v) mainly as bleaching agent for cotton, linen and wood pulp.

Sodium hypochlorite

- Sodium hypochlorite, also called as liquid bleach, is a powerful oxidizing agent that is widely used as a disinfecting and bleaching agent.
- The chemical formula of sodium hypochlorite is NaClO, and its molar mass is 74.44 g/mol.
- **Preparation:** It is prepared industrially by the Hooker process, in which dilute sodium hydroxide is reacted with chlorine gas, to produce NaClO, along with sodium chloride and water.
- 2 NaOH + $Cl_2 \rightarrow NaClO + NaCl + H_2O$
Physical properties:

- In the pure state, it exists as an unstable light green solid
- Density 1.11 g/mL,
- Melting point -18 °C
- Boiling point 101 °C.
- It is more commonly found as an aqueous pale greenish or yellow solution

Chemical properties:

- Sodium hypochlorite is a good oxidizing agent.
- It reacts with protic acids such as HCl, to form salts while releasing toxic chlorine gas.
- It also reacts with some acids to form hypochlorous acid (HClO).
- In water, it decomposes into sodium and chloride ions, as well as the powerful oxidizing agent, hydroxyl radical (OH[•]).
- NaClO also decomposes into sodium chloride and oxygen.

- Uses:
- Its main uses are as a bleaching agent and disinfectant for both household and industrial purposes.
- It is also used in water treatment plants, swimming pools, in some medical and dental treatments
- In the food industry as a disinfecting agent,
- In homes as a deodorizing and cleaning agent, and
- In laundry detergents as a stain remover and bleach.

Health effects/safety hazards:

- Sodium hypochlorite is a toxic and corrosive compound at higher concentrations.
- When swallowed, it can be very toxic.
- It also reacts with some acids as well as ammonia to produce toxic gases such as chlorine, which can lead to severe eye irritation and respiratory problems.
- Strong solutions of bleach can also cause skin burns.

HYDROGEN PEROXIDE

- A peroxide is any compound which has two oxygen atoms bonded together.
- The O-O group is the peroxide group of the compound.
- And Hydrogen Peroxide is the simplest peroxide.
- The chemical formula for hydrogen peroxide is H₂O₂.
- It is a water molecule with one extra atom of <u>oxygen</u>.
- It has various uses ranging from disinfectant to propellant for rockets.

- PREPARATION
- FROM SODIUM PEROXIDE[MERCK'S PROCESS] Hydrogen peroxide is prepared by adding calculated amount of sodium peroxide to ice cold dilute solution of sulphuric acid. The addition is carried out slowly in small amounts with constant stirring.

 $Na_2O_2+H_2SO_4 \rightarrow Na_2SO_4+H_2O_2$

Upon cooling, crystals of Na₂SO₄ .10H₂O separate out. The crystals of Na₂SO₄ .10H₂O are decanted leaving behind solution of hydrogen peroxide.

- FROM BARIUM PEROXIDE
- In this method, a paste of hydrated barium peroxide is prepared in ice cold water and is treated with about 20% ice cold solution of sulphuric acid.

 $BaO_2.8H_2O+H_2SO_4 \rightarrow BaSO_4+H_2O_2+8H_2O_2$

• The white precipitate of $BaSO_4$ is removed by filtration leaving behind about 5% solution of H_2O_2 .

PHYSICAL PROPERTIES:

- i. Pure H_2O_2 is a thick syrupy liquid with pale blue color.
- ii. It is more viscous, less volatile and dense than water.
- iii. Its density is 1.44g/cm³
- iv. Its melting point is 272.4K and boiling point is 358K at 68mm of Hg pressure.
- v. It is completely miscible with water, alcohol and ether in all proportions. It forms a hydrate with water as H₂O₂. H₂O[m.p.221K]

Chemical properties:

- Hydrogen peroxide in both acidic and basic medium acts as an oxidizing as well as the reducing agent.
- Oxidizing nature in an acidic medium PbS(s)+4H₂O₂(aq)→PbSO₄(s)+4H₂O(l)
- The reducing nature in an acidic medium HOCl+H₂O₂→H₃O⁺+Cl⁻+O₂
- Oxidizing nature in a basic medium Mn²⁺+H₂O₂→Mn⁴⁺+2OH⁻
- Reducing nature in a basic medium $I_2 + H_2O_2 + OH^- \rightarrow 2I^- + 2H_2O + O_2$

Storage of Hydrogen Peroxide:

- It must be kept in wax lined colored bottles because the rough glass surface causes its decomposition.
- ii. A small amount of phosphoric acid, glycerol or acetanilide is generally added which retard the decomposition of H₂O₂. These are also called negative catalysts.

• Uses of Hydrogen Peroxide:

- Since hydrogen peroxide acts as both an oxidizing as well as a reducing agent and it has a vast area of application:
- The textile and paper industry use it as a bleaching agent.
- It is used as hair bleach in our day to day life and also as a mild disinfectant.
- It is used for the synthesis of tartaric acid, food products, and many pharmaceuticals.
- It is used in the manufacture of chemicals which in turn are used in making of high-quality <u>detergents</u>.
- Its most significant use is in environmental chemistry where it is used in pollution control treatment of domestic waste and industrial effluents.

Chlorine Dioxide

- Chlorine dioxide is a reddish to yellowish-green gas. It does not occur naturally in the environment. When added to <u>water</u>, chlorine dioxide forms <u>chlorite</u> ion, which is also a very reactive chemical.
- Preparation (Technical grade)
- Chlorine dioxide (ClO₂) is produced from the oxidation of sodium chlorite (NaClO₂) by hypochlorous acid (HOCl). Hypochlorous acid is prepared by combining solutions of sodium hypochlorite (NaOCl) and hydrochloric acid (HCl)

$$2NaClO_2 + HOCl + HCl --- \rightarrow 2ClO_2 + 2NaCl + H_2O$$

- Preparation (Reagent grade)
- Chlorine dioxide (ClO₂) is produced by the acidification of sodium chlorite (NaClO₂) solution with sulfuric acid (H₂SO₄):
- $4\text{NaClO}_2 + 2\text{H}_2\text{SO}_4 \longrightarrow 2\text{ClO}_2 + \text{HCl} + \text{HClO}_3 + 2\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}_3$

Properties

- Molar mass: 67.45 g/mol
- Density: 1.64 g/cm³
- Boiling point: 9.7 °C

Uses

- Chlorine dioxide is a disinfectant when added to drinking water
- Chlorine dioxide is used in dentistry as an oxidizing biocide compound to <u>treat bad breat</u>
- Chlorine dioxide can be used as an <u>antimicrobial agent</u> in water used in poultry processing and to wash fruits and vegetables
- In hospitals and other healthcare environments, chlorine dioxide gas helps to sterilize medical and laboratory equipment, surfaces, rooms and tools.
- Chlorine dioxide is used in the electronics industry to clean circuit boards and as a bleach in the paper and textile manufacturing processes

Estimation of available chlorine

- AIM
- To determine the percentage of available chlorine in the given sample of bleaching powder.

• **REQUIREMENTS**:

- Standard Sodium Thiosulphate
- Potassium Iodide 10%
- Glacial Acetic Acid
- Bleaching Powder
- Starch Solution

- APPARATUS
- Burette
- Pipette
- Conical Flask
- Funnel
- Beaker
- Dropper
- Mortar n pestle
- Filter paper
- INDICATOR: Freshly prepared Starch Solution.
- **END POINT:** Deep blue colours disappear.

PRINCIPLE

 Available chlorine is the amount of chlorine liberated by the action of an acid on bleaching Powder (CaOCl2) as shown in the following reaction.

$CaOCl_2 + 2 CH_3COOH \rightarrow (CH_3COO)_2 Ca + H_2O + Cl_2 \uparrow$

- The liberated chlorine oxidize KI and liberated out the lodine in equal amount that may be titrated against Standard hypo solution using freshly prepared starch solution as an indicator.
- $Cl_2 + 2Kl \rightarrow 2KCl + l_2$
- $I_2 + 2 \operatorname{Na}_2 S_2 O_3 \rightarrow 2\operatorname{Nal} + \operatorname{Na}_2 S_4 O_6$
- Starch + $I_2 \rightarrow starch-iodide complex (Deep blue Colour)$

- **PROCEDURE**:
- Step I: PREPARATION OF BLEACHING POWDER SOLUTION
- Weigh out accurately 3 g of bleaching powder in a cleaned and pre-weighed weighing bottle.
- Transfer it into a mortar, crush with a pestle and little distilled water.
- Make a thin paste of bleaching powder sample with distilled water.
- Transfer the paste into 250 ml volumetric flask.
- Wash the mortar and pestle with distilled water and transfer it into the flask to make 250ml.
- Shake well to get homogenous suspension of bleaching powder.

• Step II: ESTIMATION OF AVAILABLE CHLORINE

- Wash the burette with distilled water and rinse with standard hypo solution then fill the burette.
- Pipette out 10ml of homogenous solution of bleaching powder in the conical flask.
- Put 04ml of potassium iodide (KI) and about half test tube of glacial acetic acid into the flask.
- Titrate the liberated iodine against standard hypo solution till a pale yellow colour is obtained.
- Now added 04 drops of starch indicator to get a deep blue colour.
- Continue adding the hypo solution till blue colour disappears. (End point)
- Repeat the experiment to get the concordant reading.

- CALCULATION:
- Bleaching Powder Vs Sodium thiosulphate solution

$$N_{1} V_{1} = N2 V_{2}$$

$$N_{1} \times 10 = 1/10 \times V_{2}$$

$$N_{1} = V2/100$$
Strength of available chlorine = N_{1} \times 35.5 (Eq Wt of chlorine)
% of available chlorine = N_{1} \times 35.5 \times 250/1000 \times 100/W

RESULT:

Amount of available chlorine present in bleaching powder is %

PRECAUTIONS:

- Wash the glass apparatus with the distilled water.
- All the reagents should be freshly prepared.
- Pipette out 10ml of bleaching powder solution accurately.
- The amount of starch indicator should be same in all the titration.
- The end point of the titration should be carefully observed.

Determination of strength of hydrogen peroxide

 The strength of H₂O₂ is expressed in two ways-Volumetric: In this way, the strength is expressed as the volume of oxygen gas liberated from one unit of H₂O₂ liquor under standard condition (i.e. N.T.P.)

For example: If 1cc of H_2O_2 liberates 100cc oxygen at S.T.P. The strength of H_2O_2 will be called 100 volumes H_2O_2 .

Percentage (%w/v): This is the weight of H2O2 per unit volume. This is more commonly used in our country.

Generally 35% H_2O_2 and 50% H_2O_2 used in textile sector in our country. But 50% H_2O_2 is most widely used. If 50 gm H_2O_2 is present in 100cc solution, then it will be called 50% $H_2O_2^2$.

