APPLIED CHEMISTRY II

1. Answer any five from the following (15 M)

a. Select the compound which possesses highest octane number and highest cetane number out of n-heptane, n-octane and isooctane.

Ans:

Octane number:
n-heptane → 00
n-octane → 60
isooctane → 100

Cetane number:
n-heptane → 100
n-octane → 00
isooctane → 60

∴ The highest octane number is of n-heptane and highest octane number is of isooctane.

b. Iron does not rust even if the zinc coating is broken in a galvanized iron pipe. Give reasons.

Ans:

1. Anodic coating type of coating protect base metal "sacrificially". Corrosion of iron does not enhance even on breaking "anodic coating" as it heals its film.
2. The iron, coating metal is at lower electrode potential than zinc base metal.
3. Galvanizing is a process of coating iron with thin coat of zinc to protect them from rusting.
4. The iron sheets are cleaned with dilute H_2SO_4 i.e. pickling to remove impurities. In this process, NH_4Cl flux is used.
5. Molten zinc is maintained at 425-430^{0}C and it becomes the reason of iron and rusting even of zinc coating is broken in a galvanized iron pipe.

c. Calculate the higher and lower calorific values of coal sample contains 84% carbon, 1.5% sulphur, 0.6 Nitrogen, 5.5% hydrogen and 8.4% oxygen.

Ans:

Dulong Formula

$G.C.V = 1/100[8080C + 34500(H\text{-}O/8) + 2240S]$ kcal/kg

$= 1/100[8080*84+34500*(5.5 – 8.4/8) + 2240*1.5]$kcal/kg

$= 1/100[678720+153525+3360]$

$= 1/100[835605]$

$= 8356.05$ kcal/kg

$\therefore$ G.C.V $= 8356.05$ kcal/kg

Net calorific value $=$ G.C.V $-$ [9H/100 *587]kcal/kg

$= 8356.05 - [9*5.5/100*587]$

$= 8356.05 - 290.57$

$\therefore$ N.C.V $= 8065.48$ kcal/kg

d. What are drawbacks of plain carbon steel

Ans:

1. With increasing percentage of carbon the ductility decreases and brittleness increases.
2. Plain carbon steel cannot be deep hardened on heat treatment, because due to effect of heat, only surface of steel get hardened while the inner layer of the steel remains soft.
3. During the use the mechanical properties of plain carbon steels get deteriorated at higher temperature. Thus the use of plain carbon steel to make various machine parts has limitations of temperature.
4. The corrosion resistance of plain carbon steel has limited use in manufacturing various machine parts, though strengths and welding characteristics may be suitable.

e. Explain the principle 'Prevention of waste' in green chemistry.

Ans:

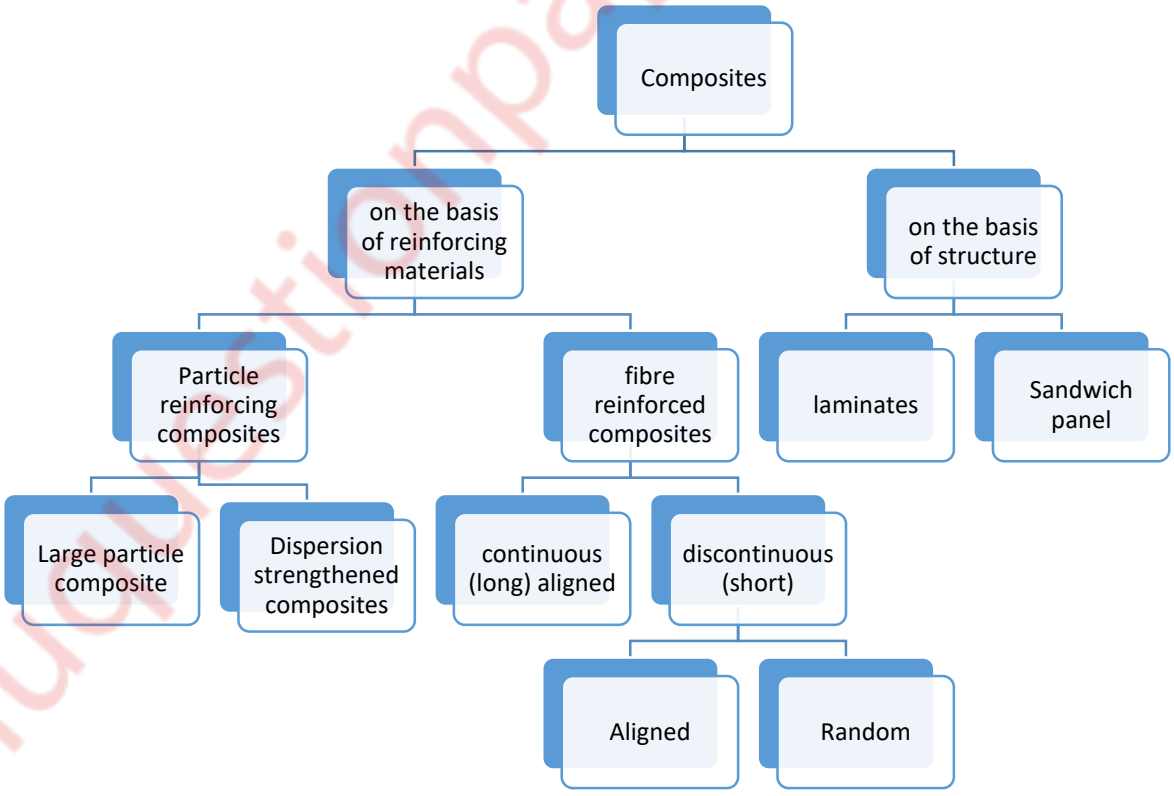
1. It is better to prevent waste than to treat and clean up waste after it is formed.
2. It has been a common practice to dump waste on land or in water or release in air. This resulted in soil, water and air pollution.

3. This made the legislation to be stringent on industries and hence there was compulsion to have waste treatment and disposal units attached to the manufacturing plants. Thus the cost of process increased considerably.
4. Thus green chemistry, involves to design chemical synthesis in such a way that the process involving pathway to give products, leaving no waste to treat or clean up.

f. Define and classify composite materials.

Ans:

1. Composite is defined as "A multiphase product made by two or more existing materials which exhibits properties of its constituents as well as shows certain unique properties of its own".
2. The composite materials are classified on the basis of reinforcing materials or structure as follows:



g. Mention three functions of thinner in paint.

Ans:

Functions of thinner in paint are:

1. To adjust viscosity and formulation in plant.
2. It helps in drying of the paint.
3. It suspend the pigment and dissolve film forming material.

Q.2.a) Define corrosion of metals. Explain the electrochemical theory of wet corrosion, giving its mechanism. (6 M)

Ans:

1. Any process of destruction and deterioration of any material is known as corrosion.
2. When metal is in immediate contact of aqueous /acidic/alkaline/natural/electrolytic solutions, the short circuited galvanic cells get set all along the surface of metal. This gives rise to corrosion which proceeds by electrochemical principles.
3. Wet corrosion is more common than dry corrosion.
4. The co-ordinating metals behave like galvanic cells thereby the parts of metal acting as an anode is consumed while the other part which is acting as cathode remains unchanged.

Mechanism:

Corrosion, by this mechanism occurs usually if environment to the metal is acidic.

Example:

Pipe lines made of iron metal get corroded if industrial waste material, or solutions of non-oxidising acids is transported through them.

The following reaction occurs:

$$Anode \xrightarrow{e-} Cathode$$

$$Fe \rightarrow Fe^{+2} + 2e^{-} \rightarrow 2H^{+} + 2e^{-} \rightarrow H_2$$

From above reactions, we can say that the flow of electrons take place from anode to cathode. These electrons are gained by cathodic reaction, and at cathodic H^+ ions are eliminated as H^2 gas. The overall mechanism can be represented as

$$Fe + 2H^{+} \rightarrow Fe^{+2} + H^2$$

Thus displacement of H^2 ions from acidic solutions by metal ions takes place. Thus all metals have tendency to get dissolved in acidic solution with simultaneous equations of the H^2 gas.