- Apparatus Beaker
- Pipette
- Stirrer
- Graduate cylinder
- Electronic balance
- Reagents
 0.1 N KMnO₄
- 10 % H₂SO₄
- And $H_2 \overline{O}_2$



End Point: The end point is determined when the colorless solution becomes permanent pink in color.

• Calculation:

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

Strength of Hydrogen peroxide =(NXV)KMNO₄x100/ml of sample

Manufacture of Hydrogen Peroxide

- By electrolysis of 50% H₂SO₄
- Hydrogen peroxide is manufactured by the electrolysis of a cold 50% solutions of H₂SO₄ in an electrolytic cell using platinum as anode and graphite as cathode. The reactions taking place are:
- At cathode: $H_2SO_4 \leftrightarrow H^+ + HSO_4^-$
- At anode : $2HSO_4^- \leftrightarrow H_2S_2O_8 + 2e^-$
- Peroxydisulphuric acid formed around anode is withdrawn and then distilled with water under reduced pressure. The low boiling H₂O₂ distils over along with water leaving behind high boiling H₂SO₄ which is recovered and recycled.

• Modification

- Recently, it has been observed that if instead of 50% H_2SO_4 an equimolar mixture of H_2SO_4 and ammonium sulphate is electrolysed, a more concentrated solution of H_2O_2 is obtained.
- At Anode: $2(NH_4)_2S_2O_8 \leftrightarrow (NH_4)_2S_2O_8+2e^-$
- At cathode: $2H^++2e^- \leftrightarrow H_2$
- Ammonium persulphate formed around anode is withdrawn and distilled with water to give H₂O₂

•

- . By autoxidation of 2-ethylanthraquinol
- This is a new method and is widely used in U.S.A. In this process, air is bubbled through a 10% solution of 2-ethylanthraquinol in benzene and cyclohexane when 2-ethylanthraquinol is oxidized to 2-ethylanthraquinone and is formed according to the following equations.



- The thus formed (about 1%) is extracted with water and the aqueous solution is concentrated by distillation under reduced pressure to give 30% (by weight) H₂O₂solution.
- 2 Ethylanthraquinone so produced can be reduced back to the starting to the material i.e.,2-ethylanthraquinol by hydrogen using palladium catalyst.
- Thus, we find that the raw material are H₂ and O₂ only.

COLORANTS

INTRODUCTION

A dye or a dyestuff is usually a coloured organic compound or mixture that may be used for **imparting colour** to a **substrate such as** cloth, paper, plastic or leather in a reasonably **permanent fashion**.

All the dyes may not necessarily be coloured substances. Previously dyes were obtained from animal and vegetable sources. Today most of the available dyes are synthetic dyes prepared from aromatic compounds, which are obtained from coal tar or petroleum.

REQUISITES OF A TRUE DYE

All colored substances are not dyes. However, requisites of true dye are as follows:

- > It must have a **suitable colour**.
- > It must have an **attractive colour**.
- It must be **able to attach** itself **to material** from solution or to be capable of fixed on it. e.g. azobenzene is coloured but cannot fix itself to a fabric. Therefore, azobenzene is not a dye.
- It must be soluble in water or must form a stable and good dispersion in water. Alternatively it must be soluble in the medium other than water.
- The substrate to be dyed must have a natural affinity for an appropriate dye and must be able to absorb it from solution or aqueous dispersion under suitable conditions of concentration, temperature and pH.
- When a dye is fixed to a substrate it must be fast to washing, dry cleaning, perspiration, light, heat and other agencies.
- The shade and fastness of a given dye may vary depending on the substrate due to different interactions of the molecular orbital's of the dye with the substrate.

CIASSIFICATION OF DYES

Dyes are **classified in various ways** according to

- > The methods of application to the fiber
- > Their chemical constitution
- > The types of materials to be dyed
- > The intermediates from which they are prepared

۶

Classification of dyes according to application

Dyes are classified according to application method, for convenience of the dyer.

1. Acid Dyes

These dyes are usually the **sodium salts** of the **colour acids** which may **contain sulphonic acid** or **phenolic group**. These dyes give very bright colour and have a **wide range** of **fastness properties**.

Acid dyes are **used to dye** fibers having **basic groups**, such as wool, silk and polyamides and are applied under acidic condition that causes **protonation of the basic groups**.

 $Dye^- + H^+ + Fiber \longrightarrow dye^- - H^+ - Fiber$

Generally the acid dyes can be **removed by washing**. The **rate of removal** depends on the rate at which the dye can diffuse through the fibber under condition of washing and

the **rate of diffusion** depends on temperature, size & shape of dye molecule and number & kind of linkage formed on fibers.

E.g. Picric acid, metanil yellow, naphthol yellow, orange II etc

2. Basic or Cationic dyes

They have a **basic amino group** which is protonated **under acidic condition** of fibers. This give intense and brilliant shades but has poor light fastness.

These are **used for dyeing** silk and wool directly but for dyeing cotton the basic dye needs mordant like tannic acid or some synthetic organic substance.

Methyl violet, methylene blue, crystal violet, rhodamine etc

3. Direct Dyes

They usually **bear sulphonic acid groups** and become strongly adsorbed on cellulose. However it is **not acid** dyes because **sulphonic acid** groups are **not used** as a means of **attachment to the fiber**. The **dyeing process** with this type of dye is **reversible** because they are held in cellulosic fiber by **adsorption**. They have **poor fastness** to washing but may be improved by treating with resins and dye fixing agents. **E.g.** Congo red

Special types of direct dye having amino groups which is first diazotized and then coupled on the fiber to improve washing fastness. **E.g.** Direct Black K 17

4. Mordant or Adjective Dyes

These dyes have **poor affinity** for **fiber**, these dye **require** a **pretreatment** of **fiber** with a mordant which bind the dye. The **mordant** gets attached to the fiber and then combines with the dye to form an **insoluble complex** called a **'Lake'**. **Mordents** such as aluminum, chromium and iron salt are used depending upon the fiber and the class of dyes.

- > **Chromium salts** for dyeing wool and for printing cotton with mordant azo dyes
- > Aluminum salts for dyeing and printing cotton with alizarin
- > **Iron salts** for printing of cotton with o-nitrosophenol.

5. Azoic Dyes

These dyes are **produced inside textile fiber** by **azo coupling**. The dye is fast to washing. A **variety of colours** can be developed by **proper choice** of **diazo** and **coupling components.** In usual procedure, the fiber is first impregnated with an alkali solution of the coupling component. This is then treated with a solution of the diazonium compound. Finally the dyed goods are soaped and rinsed.

The major application of azoic dyes is dyeing and printing of cellulosic fiber especially cotton giving shades of high standard light fastness.

6. Oxidation Dyes

These dyes are **produced by oxidation of colourless compound**. **E.g.** aniline is oxidized in cotton with sodium dichromate in the presence of a metal catalyst to produce an aniline black. This process of dyeing is an **economical way** to produce **full black shades**. The appearance and fastness of the dyeing may be varied over wide range by choice of oxidant condition and catalyst.

7. Ingrain Dyes

The term **ingrain applicable to** all types of **dye formed on** the **substrate** by the development or coupling of **intermediate compounds** which **are not themselves** true **finished dyes**. These groups thus included azoic and oxidation dyes e.g. the very bright blue copper phthalocyanine is produced inside cotton fiber. These types of dyeing are extremely fast to that light and washing.

8. Vat Dyes

These are **insoluble**, but their **reduced forms** which are **soluble**. These dyes are applied in their reduced forms which are obtained by treating it with reducing agent such as alkaline sodium hyposulphite in large wooden vats from which the name Vat dyes has come.

The cloth is immersed in the vat, having a reduced vat dye for sufficient time, then it dried in air, **due to oxidation** of dye on fiber the original **insoluble coloured dye** is obtained which is very fast to washing, light and bleaching as well e.g.



These dyes offer excellent fastness; these dyes are most often used on cotton fabrics which are subjected to the severe conditions of washing and bleaching. It can also be used for dyeing wool silk and cellulose acetate.

9. Sulfur Dyes

These dyes are **insoluble dyes** and when **reduced** with sodium sulfide they become **soluble**. These dyes are adsorbed on the fiber and on exposure to air they are **deoxidized to original insoluble dye** inside the fiber and they become very resistant to removal by washing but their brightness and fastness to bleaching are often inferior.

Sulfur dye **contain sulfur both** as an integral part of chromophore and in attached polysulfide chain

E.g. Heating m-dinitrophenol with sodium polysulfide gives m-toluenediamine which is fused with sulfur gives brown sulfur dye.

Dye-S-S-Dye (Sulfur dye/Insoluble form) 🗢 2 Dye-SH (soluble form)

10. Disperse Dyes

These dyes are **water insoluble** dyes originally introduced for dyeing cellulose acetate and are usually applied from fine **aqueous dispersion**.

The molecules are generally small and some -OH or -NH₂ groups to give finite water solubility at dyeing-temperature.

Dispersed dye may be applied by a dry heat process to polyester fibers. Here the dye achieves molecular form by sublimation from the solid dye to the fiber process. **Extremely small sizes of particles** are important to the fiber process. It gives excellent washing fastness. This dye is also used to dye cellulose acetate, nylon polyester and polyacrylonitrile fibers.

E.g. Cellitone scarlet B and cellitone fast violet 6B

11. Reactive Dyes

They are relatively new class of the dye, which **forms covalent bond** with fibers possessing hydroxyl and amino groups.

An important type of reactive dye has chlorine atoms which react with hydroxyl groups in cellulose when applied in presence of alkali. It is evident that there is an ether linkage between the dye and fiber is established.

Another important type of this dye involves an activated vinyl group, which can reacts with a cellulose hydroxyl group in the presence of base.

 $Dye - SO_2-CH_2-CH_2-OSO_2Na \longrightarrow Dye -SO_2-CH=CH_2$

 $Dye - SO_2-CH = CH_2 + HO - cellulose$ \longrightarrow $Dye - SO_2CH_2-CH_2 - O - cellulose$

These dyes offer excellent fastness to washing, as they become the part of fiber. The other property depends on the structure of colored part of molecule and by what means it gets attached to the reactive part. **E.g.** Procion red dye and Procion brilliant red

12. Solvent Dyes

These dyes do not contain sulphonic acid or other water soluble groups and are **soluble in organic solvent**. The nature of which varies according to application. They are

used in manufacture of stains, varnishes, inks, lacquors, typewriter ribbons, candles, shoe polishes, soap and cosmetics etc.

Instead of water, **tetrachloro ethylene** as used in suitable dyeing processes especially for the dyeing of the polyester fibers.

13. Solubilised Vat Dyes

It is difficult to store the sodium salts of leuco compounds of vat dyes because they are prone to air oxidation.

However, the solublised vat dyes, the sulphuric esters of leuco compound are fairly stable and could be stored without oxidation. They are vat dyes derivatives from with the parent vat dye could be produced on the fiber by the oxidation with an acid (dilute sulphuric acid) and on oxidizing agent (sodium nitrate).



14. Sulphurised vat dyes

The method of application is **similar to those vat dyes** because they have either a quinonoid structure or other structure basically similar to that of quinonoid. They are prepared by thionation of certain anthraquinone and indophenol derivatives.

15. Disperse Reactive Dyes

These dyes have **dual characteristic** properties. They are obtained as microfine aqueous paste and have reactive grouping. These are **applied on polyamide** fiber from **aqueous dispersion** as a dispersive dye and subsequently **dyed as a reactive** dye under alkaline conditions to facilitate the reaction of the dye with the fiber.

16. Synthetic fiber Dyes

Nylon: As it is basic, it may be **dyed with acid** as well as with **disperse dyes**. Although acid dyes have good wet as well as light fastness, they cause the variation in the nylon fiber and hence not much used, similarly for acid mordent dyes.

When the disperse dyes are used to dye nylon, they give wet fastness but do not build heavy shades with good wet fastness.

Terylene (polyester, Dacron): It is **dyed by** the **disperse dyes**, which slowly penetrate but their wet fastness is good sometime diphenyl or orthophenyl phenol is used with dispersed dye in dyeing of terylene because they acts carriers for accelerating the penetration in the fabric.

Orlon (polyacrylonitrile): It is acidic, it may be **dyed with basic dyes** and also with **disperse dyes** or certain **vat dyes**, the drawback of disperse dye is that they do not have good penetration in to fabric, which can be increase by dyeing at 120°C under pressure.

COLOUR AND CHEMICAL CONSTITUTION

Bathochromic and Hypsochromic effects

If a **structure change** in a dye molecule **shifts** the **absorption** towards **higher wavelengths**, it will **deepen** the **colour** of the dye in accordance to the following sequence. Yellow ► Orange ► Red ► Purple ► Violet ► Blue ► Green

Any **group** or **factor** that produces the **deepening** of the **colour** in accordance to the above sequence is known as **Bathochrome** and the **effect** i.e. the deepening of colour, is known as **Bathochromic effect** e.g.



Figure: Absorption spectra of benzene, aniline nitrobenzene and p-nitroaniline If a **structural change** in a dye molecule **shifts** the **absorption** from higher to **lower**

wavelengths, it will lighten the colour of the dye in accordance to the following sequence

Green► Blue► Violet ► Purple► Red ► Orange ► Yellow

Any group or a factor that will lighten the colour of the dye in accordance to the above sequence is known as **hypsochrome** and its effect produced is known as **Hypsochromic effect**

Changes in the structure of a dye due to which the **intensity of absorption increases** are said to be **hyperchromic** on the other hand, structural changes which **decrease the intensity** of **absorption** are termed as **hypochromic**.

Bathochromic, hypsochromic, hypochromic and hyperchromic effects are represented by the absorption spectra as show in the figure



The introductions of certain group in a dye molecules cause the Bathochromic and Hypsochromic effects. This is summarized in the following facts:

> The **bathochromic effect** is produced by the **introduction of** additional **auxochromes**

such as -OH and -NH₂ groups in a dye molecule. For example, when an additional - NH_2 group comes in the aniline yellow, chrysodine is produced which is in orange coloured dye.



- In addition to the auxochromes, the o-and p- directing groups when presence on the aromatic ring also deepens the colour. For example alkyl, aryl and halogens deepen the colour and are therefore known as Bathochrome.
- When the alkylation of amino group is done, it produces the bathochromic effects on the other hand when the alkylation as well as acylation of phenolic groups are done, these will produce hypsochromic effect. A good example of illustrating the bathochromic effect is to introduce six methyl groups in pararosaniline (red dye) nucleus to give crystal violet(violet colour)

 $-NH_2 \rightarrow -NH(CH_3)_2$

Bathochromic effect

 $-OH \rightarrow -OCH_3 \text{ or } -OCOCH_3$

Hypsochromic effect

The bathochromic effect is also produced by salt formation because it increases the possibility of resonance, which is again due to the formation of dye ions.

Colour

The **psychological sensation** which is **produced** when the **light** of **certain wavelength** reaches the eye is known as the **colour**. Colour is dependent on and varies with the nature of the light illuminating the coloured substance.

The ordinary light can be categorized in following three groups or types

| Part of Light | Range of Wavelength of light | | |
|----------------------------|------------------------------|--|--|
| Ultraviolet light | 1000 - 4000° A | | |
| Visible part (White light) | 4000-7500°A | | |
| Infrared | 7500-1,00,000° A | | |

The **range of wavelength visible** to **human eyes** is consisting of electromagnetic radiation's covering rays of wavelength in the **region 4000 to 8000°A**. In this region (visible region) **seven different colours** namely violet, indigo, blue, green, yellow, orange and red are present (**VIBGYOR**). The sequence of UV, visible and IR is shown below.

| Ultraviolet | Violet | Indigo | Blue G | Green | Yellow | Orange | Red | Infra Red |
|-------------|--------|--------|--------|--------|--------|--------|--------|-----------|
| (UV) | (V) | (I) | (B) | (G) | (Y) | (O) | (R) | (IR) |
| Invisible | | | v | isible | | | | Invisible |
| | 4000°A | ١ | | | | 8 | 8000°A | |

When white light is incident on a substance, colour is obtained in the following different ways :

- > If the white light **reflected completely**, the substance will appear **white**
- > If the white light is **absorbed completely**, the substance will appear **black**.
- If all the wavelengths of white light are absorbed except a single narrow band, which is reflected, the colour of the substance will be colour of the reflected band.
- If only a single band of white light is absorbed, the substance will have the complementary colour of the absorbed band, which is shown below.

| Wavelength | Colour absorbed | Colour visualized |
|-------------|-----------------|-------------------|
| 4000-4350 | Violet | Yellow-Green |
| 4350-4800 | Blue | Yellow |
| 4800-4900 | Green-Blue | Orange |
| 4900-5000 | Blue-Green | Red |
| 5000 - 5600 | Green | Purple |
| 5600-5800 | Yellow-Green | Violet |
| 5800-5950 | Yellow | Blue |
| 5950 - 6050 | Orange | Green - Blue |
| 6050 - 7500 | Red | Blue - Green |

Relation between colour and chemical constitution

The colour of compound is related to its chemical constitution. **Graebe and Libermann** have stated that **reduction** of coloured organic compound results in the **loss of colour** and **oxidation** of the reduced compound **regenerates** the **original colour**. Hence they concluded that unsaturation was responsible for development of colour.

WITT'S THEORY

According to this theory, there existed a relationship between colour and chemical constitution, a dye is made up of two parts, **chromophores and auxochromes.**

Chormophores

The colour usually appears in an organic compound if it contains certain **unsaturated** group called Chormophores. (Chromo-colour and phores -bearing)Typical chromophores are shown below

| - N = O Nitroso | K) | o - quinonoid |
|---------------------|----------|---------------------------------|
| C = S Thio Carbonyl | - CH = N | azo methine |
| -N = N - azo | - N 20 | Nitro |
| -N = NO azoxy | -N=N-NH | azo amino |
| C = O carbonyl | =(= | p- quinonid |
| C = C ethylenic | | |

There are two types of chromophores Independent chromophores

When a **single chromophores** is sufficient to import colour to the compound, then it is called independent chromophores e.g. -N=O, N02, -N=N, -N=NO, -N=N-NH, p-quinonoid etc.

Dependent chromophores

When more than one chromophores are required to impart colour to a compound, then it is called dependent chromophores

Acetone containing one carbonyl group is colourless while biacetyl containing two carbonyl group is yellow

H₂C-

Acetone (Colourless)

-CH₂

Biacetyl (Yellow) Similarly Diphenylpolyenes having formula

 $Ph-(CH = CH)_n-Ph$ here if,

n = 1 or 2 the compound is colourless

n = 3 the compound is yellow

the compound is orange n = 5

the compound is copper - Bronze. n = 7

n – 11 the compound is violet - black

Shade of the colour is also influenced by the **proximately of chromophores**, If these are separated by other groups, the compounds become colourless.

| 0 0 | 0 | 0 |
|----------------------------|-------------------|---|
| IK 11 | . | 1 |
| $H_3C - C - C - CH_3$ | $CH_3 - C - CH_2$ | – CH ₂ – C – CH ₃ |
| Biacetyl (yellow coloured) | Diketo hexa | ne (colourless) |

Compound containing Chromophores then it is called as Chromogen.

Auxochromes

The presence of **certain groups** in a **chromogen** leads a **deepening** of the **colour**, even though they are **not chromophores** and **do not impart colour** to the compound when present without chromophores, Witt's called these groups as auxochromes. (Auxein means to increase and chroma means colour) Some typical auxochromes are as shown below.

| Amino | -NH ₂ | Chloro | -CI |
|-----------------|------------------------------------|-----------|--------------------|
| Methyl amino | -NHCH ₃ | Methyl | -CH₃ |
| Dimethyl amino | - N(CH ₃) ₂ | Methoxy | -OCH ₃ |
| Sulphonic acid | -SO₃H | Cyano | -CN |
| Hydroxy | -OH | Acetyl | -COCH ₃ |
| Carboxylic acid | -COOH | Acetamide | -CONH ₂ |

These auxochromes serve two functions

- > They **increase** the **intensity** of the colour.
- > They **make the chromogens a dye** by fixing it the fabric or the material to dyes either by association or by salt formation.

Auxochromes are of two types

Bathochromic Auxochromes

These are the groups which increases the depth of the colour. These shift the absorption maximum from the violet towards the red and bring deepening of colour. It is called "<u>Red Shift</u>" e.g. H-atoms are replaced by 'R' in amino group.

Hypsochromic Auxochromes

These are the groups which decreases the depth of colour. These shift the absorption maxima from red toward violet and result in the fading of colour. It is called "<u>Blue shift</u>" e.g. Hatom is replaced by acetyl group in hydroxyl or amino group.

ARMSTRONG'S THEORY

According to theory, all the **coloured compounds** could be represented by **quinonoid structures**

> Benzene is colourless whereas benzo-quinones are coloured



If phenolphthalein is present in benzoquinone structure it is coloured, and if it is present in benzonoid structure it is colourless



Limitations

This theory could not explain colouring characteristics of the entire compound, e.g. even though iminoquinone and di-iminoquinone have quinonoid structure, yet they are colourless.



There are other **compounds**, which are **coloured**, **but do not have quinonoid structure** e.g. biacetyl, Fluvene and azobenzene.