Q.2.b.i) 1.56g of coal sample was kjeldahlished and NH_3 gas thus evolved was absorbed in 50ml of 0.1N H_2SO_4. After absorption to excess (residual) acid requires 6.25ml of 0.1N NaOH for exact neutralisation. Calculate the percentage of N in the coal sample. (3 M)

Ans: Calculation of Nitrogen percentage

Weight of coal = 1.56gm

Volume of H_2SO_4 = 50 ml

Volume of NaOH = 6.25 ml

Normality of H_2SO_4 and NaOH = 0.1 N

H_2SO_4 consumed = 50-6.25 = 43.75 ml

Equivalent of H_2SO_4 = 43.75*0.1

= $4.375 * 10^{-3}$ milli equivalent

$N_2 = 4.375 * 10^{-3} * 14$

= wt. of nitrogen / wt. of coal sample * 100

= $4.375 * 10^{-3} *14 / 1.56 *100$

= 3.93 %

Q.2.b.ii) What is supercritical CO_2? Why is it considered a green solvent. (2 M)

Ans:

1. Supercritical fluids possesses properties of gases and liquids in an intriguing manner, which could after a range of applications in both synthetic and analytical chemistry.
2. **The green solvents:** A newer concept involves the technology which has been popularly preferred over conventional solvents extraction process because of environment concerns, such as the need to organic solvents and to find appropriate technologies for their disposal. **Eg.** Ionic liquid CO_2, propylene glycol, etc.

Q.2.c) Write a short note on Particle reinforced composites. (4 M)

Ans:

The size of the particle is in dispersed phase are of nearly the same in all directions.

Large particle composites:

In this sub type of composites, particulate phase should have following characteristics:

1. Stiffer and harder as compared to matrix phase.
2. It acts as reinforcing material.
3. It restrains the movement of matrix surrounding to itself.
4. The bond strength between two phases governs mechanical properties of composites.

Q.3.a) What is cracking? Explain in detail – fixed bed catalytic cracking. (6 M)

Ans:

1. Cracking is a process of converting heavy oil with higher molecular weight hydrocarbons to the oil with lower molecular weight hydrocarbons which is known as gasoline.
2. Generally on cracking a mixture of hydrocarbons is obtained which is allowed to undergo fractional condensation to separate gasoline.

Thermal Cracking:

a. Liquid phase thermal cracking: By this any type of oil can cracked. In this method the oil is pumped into the coil kept at 420^0C to 550^0C under pressure of 15 to 100 kg/cm^2 .
b. Vapour phase thermal cracking: in this method the heavy is treated at 400^0c to convert it into the vapour and then these vapours are passed to the reaction chamber.

Catalytic cracking:

a. It is a process in which heavy is oil is heated in presence of catalyst. Generally used catalyst are crystalline substances.

Eg: bauxite, zeolite, crystalline alumina silicate, etc.

Fixed bed catalytic cracking:

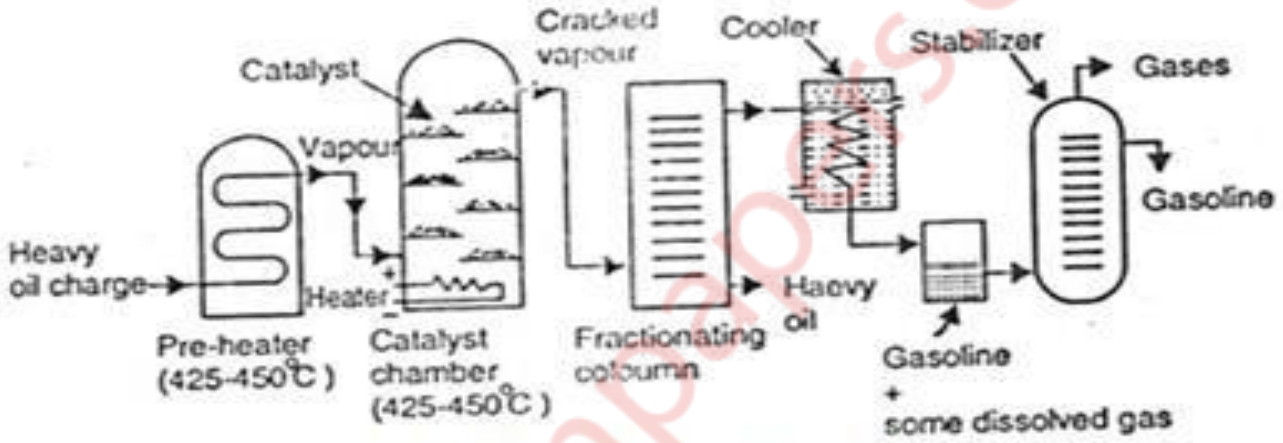


Fig.4. Fixed-bed catalytic cracking.

1. In this method vapours of heavy oil is treated in the presence of catalyst due which a better yield of petrol is obtained.
2. In this method heavy oil is vapourised by heating in an electrical heater. Then the vapours are passed over a series of trays containing catalyst. Generally the catalyst used are crystalline alumino-silicate, bauxite and zeolite.
3. The reaction chamber is maintained at 425^0c to 450^0c and under pressure of 1.5 kg/cm^2.
4. The cracked gases are taken out from the top of the reaction chamber and are allowed to pass in the fractionating tower, where gasoline fraction is collected. The octane value of this gasoline is about 80-85.
5. During the cracking, free carbon is also formed which deposits in catalyst, then the flow of vapours of heavy oil is passed over the second set of reaction chamber and catalyst in earlier chamber in regenerated by burning the carbon deposits with help of air.

Q.3.b.i) Write a note on heat resistant steel (3 M)

Ans:

These are steels which are exposed to high temperatures during proportion of equipment.
Heat resistance is obtained by adding specific metals in appropriate proportion.
Following metals are used/added in stainless steel in order to make them heat resisting.
Molybdenum: 3.5% addition of this metal improves heat resistance of steel.

Chromium: though this is the component in steel, but it is added more than 12%, it imports high grade heat resistance to steel. Such a steel is called as 'nichrome'.
Uses:
For making equipment facing high temperature i.e. gas turbines, retorting, parts of boilers, steam – linings, aero engine valves, etc.

Q.3.b.ii) A metal rod half immersed in water starts corroding at the bottom. Give reasons. (2 M)

Ans:

A metal rod when partially dipped in water or dilute solution of salt; like Nacl and if solution is not agitated properly then the parts of the strip above and closely adjacent to the water line are more strongly aerated, because they have more strongly aerated, and have more supply of oxygen while remaining parts of rod which is immersed to greater depth have less supply of oxygen and these are poorly aerated and show lower oxygen concentration and hence a metal rodhalf immersed in water starts corroding at the bottom.

Q.3.c) Calculate the percentage of atom economy for the following reaction with respect to allyl chloride. CH_3-CH=CH_2+Cl_2 → Cl-CH_2-CH=CH_2+HCl (4 M)

Ans:

CH_3-CH=CH_2+Cl_2 → Cl-CH_2-CH=CH_2+HCl

Prpene (42) (71) Allyl chloride (76.5) (36.5)

% Atom economy = molecular weight of product/total mol. Weight of reactants * 100

=76.5/42+71 * 100

=76.5/113 * 100

= 67.7%

% Atom economy = 67.7%

Q.4.a) Explain how the following factors affect the rate pf corrosion (6 M)

i) pH

Ans: In acidic pH the rate of corrosion is higher, because the mechanism of electrochemical corrosion proceeds by evolution of hydrogen gas at cathode. On the contrary, in alkaline or neutral electrolytic medium the electrochemical corrosion occurs by following the mechanism of absorption of oxygen, thereby forming as oxide film as a cathodic product. Such a film gets adhered to the surface of the metal and further rate of corrosion is governed by nature of corrosion product which is discussed as above.

ii) Ratio of anode to cathode areas.