Armstrong attempted to explain the colour of **p-nitrophenol**, on the basis of **quinonoid structure**, **but** there was **no evidence** for their **existence of a structure**.

Then Hantzesh proved that there exists the phenomenon tautomarism in nitrophenol is by preparing ester form it.



According to hantzsch the change in colour of compound could be attributed to a change in structure from benzenoid to quinonoid or vice versa i.e. colour is an additive

property.



For example the groups -NO₂ and -ONa, both are present then impart colour, but if present alone do not do so. This means that the two groups must be interchange to yield a new structure for the molecule. This phenomenon is known as chromo-isomerism.

BAEYER'S THEORY

According to this theory, the **colour**, is might be **due to** the **structural oscillation** of the **quinonoid** condition between the **two benzenerings**.

Fuchsonimine, (I) is colourless, but if amino groups is introduced in one of the benzene rings, it introduces deeply coloured Doebner's violet.



Fuchsonimine

This is because of structural oscillation of the quinonoid condition between two benzene rings as shown in figure (II) & (III).





Fuchsonimine (Colourless)

Doebner's Violet (Coloured)

NIETZKI'S THEORY

According to this theory, the **colour** of dye is **deepen by** the **addition of substituent** and due to **increase** in **molecular weight**.

But for the **deepening** of colour, **nature of the group** added is important and not its weight this can be explain by following example

CH₃ -(CH₂)_a - X - (CH₂)_b-CH₃

Here X is chromophores, if X remain same and a & b are having different values, the depth of colour is not affected or no deepening of colour occurs.

WATSON'S THEORY

Besides the length of conjugated chain, other factor are also has effect on colour change of compound. If weight of dye is increased without changing the length of conjugated chain, the shade becomes deeper, because vibration becomes slower due to increase in molecular weight, e.g. Fluorescein on bromination gives eosin (tetra bromo-fluorescein) which has much deeper colour then Fluorescein due to the molecular weight.

MODERN THEORIES OF COLOUR AND CONSTITUENTS

There are two most important theories called valence bond and molecular orbital theory. These theories are based upon following concepts.

1. Quantization of light energy

Light is quantized in the units of energy called quanta or photons.

2. Absorption of Radiation by molecules
The amount of light energy absorbed in the visible spectrum is the only responsible

factor for the **shade** of the colour. The main function of absorbed energy is to raise the energy of the molecule from ground state to excited state.

 $\Delta E = E_1 - E_0 = hc/\lambda, = hv$

Where,

 ΔE = Quantum energy h = Plank's constant

- E₁= Energy of excited state
- λ = Wavelength of the absorbed radiation c = Velocity of light
- E₀= Energy atground state v =Frequency of light

The amount of energy absorbed i.e. ΔE depends upon the structural configuration of dye. For instance

- If the electrons are tightly bound, as in saturated compound, no light of visible region will be absorbed and hence the compound will appear colourless.
- If the electrons of a molecule are loosely bound as in unsaturated compounds, the absorption may occur in the visible region and the substance will then appear coloured.

For a coloured substance the values of ΔE lie between 71.0 and 35.5 kcal/mole as we go from 4000 to 8000°A.

As the electrons occupy definite orbital, it means that ΔE and hence frequency of light absorbed must have definite values. As each values of a frequency is associated with a

particular line of spectrum. Thus the spectrum of the compound will consists of large number of lines corresponding to a large number of excited states of the large number of molecules constituting the compound. These lines then appear as band because of value of E which very close to each other. The existence of the bands in definite parts of the spectrum which produces the color.

3. Dipole moment

The **molecule** can **absorb light** only if its **dipole moment changes**. The more the molecule is symmetrical, the smaller the transition dipole and molecule absorbs light very slowly, and vice versa. Thus if the group which is introduce in a molecule, decreases the symmetry and increases transition dipole of molecule, the intensity of the absorbed light will increased.

VALENCE BOND THEORY OR RESONANCE THEORY

Postulates of theory

The *π*-electrons of groups of atom (i.e. chromphores) which may get transferred from ground state to excited state by the absorption of radiation, thus producing the colour.

- Auxochromes are groups, which tend to increase resonance by interacting the unshared pair of the electrons on nitrogen or oxygen atoms of the auxochromes with *n*-electron of the aromatic ring. This increase in resonance increases the intensity of absorption of light and shift the absorption bend to longer wavelength deepening the colour.
- > The **dipole moment changes** as a result of the **oscillation of electron pairs**. For the ease of excitation of groups, the following order has been observed.

$$N = O > C = S > N = N > C = O > C = N > C = C$$
 (light)

The colour deepens in the opposite direction.

The more the possibility and longer the path for a charge to oscillate in a compound, the more long wavelength of light will be absorbed. And therefore more deeper would be the color of the compound.

Consider the following examples.

a) Explain Benzene is colourless, nitrobenzene is pale yellow and p-nitro aniline is dark yellow In benzene, two kekule structures (I & II) are major structures contributing to its

resonance hybrid. Also a number of charged canonical structures are possible (as shown in figure III). But they contribute relatively little to either ground or excited state and thus benzene absorbs in the U.V. region also benzene is symmetrical. Therefore, it is colourless. Also it has no chromophoric group.



In **nitro benzene charged structures contribute** much more to its **resonance hybrid**.

And due to **loss of symmetry** of the molecule, the absorption is shifted to longer wavelength, thereby produces **pale yellow**.



Due to chromophore also colour deepens.

Similarly in **p-nitroaniline** the **contribution** of the **charged structure** is **still large** and hence the light of longer wavelength is absorbed. Thus deepening colour occurs to **dark yellow.**



The **comparison** of the **dipole moment** for nitrobenzene (0.21D) aniline (1.48D) and pnitroaniline (6.1D) also gives an idea that there is relatively high contribution of the charged structure to resonances, hybrid of p-nitro aniline.

Here in p-nitroaniline each of amino and nitro groups cooperatively helps the other in shirting the actual state of the molecule in the direction of charged structures.

b) Pure p-nitrophenol is colourless but yellowish in alkaline solution.

It is evident from the fact, that in **alkaline solution** the **nitropheno**l exists as **nitrophenoxide ion** in which only the charged structures are contributing to its resonance hybrid. Therefore compound absorb light energy at higher wavelength.



c) p-or o-quinones has yellow colour which can be explained by resonance theory

Here due to **two oxygen atoms**, there occurs **greater contribution** of the charged structure to the **resonance hybrid**. Thus these compound absorbed light of the higher wavelength and compound appear coloured.



d) Explain p-aminozaobenzene is yellow but in acidic solution it becomes violet.



The **deepening** of colour is due to **contribution** of **both charges structures** in resonance hybrid, while in case of **p-aminoazobenzene** only **one charged structure**

contribute to the resonance hybrid.

e) All the triphenylmethane dyes has much deeper colour this can be explain by resonance theory.



Doebner's violet

This is due to the **delocalisation of unit electrical charge** over a long path. If **one** of the **amino grou**p of Doebner's violet **is replaced by H-atom** then the molecule formed i.e.

p-amino triphenylmethane is **colourless** because here **no oscillation of +ve charge** takes place.



f) Crystal violet has one principle absorption peak (λ max 5900°A) while malachite green has two absorption peaks.



Melachite green, the molecule is **unsymmetrical** and as **two axes of polarisability** differing in degree lying at right angle, also here the possibility of the **oscillation for +ve charge** is **restricted to two benzene ring**, hence it shows **two peaks** at 4230 - 6250°A.

Crystal violet has **center of symmetry** in which **all three benzene rings** participate in resonance as shown in above structures. **Polarisability** becomes **equal** in **all directions** in the **plane of the molecule** and hence there is only **one absorption peak**. Also the **oscillation** for **+ve charge** is **not restricted**, but oscillates in all benzene rings.

g) Effect of conjugation on resonance

The **longer** the **conjugation** in a molecule, the **deeper** will be the **colour** because the conjugation system of the **double bonds** provides a **long path** of resonance. This **shifts** the **absorption to longer wavelength**. **E.g.** diphenylpolyenes. The colour change as 'n' increases which shift the change absorption to higher wavelength side and colour becomes deeper.

According to **Lewis and Calvin** the **deepening** of colour with **increase** in **length of conjugation** which has been attributed to increase in number of electrons which are participating in conjugation. In some compound increasing in conjugated system is also able to increase the deep colour, which do not have aromatic nucleus.



 β – carotene (orange red)

As the **number of fused rings increases**, the **colour deeper** more and more for examples.





Graphite (Black)

If the **conjugated system** also has **atoms** as **N**, **O**, **S**, etc, it **absorbs** light of **longer wavelength** than the corresponding compounds which consists of conjugated system of only the carbon atoms.

MOLECULAR ORBITAL THEORY

According to this theory, the excitation of a molecule means the transference of one e-from an orbital of lower energy to higher energy. This electrons may be σ , π or n.

The higher energy states are commonly known as "Anti bonding" orbital. It's association with σ and π bonds are called σ * and π * but there are no antibonding orbitals associated with 'n' electrons because they do not form bonds.

σ* Anti bondingπ* Anti bondingnLoan pair, non-bondingπ Bondingσ Bonding

Figure: schemes showing molecular orbitals

The electronic transition can occur by the absorption of ultra-violet and visible radiation. Although several transitions are possible only the following types are allowed. (1) $\sigma \rightarrow \sigma^*$ (2) n $\rightarrow \sigma^*$ (3) n $\rightarrow \pi^*$ and (4) $\pi \pi^* \rightarrow$

This **transition** may be arranged in their **decreasing order of energy**.

 $\sigma \longrightarrow \sigma^* > n \longrightarrow \sigma^* > \pi \longrightarrow \pi^* > n \longrightarrow \pi^*$

 σ $\overline{\sigma}$ type of **transition** requires a **very large amount** of **energy** as σ - electrons are very tightly bonded. The saturated hydrocarbons which do not have any π or n electrons may undergo only π π^* transition and are **not absorbed** in the ordinary **ultraviolet region** e.g. ethane absorb at 1350°A.

If a compound has non-bonding e- pair then $n \rightarrow \sigma^*$ transition take place also in addition to the σ σ^* transition. Compounds having **non-bonding electrons** on **hetro atom** like O,N,S etc. can undergo $n \rightarrow \sigma^*$ transitions also in addition to the $\sigma \rightarrow \sigma^*$ transition. But non-bonding electrons are much more loosely held then the σ electrons. Therefore the energy required for $n \rightarrow \sigma^*$ will be much lower than that for $\sigma \rightarrow \sigma^*$ transitions and hence they are usually absorbed in **ordinary U.V. region** e.g methyl iodide shows λ max. at 2580°A. while trimethylamine at 2270°A.