Ans:

1. If two dissimilar metals are in contact one forming anode while another cathode, then the corrosion of the anodic metal is directly proportional to the ratio of the areas occupied by cathode and anode.
   Thus, corrosion at anode
   α = area of cathodic part / area of anodic part

2. Hence, if cathode is large and anode is small, then corrosion at anode is higher and vice – versa.

iii) Position of metal in galvanic series.

Ans:

1. This is the major factor for corrosion of metals are in corroding environment, the metal having higher electrode potential in the galvanic series undergoes corrosion, i.e. it act as a anode.

Q.4.b.i) Write a brief note on products obtained from natural materials. (3 M)

Ans:

1. Plants have been playing an important role in the field of pharmacy, not only in ancient time but also in arena of modern drug discovery.
2. The chemical diversity of plant gives the important dew for synthesis of different efficient pharma cophore in pharmaceutical during design.
3. Example like merpidine, pentazoine, are totally synthetic drugs for which opiates such as morphine and codeine were the models
4. Japanese research group has recently isolated stilbane derivatives from the bark of a shorea hemsleyana and roots of cyphostomma bainessi.
5. The active compounds identified is hemsleyanol – D is potent anti-bacterial agent methicillin resistance staphylococcus aurous responsible for variety of human diseases.

Q.4.b.ii) Define structural composites. (2 M)

Ans: A structural composites consists of both homogenous and composites materials. Their properties of the constituent materials as well as the geometric design. Structural composites are of two types such as,

a) Laminar composites: eg. Plywood
b) Sandwich composites: eg. Honeycomb core.

Q.4.c) Define shape memory alloys and mention its applications. (4 M)

Ans: The shape-memory alloys are metals alloys undergo deformed at one temperature, but on rising or falling temperature, they return to their 'original' shape.

Applications:

1. Orthopaedic applications:
   - Microstents simon filter micro wrapper.
2. cardiovascular applications are:
   - microsurgery
   - reinforcing week blood vessels
   - microstents.
3. Intravascular therapy:
   - Micro assembly for MEMS devices
   - Facilitates access to intricate regions of the body
   - Grab tiny foreign objects for removal from the body

Q.5.a) A sample of coal was found to contain the following constituents. C = 81%, O = 8%, S = 1%, H = 5%, N = 1% and Ash = 4%. Calculate the minimum weight and volume of an required for the complete combustion of 1kg of coal. (6 M)

Ans:

Let us calculate the 0_2 required for 1kg of coal first

Weight of carbon = 81 / 100 * 1 = 0.81 kg

Weight of hydrogen = 5 / 100 * 1 = 0.05 kg

Weight of sulphur = 1 / 100 * 1 =0.01 kg

Weight of oxygen = 8 / 100 * 1 = 0.08 kg

Calculation of O_2 needed for 1 kg of coal

CO_2 = 0.81 * 32 /12 = 2.16 kg

$2H_2O$ = 0.05 * 32 / 12 = 0.4 kg

SO_2 = 0.01 * 32 / 12 =0.01 kg

Total O_2 required = 2.57 kg

Less O_2 available = -0.08

Net O_2 required = 2.49 kg

Weight of air required = weight of O_2 / 23 *100

= 2.49 / 23 *100

= 10.82 kg of air

Volume of air:

$\therefore 28.94$ kg of air $= 22400$ ml volume at NTP

$\therefore 10.82$ kg of air $= 22400 * 10.82 / 28.94$

$= 8374.84$ ml

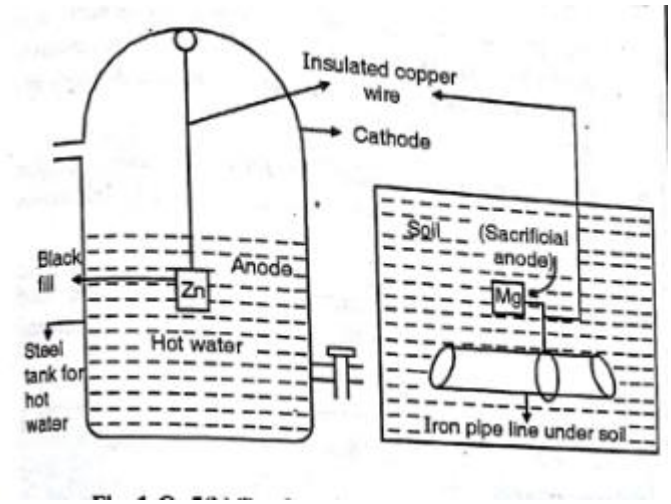
air $= 8.375$ litres of air

Weight of air requires $= 10.28$ kg

Volume of air required $= 8.375$ Litres.

Q.5.b.i) Discuss in brief sacrificial anode method of corrosion protection. (3 M)

Ans:



1. To achieve protection by sacrificial anode method, the metal to be protected from corrosion is connected by a wire to another piece of metal which is more reactive than the base metal itself.
2. This results in the corrosion of the piece of metal, connected thereby saving base metal.
3. Since the more active metal sacrifices itself, by undergoing corrosion and saving the base metal the method is named as sacrificial anode or auxiliary anode method.
4. The metal normally used are Mg, Zn or Al.
5. The method is generally used to protect cable or iron pipelines, by connecting them to Mg blocks, and in case of marine structures, ships are protected by suing Zn plates as sacrificial anode. Even water tanks, boilers are protected by using Zn metal.

Q.5.b.ii) What is powder metallurgy? Mention any two advantages and two limitations of powder metallurgy. (2 M)

Ans:

1. Powder metallurgy is the process which deals with the product of useful components from fine metal powders, from individual, mixed or alloyed with or without the inclusion of non-metallic constituents.
2. In this process,
   - Metal is obtained powder form
   - Powdered metal is mixed with other elements in powder form
   - It is then subjected to high pressure so s to get compressed into desired shape
   - The shaped is then finished finished into final form various combinations with metal and non-metals are possible.

Advantages:

1. By PM, materials can be made using, metal or non-metal in any desirable composition
2. Dimensional accuracy and finish of the materials are excellent.

Limitations:

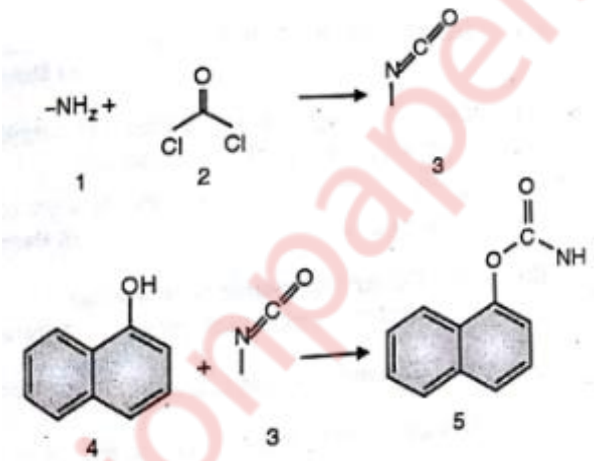
1. Storage of metal powder requires precautions, because powder metals get oxidised in air if exposed. This cause wastage.
2. Process is not suitable to produce large size components because process available for compaction are of limited capacity.