 $n \longrightarrow \pi$ *and $\pi \longrightarrow \pi$ *are of lower energy than both the $\sigma \longrightarrow \sigma$ *and $\pi \xrightarrow{\bullet} \sigma$ * transition and therefore, take place at longer wavelengths.. Furthermore, $\pi \xrightarrow{\bullet} \pi$ *transitions are of lower energy than the $n \longrightarrow \pi$ * but require more energy than the $n \longrightarrow \sigma$ *.

E.g. Acetaldehyde shows two absorptions, one at 1800°A.Corresponding to $\pi \longrightarrow \pi^*$, while the other at 2900°A, corresponding to n $\longrightarrow \pi^*$ transition. Considered the data of following table

| Compound | Transition | Absorption band(max) |
|-----------------------|--|----------------------|
| $H_2C = CH_2$ | $\sigma \longrightarrow \sigma^*, \pi \longrightarrow \pi^*$ | 1750°A |
| $H_2C = CH-CH - CH_2$ | π → π* | 2170°A |
| B-Carotene | π → π* | 4510°A |

From above absorption it is concluded that as conjugate of double bond increases, energy required for $\pi \pi^* r$ ansition decrease and absorption shift to longer wavelength.

> Explain Benzene which is symmetrical, possesses no transition dipole, does not absorb

visible light and is colourless. While **nitro-benzene** is **not symmetrical** and thus its Catoms are unequally charged. The introduction of NO_2 group in the benzene molecule extends its conjugation, the decreases the energy difference between the highest level of the ground state and the lowest level of the excited state and hence absorption are expected at longer wavelength then the benzene and thus nitrobenzene appears **yellow**.

Consider aniline molecule, in which the lone pair of electrons present on nitrogen atom is in conjugation with the benzene ring and therefore it possesses dipole transition due to this aniline absorbs light of longer wavelength than that of benzene. In acid solution the lone pair of electron of nitrogen atom is coordinated with proton.

This destroy conjugation and transition dipole due to this the absorption maxima of anillinium ion is almost the same as that of benzene.

AZO DYES

The dyes containing soluble azo group (-N=N-) are known as azo dyes.

The dyes containing insoluble azo group (-N=N-) are known as azoic dyes. These dyes are not found in readymade form. Azoic dyes are produced by a reaction between two components. The components are:

- 1. Coupling Compound (Naphthol)
- 2. Di-azo -compound or diazo base or diazo salt.
- The colored substance formed from this colorless compound is insoluble in water and washing fastness of this shade is excellent.
- Azo dyes contain the characteristic azo group –N=N– which is present to a greater or lesser degree in nearly all classes of dyes.
- Over half of all commercial dyestuffs belong in this general category.
- By varying the chemical composition it is possible to produce acid, basic, direct, reactive, disperse and mordant dyes containing the azo chromophore.
- These dye stuffs always contain Azo groups in its chemical structure.
- Light fastness property is admirable. Brightness of shade is also admirable.
- It is directly insoluble in water.
- These dye stuffs are always used in dyeing cellulosic material.

• Here dyeing operation is completed by two bath arrangement. One is called impregnation bath and another is called developing bath

- Alkali resistance is poor to good, Index 2-4.
- Suitable for lighter shade dyeing (Light resistance: Poor to very good, Index 2-7).
- This dye stuff is called developed dye due to formation of dye in fiber during dyeing process.
- •Addition of salt increases the substantivity.

Synthesis of Methyl Orange

In this experiment the azo dye methyl orange is prepared by a electrophilic substitution with arene diazonium salts (diazo coupling).



p-Dimethylamino-Azobenzenesulfonic Acid (Methyl Orange)

Methyl orange is a pH indicator and due to its clear color change it is very often used in titrations.

Methyl orange changes color at the pH of a mid-strength acid and is usually used in titrations for acids.

Unlike a so called universal indicator, methyl orange does not have a full spectrum of color change, but has a sharper end point.

Methyl orange is not generally used as dye because it is sufficiently fast to light and soap. However, Its sodium salt is used as indicator in acidimetry and alkalimetry because its sharp colour change over small pH range.

It gives yellow colour in alkaline solution (above pH 4.4) and red in acidic solution (below pH 3.1).

The change in colour of the compound in different media has been ascribed to the difference in its structure in the two media.

Chemically it is sodium **p-dimethylaminoazobenzene** – **p'** – **sulfonate**.

It is acidic azo dye.

It is obtained by coupling diazotized sulfanilic acid with dimethyl aniline.

Dye generally isolated as sodium salt. The hydrochloride of methyl orange is called *"Kelianthin"*

−NMe2 NaOH NaO3S-NMe₂ •N₂C| + ⟨

METHYL ORANGE

DETAILED PROCEDURE

Preparation of the diazonium salt of sulfanilic acid

Although sulfanilic acid is insoluble in acid solutions, it is nevertheless necessary to carry out the diazotization reaction in an acid (HNO_2 , nitrous acid) solution. This problem can be circumvented by precipitating sulfanilic acid from a solution in which it is initially soluble. The precipitate which is formed is a fine suspension and reacts instantly with nitrous acid. The first step is to dissolve sulfanilic acid in basic solution.



Formation of nitrosonium ion

In order to obtain the nitrosonium ion (NO⁺), sodium nitrite has to be treated with hydrochlorid acid. During the addition of the acid, the sulfanilic acid is precipitated out of solution as a finely divided solid, which is immediately diazotized (see below).





Addition to N,N-dimethylaniline

The finely divided diazonium salt is allowed to react immediately with dimethylaniline in the solution in which it was precipitated.



Methyl orange is often used as an acid-base indicator. In solutions that are more basic than pH 4.4, methyl orange exists almost entirely as the **yellow** negative ion. In solutions that are more acidic then pH 3.2, it is protonated to form a **red** dipolar ion.





Due to these properties, methyl orange can be used as an indicator for titrations that have their end points in the pH 3.2 to 4.4 region. The indicator is usually prepared as a 0.01% solution in water. In higher concentrations in basic solution, of course, methyl orange appears **orange**.

CONGO RED

It is **Basic azo dye**. It is simple benzidine bisazo dyestuff. Prepared by **coupling** tetraazotised (bis diazotised) benzidine with two molecules of naphthionic acid. Blue dye so obtained is converted into its disodium salt having red colour using NaCl. The **red salt** is capable of dyeing cotton only.



DISODIUM SALT (RED)

Red salt is very sensitive to acids, the colour turns from red to deep blue in the presence of strong mineral acid and dull purple in by organic acid.

The change in colour from red to blue in the presence of inorganic acids may be explained due to occurrence of resonance as follows.

Congo red is used as an indicator in acid-base titration.

Congo red paper is used for testing acidity of the solution



In the first step of the synthesis, anthranilic acid is reacted with hydrochloric acid (HCl) and sodium nitrite (NaNO₂) to produce an intermediate compound called a diazonium salt.

Once the diazonium salt is formed, the second step involves reaction with a compound known as dimethylaniline which actually gives methyl red as the final product



Uses

- As indicator in 0.1% alcoholic solution; pH: 4.4 red, 6.2 yellow.
- Used for titrating NH₃, weak organic bases, e.g., alkaloids; not suitable for organic acids, except oxalic and picric acid.
- Methyl red is easily reduced, thereby losing its color, and readings should be made promptly.
- It is gradually being replaced by sulforphthalein indicators, such as bromocresol green, which are more stable and exhibit a sharper change in color.

| Questions | opt1 | opt2 | opt3 |
|--|--|--|---|
| | | | |
| The nitrating agent is a reactant. | Electrophilic | Nucleophilic | both |
| enters? | Ortho | Para | Meta |
| The Nitration reaction serves to introduce one or more groups into a reacting molecule. | Nitro group | Nitrite group | Ammonia group |
| Amination by reduction involves the synthesis of what by reductive methods? | Toluene | Phenols | Amines |
| Which of the following is the Tertiary amine? | NH3 | R-NH2 | R-NH-R' |
| What is the formula of Methylamine? | CH3-NH2 | C2H5-NH2 | CH3-NH-CH3 |
| Which one of the following is the most important halogen in terms of preparations? | Bromine | Chlorine | Iodine |
| Introduction of -SO2CL, Which type of Sulfonation is it? | Sulfoxidation | Sulfochlorinati on | Sulfoalkylatio n |
| Amination by ammonolysis is a process of formation of what? | Phenols | Amines | Alcohols |
| Which of the following processes can saponification be used for? | For the production of plastics | In blow glass artistry | To make soap |
| Which of the following term describe saponification? | Cleaving of ester molecules into carboxylic acid and alcohol | Dehydration synthesis by removing water | Hydrolysis of a salt by adding a weak acid |
| Which of the following is considered a useful alkali in saponification reactions? | CCl4 | Cl– | NaOH |
| Saponification value is the number of milligrams of KOH required to saponify what present in the 1g of oil or fat? | Salts | Hydrocarbon | Fatty acids |
| Which of the following is used as a reactant for the nitration of benzene to form nitrobenzene? | HNO2 | HNO3 | Mixture of HNO2 AND HNO3 |
| What is meant by Halogenation? | Introduction of Halogen atom | Removal of Halogen atom | Introduction & Removal of Halogen atom |
| Which is the most important Nitrating medium? | Nitric acid and H2SO3 | Nitric acid and Sulphuric acid | Nitrogentetrao xide and - H2SO4 |
| What is the mixture of Nitric acid and Sulphuric acid called? | Nitrite ion | Combined acid | Addition acid |
| What is meant by an Electrophilic nitro group? | Repels electron | Attracts electron | Free radical atoms |
| In Sulfonating, which acid group is used? | ОН | SO-OH | -SO2-OH |

| opt4 | Answer |
|---|--|
| | Electror 1:11: |
| neutral | Electrophilic |
| In all positons | In all positons |
| None of the mentioned | Nitro group |
| Alkyl | Amines |
| R-N(R')-R" | R-N(R')-R" |
| CH3-N (CH3)- CH3 | CH3-NH2 |
| Fluorine | Chlorine |
| Sulfoacylation | Sulfochlorinati on |
| Halogens | Amines |
| The formation of alloys | To make soap |
| Synthesis of two alkyl groups to make an ether | Cleaving of ester molecules into carboxylic acid and alcohol |
| Pb+ | NaOH |
| unsaturation | Fatty acids |
| Mixture of HNO2 and H2SO4 | Mixture of HNO2 AND HNO3 |
| Introduction of Hydrogen atom | Introduction of Halogen atom |
| Nitric acid and HCl | Nitric acid and Sulphuric acid |
| Mixed Acid | Mixed Acid |
| Attract protons | Attracts electron |
| -SO3-OH | -SO2-OH |

| Sulfation involves placement of which group on carbon atom? | -OSO2OH | -SO2-OH | -ClS03H |
|--|--------------------------|--------------------------|----------------------|
| Why is aq. NH3 used as an amminating agent in majority of cases? | Handling | More energy | Lower reaction rate |
| Ethyl acetate is produced by the mixture of ethanol with what? | Acetic acid | Carboxylic acid | Ketones |
| It is of fatty oils which leads to formation of soaps. | Alkaline hydrolysis | Alkaline electrolysis | Hydrolysis |
| Aspirin is | acetyl salicylic acid | sodium salicylate | methyl salicylate |
| Cleaving of ester molecules into carboxylic acid and alcohol is called | saponification | oxidation | Hydrolysis |
| Introduction of Halogen atom is called | saponification | Halogenation | Hydrolysis |
| Production of soap is by | saponification | oxidation | Hydrolysis |
| The widely used drug Aspirin is synthesized by | esterification | saponification | oxidation |
| The reaction used in synthesis of explosives | esterification | saponification | Nitration |
| The conversion of Ar/R-H to Ar/R-X is | saponification | Halogenation | Hydrolysis |
| The conversion of Ar/R-H to Ar/R-SO3H is | sulphonation | Halogenation | Hydrolysis |
| Catalytic hydrogenation of an aldehyde or ketone in the presence of ammonia is | sulphonation | Halogenation | Hydrolysis |
| Dimethyl terephthalate is obtained by esterification of what? | Benzene | Ethanol | Terephthalic acid |
| TNT, Nitrobenzene, m-dinitrobenzene are products of what type of reaction | esterification | saponification | Nitration |
| Saccharin is prepared by | sulphonation | Halogenation | Hydrolysis |
| The process used in the manufacture of polyethylene terephathalate | esterification | saponification | oxidation |
| Nitrating phenol with sodium nitrate yields | Aspirin | Paracetamol | Ibuprofen |
| Ester and alkali plays major role in which reaction | saponification | Halogenation | Hydrolysis |
| ArH +> ArNO2 + H2O. | HNO | HNO2 | HNO3 |
| The rate of Nitration depends upon what? | Temperature | Concentration | Pressure |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |

| HCl | -OSO2OH |
|------------------|--------------------------|
| less energy | Handling |
| Amides | Acetic acid |
| Electrolysis | Alkaline hydrolysis |
| ethyl salicylate | acetyl salicylic acid |
| amination | saponification |
| amination | Halogenation |
| amination | saponification |
| Hydrolysis | esterification |
| Hydrolysis | Nitration |
| amination | Halogenation |
| amination | sulphonation |
| Reductive | Reductive |
| amination | amination |
| Methanol | Terephthalic acid |
| Hydrolysis | Nitration |
| amination | sulphonation |
| Hydrolysis | esterification |
| Brufen | Paracetamol |
| amination | saponification |
| Not needed | HNO3 |
| time | Concentration |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |

| Questions | opt1 | opt2 | opt3 |
|---|---|--|---|
| What is the electrophile in the electrophilic substitution reaction of benzene using oleum and conc. H2SO4? | SO ₃ | NO ₃ | NO2+ |
| What is the electrophile in the acylation of benzene? | AlCl ₃ | CO+ | Cl+ |
| In which condensation an enol or an enolate ion reacts with a carbonyl compound to form a β -hydroxyaldehyde or β - hydroxyketone (an aldol reaction), followed by dehydration to give a conjugated enone happens? | Aldol | Claisen reduction | Henry condensation |
| Which of the following halide can give best SN2 reaction? | Primary alkyl halide | Tertiary alkyl halide | Secondary alkyl halide |
| Which of the following statement is incorrect about nucleophiles? | Nucleophiles have an unshared electron pair and can make use of this to react with an electron deficient species | The nucleophilicity of an element (an electron donor) generally increases on going down a group in the periodic table | A nucleophile is electron- deficient species |
| In a free radical reaction, free radicals are formed at | initiation step | propagation step | termination step |
| An acceptor of pair of electron is termed as | nucleophile | electrophile | carbocation |
| Formation of radicals which attack reactants molecules generate more free radicals. This step is a | initiation step | propagation step | termination step |
| Alkenes mostly follow reaction of | addition reaction | elimination reaction | substitution reaction |
| Condensation reaction is the reverse of which of the following reaction? | lock and key hypothesis | hydrolysis | glycogen formation |
| Condensation reaction always results in the formation of complex sugar (disaccharide or polysaccharide) and which of the following? | amino acids | lipids | water |
| a reaction in which one molecule combines with another to form a larger molecule with no other products. | Addition | Substitution | Elimination |
| is a chemical reaction during which one functional group in a chemical compound is replaced by another functional group. | Addition | Substitution | Elimination |

| opt4 | Answer |
|----------------|-----------------|
| | |
| | |
| NO+ | SO ₃ |
| D CO I | |
| R-CO+ | K-CO+ |
| | |
| | |
| Knoevenagel | Aldol |
| condensation | condensation |
| All can give | |
| SN2 reaction | Primary alkyl |
| at same rate | halide |
| | |
| | |
| | |
| | |
| All good | |
| nucleophiles | |
| are good bases | A nucleophile |
| when we deal | is electron- |
| across the | deficient |
| period | species |
| hoth A and D | both A and D |
| both A and B | both A and B |
| anion | electrophile |
| | propagation |
| elimination | step |
| step | 11.4 |
| 11 0.1 | addition |
| all of them | |
| .1 | 1 1 1 . |
| oxidation | nydrolysis |
| | |
| | |
| maltose | water |
| | |
| | |
| ring opening | Addition |
| • | |
| | |
| | |
| ring opening | Substitution |

| Additon reaction takes place in | saturated compounds | Unsaturated compounds | Both Saturated & Unsaturated coumpounds |
|--|---|--|---|
| Free radicals are produced by | heterolytic bond fission | homolytic bond fission | Both |
| Ions are produced by | heterolytic bond fission | homolytic bond fission | Both |
| nucleophile is an chemicals species | Electron rich | Electron deficient | Proton rich |
| Electophile is a chemical species | Electron rich | Electron deficient | Proton rich |
| SN2 denotes | unimolecular substitution reaction | bimolecular substitution reaction | bimolecular addition reaction |
| SN1 denotes | unimolecular substitution reaction | bimolecular substitution reaction | bimolecular addition reaction |
| SN1 reaction takes place in steps | 1 | 2 | 3 |
| SN2 reaction takes place in steps | 1 | 2 | 3 |
| Which of the following is rate determining step in electrophilic substitution reaction? | Generation of electrophile | Attack by an electrophilic reagent on benzene ring | Formation of product |
| Nitro group is meta-directing in electrophilic aromatic substitution reactions? | increases electron density at meta-position | increases electrons density at ortho and para- positions | decreases electron density at meta-position |
| Identify the one which does not come under the organic addition reaction | Hydration | Dehydration | Halogenation |
| What will be the reactivity of chlorobenzene in an electrophilic substitution reaction with benzene? | Reacts very slowly than benzene | Reacts in the same way as benzene | Reacts faster than benzene |
| Identify the one which on reaction with carboxylic acid at high temperature gives Ester | Ketone | Alcohol | Aldehyde |
| Why are aryl halides less reactive towards nucleophilic substitution reactions as compared to alkyl halides? | The formation of a less stable carbanion | Longer carbon halogen bond | The inductive effect |
| Which of the following is not true for SN1 reactions? | They occur through a single step concerted reaction | They are favoured by polar solvents | Tertiary alkyl halides generally react through this mechanism |

| Not in | |
|---|---|
| Unsaturated coumpounds | Unsaturated compounds |
| None of these | homolytic bond fission |
| None of these | heterolytic bond fission |
| Proton deficient | Electron rich |
| Proton deficient | Proton rich |
| unimolecular addition reaction | bimolecular substitution reaction |
| unimolecular addition reaction 4 | unimolecular substitution reaction 2 |
| 4 | 1 |
| All of the mentioned | Attack by an electrophilic reagent on benzene ring |
| decreases electron density at ortho and para- positions | decreases electron density at ortho and para- positions |
| Hydrohalogen ation | Dehydration |
| Does not react with benzene | Reacts very slowly than benzene |
| Sugars | Alcohol |
| Sp2- hybridized carbon attached to the halogen | Sp2- hybridized carbon attached to the halogen |
| Concentration of nucleophile does not affect the rate of such reactions | They occur through a single step concerted reaction |

| Which types of isomers are formed in rearrangement reactions? | structural isomers | Geometrical isomers | Optical isomer |
|--|---|---|--|
| Which of the following statement is incorrect about electrophiles? | Electrophiles are positively charged or neutral species having vacant orbitals | The electrophiles are attacked by the most electron- populated part of one nucleophile | Chemical species that do not satisfy the octet rule such as carbenes and radicals are electrophiles |
| Which of the following is the most activating in electrophilic aromatic substitution? | NO2 | NHCOCH3 | CN |
| The characteristic reaction of benzene in which a hydrogen atom is replaced by an electrophile | Aldol condensation | electrophilic aromatic substitution | Claisen reduction |
| A reaction in which two molecules combine to form a single molecule with elimination of small molecule | Addition | substitution | polymerization |
| Two molecules of aldehydes reacts with each other to form a condensed product called Benzoin.The reaction called | Aldol condensation | electrophilic aromatic substitution | Claisen reduction |
| A reaction in which two reactants add together in a single step to form a cyclic product. | Aldol condensation | Cyclo addition | Claisen reduction |
| Diels-Alder reaction is example for | Aldol condensation | Cyclo addition | Claisen reduction |
| The reaction which proceed by reaarangement of atoms or groups in the molecule is | Addition reaction | substitution reaction | Reaarangemen t reaction |
| is used in the industries for the synthesis of paracetamol. | Beckmann rearrangement | Claisen reduction | Henry condensation |
| Ultraviolet light causes splitting of chlorine molecules into chlorine atoms. This step is | Initiation | propagation step | termination step |
| Collision of any two free radicals results in | Initiation | propagation | termination |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |

| Conformationa l isomers | structural isomers |
|---------------------------------|---|
| Electrophiles are Lewis base | Electrophiles are Lewis base |
| NH2 | NH2 |
| Henry condensation | electrophilic aromatic substitution |
| condensation reaction | condensation reaction |
| Benzoin condensation | Benzoin condensation |
| Benzoin condensation | Cyclo addition |
| Benzoin condensation | Cyclo addition |
| condensation reaction | Reaarangemen t reaction |
| Aldol condensation | Beckmann rearrangement |
| Addition | Initiation |
| Addition | termination |
| | |
| | |
| | |
| | |
| | |
| | |

| Questions | opt1 |
|--|---------------------|
| | |
| Which of the following is not a suitable solvent for oils and fats? | Benzene |
| Saponification is hydrolysis | By alkalis |
| Lubrication is necessary to protect wear and tear caused due to | Electrostatic force |
| On increasing the lubrication, the efficiency of the machine | Increases |
| The additive in many soaps and detergents that greatly harm the environment is: | perfume |
| he saponification of a fat or oil is done using | KOH |
| Which of the following is a typical soap molecule? | Calcium stearate |
| The catalyst used in the addition of iodine is | Ni/ Pt |
| The number of milligrams of KOH required for the saponification of one gram of oil or fat is called | Acid number |
| Iodine number is defined as number of grams of iodine needed for the iodination of gram/grams | |
| of oil or fat. | 1 |
| amount of free fatty acids present in fat or oil? | Acid number |
| Which of the following helps in the classification of oils into drying, semi-drying and non-drying categories? | Acid number |
| Which of the following is of special value in testing the purity of butter and desi-ghee? | Acid number |
| It is of fatty oils which leads to formation of soaps. | Alkaline hydrolysis |
| Which of the following is not saponifiable? | Ground nut oils |
| The saponification value of the vegetable oil is | Very high |
| The different properties of the soaps is due to the | Nature of alkali |

| opt2 | opt3 |
|-------------------------------------|--|
| | |
| | |
| CCl | CHCl ₂ |
| | |
| In digestive tracts of human beings | By acids |
| | |
| Gravitational force | Frictional force |
| D | Domoin como |
| Decreases | Remain same |
| 1, | 1 1 / |
| salts | phosphates |
| | |
| NaOH | HCI |
| Potassium permanganate | Sodium bicarbonate |
| i otassiani pointanganato | Source of the so |
| Lewis acids | CH ₃ MgCl |
| | |
| Iodine number | Richert-Meissl number |
| | |
| | |
| 5 | 100 |
| | |
| Iodine number | Saponification number |
| | |
| | |
| Iodine number | Saponification number |
| | |
| Iodine number | Saponification number |
| Alkaline electrolysis | Hydrolysis |
| | 11901019313 |
| Mineral oils | Castor oil |
| | |
| Very low | Moderate |
| | |
| Nature of the oil | I emperature variance |

| opt4 | Answer |
|-----------------------|-----------------------|
| | |
| | |
| Water | Water |
| | |
| By salts | By alkalis |
| | |
| Magnetic force | Frictional force |
| Does not get affected | Increases |
| Does not get uneeled | |
| | nhosnhates |
| | phosphates |
| NaCl | NaOH |
| | |
| Sodium stearate | Sodium stearate |
| | |
| HgCl ₂ | HgCl ₂ |
| | |
| Saponification number | Saponification number |
| | |
| 1000 | 100 |
| | |
| Richert-Meissl number | Acid number |
| | |
| | |
| Richert-Meissl number | Iodine number |
| | |
| Richert-Meissl number | Richert-Meissl number |
| | |
| Electrolysis | Alkaline hydrolysis |
| Coconut oil | Mineral oils |
| | |
| Cannot be determined | Very high |
| | |
| Nature of the fats | Nature of alkali |

| Acid number of a lubricating oil isrequired to neutralise all acidic constituents of 1 g of oil. | Mgs of KOH |
|--|-------------------------|
| The fatty oils mostly constitute | Glycerine |
| The acid content with time. | Decreases |
| The acid value of the lubricating oil is must be less than | 7 |
| Darkening of the oil colour takes place due to | Oxidation |
| Soaps are metal salts of | fatty acids |
| Soaps are prepared by chemical treating of by strong alkaline solutions. | Oils and salts |
| Lubricating oil thickened with metallic soaps or by adding solid forms | grease |
| 99% of grease is produced from | petroleum oil |
| A good liquid lubricant must possess the property of | Low viscosity |
| Which of the following is not the liquid lubricant? | Olive oil |
| The lubricating oils must be refined to remove | Wax |
| The viscosity of an oil decrease when temperature | Decreases |
| The moisture in the environment the oxidation. | Increases |
| Oxidation in lubricants is | Desirable |
| The fire point is the lowest temperature at which the vapour of oil burns continuously for at least when a small flame is | |
| brought near to it. | 1 Second |
| be low. | coefficient of friction |
| Which of the following are the disadvantages of solid lubricants? | poor heat dissipation |

| Mgs of K ₂ SO ₄ | Mgs of NaOH |
|---------------------------------------|--------------------------------|
| | |
| Glycol | Ethanol |
| T | D |
| Increases | Remains constant |
| 0.7 | 1 |
| | |
| Reduction | Hydrolysis |
| 1 1' '1 | 1 |
| carboxylic acids | amino acids |
| | |
| Oils and fats | Salts and fats |
| | |
| vaselines | oils |
| olive oil | castor oil |
| | |
| High bailing point | High freezing point |
| ingh coming point | |
| Palm oil | Castor oil |
| | |
| Hydrocarbons | Nitrogen |
| Is constant | Increases |
| is constant | literases |
| Decreases | Neutralises |
| | |
| Undesirable | Important |
| | |
| | |
| 2 Seconds | 4 Seconds |
| | |
| calorific value | stability |
| more effective even at high | . . |
| pressures | high resistance to detoriation |

| Mgs of Na ₂ SO ₄ | Mgs of KOH |
|--|-------------------------|
| Glycerol | Glycerol |
| Becomes zero | Increases |
| 0.1 | 0.1 |
| Catalysis | Oxidation |
| inorganic acids | fatty acids |
| Fats and proteins | Oils and fats |
| petrol | grease |
| whale oil | petroleum oil |
| Low oiliness | High boiling point |
| Grease | Grease |
| Oxygen | Wax |
| 100oC | Increases |
| Do not change | Increases |
| Necessary | Undesirable |
| | |
| 5 Seconds | 5 Seconds |
| cleanliness | coefficient of friction |
| permit equipment is heavy | poor heat dissipation |

| The rate of change of the viscosity with raise in temperature is measured by an arbitrary scale called as | Arbitrary constant |
|--|-------------------------|
| The temperature expressed in | |
| multiples of 1oC at which the haze | |
| of the wax crystal appears when the | |
| oil is cooled under prescribed | |
| conditions is called | Pour point |
| The fire point of an oil is about higher than the flash | |
| point. | 5-10degree C |
| Select the incorrect statement from the following option. | Lubricant keep out dirt |
| The science of friction, lubrication and wear is called | Endiology |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |

| T T | 17 1 |
|-------------------------|----------------------------------|
| Viscosity constant | Viscosity index |
| | |
| Cloud point | Oxidation stability |
| | |
| 5-20degreeC | 5-30degreeC |
| Lubricant act on a goal | Lubricant transmit fluid a surra |
| Lubricant act as a sear | Lubricant transmit fluid power |
| Geology | Tribology |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |

| Arbitrary index | Viscosity index |
|-----------------------------|-----------------------------|
| Acid number | Cloud point |
| | • |
| 5-40degreeC | 5-40degreeC |
| | |
| Lubricant enhance corrosion | Lubricant enhance corrosion |
| | |
| Morphology | Tribology |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |

| Questions | opt1 | opt2 | opt3 |
|--|------------------------------------|----------------------------------|---------------------------------------|
| | | | |
| Select the one which is wrongly mapped | Sodium carbonate – Washing soda | Sodium chloride – common salt | Calcium carbonate – slaked lime |
| During the chloralkali process, which of the following is obtained at a node? | Hydrogen | Sodium hydroxide | Sodium chloride |
| What is the chemical formula of bleaching powder ? | Ca(OH) ₂ | CaCl ₂ | CaOCl ₂ |
| What is the chemical name of bleaching powder ? | calcium oxy chloride | calcium chloride | calcium oxide |
| Bleaching powder is prepared by passing | Chlorine over slaked lime | Chlorine over quick lime | Oxygen over slaked lime |
| Hydrogen peroxide is | stronger acid than water | weaker acid than water | An oxidising agent |
| What is chloride of lime | Sodium hydroxide | Sodium chloride | Sodium carbonate |
| The strength of hydrogen peroxide is found by titrating against | NaOH | KMnO ₄ | КОН |
| What is the chemical formula of sodium hypo chlorite ? | Ca(OH) ₂ | CaCl ₂ | NaOCl |
| Bleaching powder contains of available chlorine. | 16% | 33.30% | 66.60% |
| Which of these is used as the most common disinfectant? | Chlorine | Chlorine dioxide | Ozone |
| What is the most effective dosage of chlorine to be used as a disinfectant? | 1-6 mg/L | 6-8 mg/L | 8-10 mg/L |
| What is the process of removal of contaminating pathogenic micro-organisms from the articles called? | Decontamination | Sanitization | Disinfection |
| means the deactivation or killing of pathogens. | Reduction | Disinfection | Oxidation |
| is the process of elimination of most pathogenic micro-organisms. | Reduction | Disinfection | Oxidation |
| The amount of chlorine available in water after disinfection is | Free chlorine | Residual chlorine | Chlorine demand |
| What is the other name of bleaching powder ? | Sodium hydroxide | Sodium chloride | Sodium carbonate |
| What is the chemical formula of hydrogen peroxide ? | Ca(OH) ₂ | CaCl ₂ | CaOCl ₂ |
| What is the chemical formula of chlorine dioxide ? | Ca(OH) ₂ | CaCl ₂ | ClO ₂ |

| opt4 | Answer | |
|---------------------------------------|---------------------------------------|--|
| Sodium hydroxide – caustic soda | Calcium carbonate – slaked lime | |
| Chlorine | Chlorine | |
| H ₂ O ₂ | CaOCl ₂ | |
| calcium dichloride | calcium oxy chloride | |
| Carbon dioxide over slaked lime | Chlorine over slaked lime | |
| A reducing agent | stronger acid than water | |
| Bleaching powder | Bleaching powder | |
| HCl | KMnO ₄ | |
| CHCl ₃ | NaOCl | |
| 99.90% | 33.30% | |
| UV rays | Chlorine | |
| 10-12 mg/L | 1-6 mg/L | |
| Sterilization | Decontamination | |
| Pyrolysis | Disinfection | |
| Pyrolysis | Disinfection | |
| Residual demand | Residual chlorine | |
| Calcium hypochlorite | Calcium hypochlorite | |
| H ₂ O ₂ | H2O2 | |
| H ₂ O ₂ | ClO ₂ | |

| In lab H2O2 is prepared by | Cold H ₂ SO ₄ +BaO ₂ | HCl+BaO ₂ | H2SO4+Na ₂ O ₂ |
|--|---|--|---|
| The oxide which gives hydrogen peroxide on treatment with dil.sulphuric acid | PbO ₂ | BaO ₂ .8H ₂ O+O ₂ | MnO ₂ |
| Hydrogen perovide is | Oxidising agent | Reducing agent | Both Oxidising and Reducing agent |
| When sodium peroxide is treated with dil. sulphuric acid we get | sodium sulphate and water | sodium sulphate and oxygen | sodium sulphate, hydrogen and oxygen |
| Hydrogen peroxide is obtained by electrolysis of | water | dil.sulphuric acid | HCl |
| is used as monopropellant | Hydrogen peroxide | fused sodium peroxide | barium peroxide |
| In electrolytic synthesis of H2O2, what is added to improve efficiency of sulphuric acid | Sodium hydroxide | ammonium sulphate | Sodium chloride |
| A mixed salt of hydrochloric acid and hypochlorous acid. | Sodium hydroxide | Sodium chloride | Sodium carbonate |
| What is used as deodorizing and cleaning agent | Bleaching powder | Sodium hydroxide | Sodium chloride |
| The action of chlorine on dry slaked lime gives Sodium hydroxide is reacted with chlorine gas, to produce is used in dentistry | Bleaching powder | Sodium hydroxide | Sodium chloride |
| | Bleaching powder | Sodium hydroxide | Sodium chloride |
| | Chlorine dioxide | Sodium hydroxide | Bleaching powder |
| When sodium peroxide is added to ice cold dilute solution of sulphuric acid it gives | Hydrogen peroxide | fused sodium peroxide | barium peroxide |
| The oxidation of sodium chlorite (NaClO2) by hypochlorous acid gives | Bleaching powder | Sodium hydroxide | chlorine dioxide |
| The indicator used in iodimetric determination of available chlorine is | Methyl orange | phenolphthalein | EBT |
| The amount of chlorine liberated by the action of an acid on bleaching Powder | Available chlorine | Residual chlorine | Free chlorine |
| When 2-ethylanthraquinol is oxidized it gives | Hydrogen peroxide | fused sodium peroxide | barium peroxide |
| In the presence of cobalt chloride bleaching powder looses | Chlorine | Oxygen | calcium chloride |
| The chemical used in the manufacture of chloroform | Bleaching powder | Sodium hydroxide | Sodium chloride |

| H_2+O_2 | Cold H ₂ SO ₄ +BaO ₂ |
|--|---|
| TiO ₂ | BaO ₂ .8H ₂ O+O ₂ |
| Neither Oxidising nor Reducing agent | Both Oxidising and Reducing agent |
| sodium sulphate and hydrogen peroxide | sodium sulphate and hydrogen peroxide |
| fused sodium peroxide | dil.sulphuric acid |
| Sodium hydroxide | Hydrogen peroxide |
| Sodium carbonate | ammonium sulphate |
| Bleaching powder | Bleaching powder |
| Sodium hypochlorite | Sodium hypochlorite |
| Chlorine | Bleaching powder |
| Sodium hypochlorite | Sodium hypochlorite |
| Sodium hypochlorite | Chlorine dioxide |
| Sodium hydroxide | Hydrogen peroxide |
| Hydrogen peroxide | chlorine dioxide |
| starch | starch |
| Break point chlorine | Available chlorine |
| Sodium hydroxide | Hydrogen peroxide |
| hydrogen | Oxygen |
| hydrogen | Bleaching powder |
| For what purpose bleaching powder is used in drinking water? | Disinfection | nitration | sulphonation |
|--|-------------------|--------------------------|--------------------|
| Water molecule with one extra atom of oxygen is | Hydrogen peroxide | fused sodium peroxide | barium peroxide |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |

| hydration | Disinfection |
|---------------------|----------------------|
| Sodium hydroxide | Hydrogen peroxide |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |

| Questions | opt1 |
|---|---|
| | |
| An azo dye is fixed on fabrics by the process applicable in | Vat dyes |
| An azo dye is formed by interaction of an aromatic diazonium chloride with | A phenol |
| Alizarin belongs to the class of | Vat dyes |
| To which class of dyes does phenolphthalein belong | Azo dyes |
| Which of the following is an example of basic dye | Alizarin |
| Which of the following is a direct dye | Phenolphthalein |
| Which of the following is a vat dye and often used in dyeing jeans | Indigo |
| Which of the following is not a chromophore | -N=N- |
| The compounds used to fix a dye to the fabric is known as | Mordant |
| Methyl orange is an indicator in acid-alkali titration. It gives | Yellow colour in alkaline medium |
| An example of anthraquinone dye is | Alizarin |
| The dyes which are applied to the fabric in the colourless reduced state and then oxidised to coloured state are called | Vat dyes |
| Which of the following is a basic dyes | Aniline yellow |
| Which of the following is an azo dye | Phenolphthalein |
| A dye imparts red colour on fabric. What colour of light was absorbed by the dye | Blue |
| Which one is disperse dye | Congo red |
| The difference between a dye and a pigment is that a dye: | is held to the surface of the fiber by a resin. |
| The auxochrome chemical group of a dye chemical: | is the color producing group of the dye chemical. |

| opt2 | opt3 | opt4 |
|--|--|--|
| | | |
| Mordant dyes | Developed dyes | Substantive dyes |
| An aliphatic primary amine | Benzene | Nitrous acid |
| Mordant dyes | Substantive dyes | Reactive dyes |
| Nitro dyes | Triphenyl methane dyes | Phthalein dyes |
| Malachite green | Indigo | Orange I |
| Congo red | Alizarin | Indigo |
| Alizarin | Picric acid | Crystal violet |
| -NO | -NO2 | -NH2 |
| Azeotrope | Bleaching agents | Lake |
| Red colour in acid medium | Yellow colour in acid medium | Yellow colour in alkaline medium and red colour in acid medium |
| Basic acid | Methylene blue | Phenolphthalein |
| Mordant dyes | Developed dyes | Substantive dyes |
| Congo red | Alizarin | Indigo |
| Orange I | Methylene blue | Malachite green |
| Red | Green | Orange |
| Alizarin | Celliton | Indigo |
| is an inorganic chemical that permeates fibers | usually diffuses into the interior of a fiber from a water solution. | lays on the surface of the fiber. |
| influences the intensity of the dye. | acts as a mordant. | influences the intensity of the dye. |

| Answer |
|--|
| Developed dyes |
| A phenol |
| Mordant dyes |
| Phthalein dyes |
| Malachite green |
| Congo red |
| Indigo |
| -NH2 |
| Mordant |
| Yellow colour in alkaline medium and red colour in acid medium |
| Alizarin |
| Vat dyes |
| Aniline yellow |
| Orange I |
| Green |
| Celliton |
| usually diffuses into the interior of a fiber from a water solution. |
| influences the intensity of the dye. |

| only the Indigofera tinctoria plant. |
|---|
| alizarin, carminic acid and tartrazine |
| chlorophylls, carotenoids, and anthocyanins |
| the cochineal insect (genus Dactylopius) |
| haematin |
| an FD & C dye added to the egg |
| not enough chlorophyll. |
| chlorophylls |
| a dye color that bites into the fiber. |
| If a dye is fast to light, it will also be fast to washing. |
| must be reduced to a soluble form so that it can dissolve in the dye bath and get trapped in the cellulose fiber. |
| to preserve the food. |
| coupling reaction |
| coupling reaction |
| |

| the Indigofera plant and the woad (Isatis tinctoria) plant and over 50 plants on the African continent. | the madder (Rubia tinctorium) plant. | the Indigofera and the weld plants. |
|---|--|--|
| indigo, bixin and alizarin | tartrazine, FD&C Blue #1, and indigo | chlorophyll, yellow #6 and haematin |
| chlorophylls, carotenes and xanthophylls | chlorophyll a, chlorophyll b and carotenoids | beta-carotene, chlorophyll and alizarins |
| mollusk shells (genus Murex) | the madder plant (genus Rubia) | an anthocyanin. |
| a synthetic black dye | indigo and a mordant | no dye needed |
| a carotenoid | an anthocyanin | natural meansthe fat is just yellow. |
| the dye being washed out by moisture. | the substitution of hydrogen for magnesium in the chlorophyll molecule. | the chlorphyll molecule breaking down. |
| anthocyanins | carotenoids | xanthophylls |
| a metallic ion that attaches to fibers and causes a color emission. | a chemical that stops the dye process. | a metallic ion or salt added to the dye bath to make dyes more colorfast by forming a bridge between the dye and the fiber. |
| A dye that is fast on one type of fiber will be fast on all fabrics. | Wool is the most easily dyed fiber and the resulting color will change the least. | There are no standardized methods of testing colorfastness. |
| penetrates both the outer ring and the inner core of a piece of fiber. | remains in its soluble form inside the denim fabric. | must be in an insoluble form so that it can get trapped in the cellulose fiber. |
| to make the food more appealing to the consumer. | to give the food a longer shelf life. | to make the food not react with its container. |
| desorption | diazotization | assimilation |
| desorption | diazotization | assimilation |

the Indigofera plant and the woad (Isatis tinctoria) plant and over 50 plants on the African continent.

indigo, bixin and alizarin

chlorophylls, carotenoids, and anthocyanins

mollusk shells (genus Murex)

haematin

a carotenoid

the substitution of hydrogen for magnesium in the chlorophyll molecule.

anthocyanins

a metallic ion or salt added to the dye bath to make dyes more colorfast by forming a bridge between the dye and the fiber.

Wool is the most easily dyed fiber and the resulting color will change the least.

must be reduced to a soluble form so that it can dissolve in the dye bath and get trapped in the cellulose fiber.

to make the food more appealing to the consumer.

coupling reaction

diazotization

| Colored compounds which are formed on addition of phenol to diazonium ion are called | azo dyes |
|---|--------------------------|
| Azo dye is prepared by the coupling of phenol and which of the following compound? | Diazonium chloride |
| When diazonium salt solution is treated with KI, it forms which of the following compound? | Bromobenzene |
| Benzene diazonium chloride forms orange red dye with which of the following compound? | Nitrophenol |
| What is the general formula of Diazonium salt? | RN2+X- |
| The reactive dyes are applied to a cellulosic fiber in an alkaline dye bath, they form a with hydroxyl group of the fiber by chemicallyreacting with fiber | Covalent bond |
| The application of color to the whole body of a textile material with somedegree of fastness | Dyeing |
| Acid dyes on nylon are held by | Electrostatic attraction |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |

| colored compounds | aromatic compounds | transition metals |
|-------------------|--------------------|--------------------|
| o-nitro aniline | Benzoic acid | Chlorobenzene |
| Iodobenzene | Phenol | Acid |
| Benzophenol | Resorcinol | Methanol |
| RN+ | RXI | RN2+HSO-2 |
| Hydrogen bond | Salt linkage | vander waals force |
| Printing | Discharge style | painting |
| Hydrogen bond | Salt linkage | vander waals force |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |

azo dyes

Diazonium chloride

Iodobenzene

Resorcinol

RN2+X-

Covalent bond

Dyeing

Electrostatic attraction