Q.5.c) Explain with suitable equations conventional and green synthesis of carbaryl. Also mention the principle of green chemistry involved. (4 M)

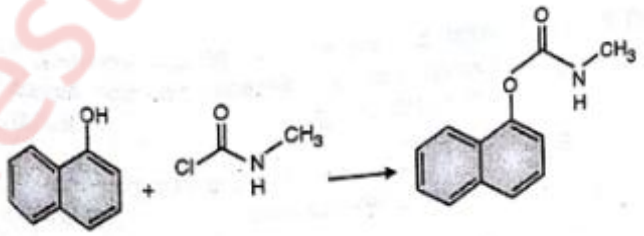
Ans:

Conventional route:

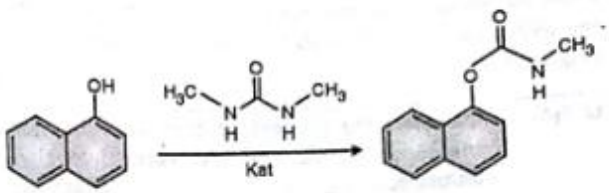
Carbonyl is prepared on large scale by treating methyl-isocynate with 1-napthol, anine is treated with phosgene to get methyl-isocynate. Carbaryl is produced by treating methyl isocynte with 1-napthol



- With using napthol-1 methylcarbomoyl chloride:

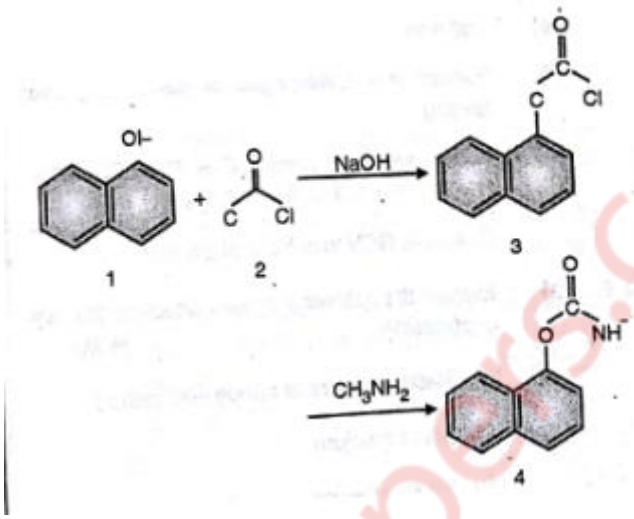


- In these route of synthesis of carbaryl highly toxic substance such as phosgene, methyl isocynate and methylcarbamoyl chloride are used.



Green route:

1. Napthol treated directly with equal quantity of phosgene is alkaline medium to get chloroformate which is then treated with methylamine to give carbary alternatively, 1-napthol is first converted to its chloroform, which is then treated with methylamine to give desired product.



2. Greener route synthesis also uses exactly the same reagent, but these are taken in different sequence. Hence, this sequence avoids the proportion of methyl isocynate. But use of phosgene and methyl amine is still needs to be avoided.

Q.6.a) Mention the composition, properties and uses of (6 M)

i. Duralumin:

Compositon:

Aluminium (Al) = 95%

Copper (cu) = 4%

Manganese (mn) = 0.5%

Magnesium (mg) = 0.5%

Properties:

1. It is light weighted, tough, highly, ductile, easily, castable, good conductor of heat and electricity and corrosion resistant.
2. It can easily be worked as it possesses high machinability. Its tensile strength can be raised by heat treatment, up to about 2000 kg-cm^2 without affecting its ductility. It approaches steel in strength and yet its density is one third of steel.

Uses:

Due to high strength with low density, it finds extensive use in aircraft industry in the form of a 'clad'. It is also used in making surgical instruments, cables, fluorescent tube caps etc. It is also used in making automobile and locomotive parts because off its high ductility and good electrical conductivity.

Q.6.a.ii) German silver

Ans:

Composition:

Cu = 25 -50%

Zn = 10 – 35%

Sn = 5 – 35%

Properties:

Possesses good strength, high corrosion resistance to electrolyte, high ductility, malleability, appears like silver.

Uses:

Decorative articles, utensils, table wares, ornaments, cutlery etc.

Q.6.a.iii) Gun metal

Ans:

Composition:

Cu = 85%

Zn = 4%

Sn = 8%

Pb = 3%

Properties:
High strong, can resist explosion, hard, tough.

Uses:

For hydraulic fittings, high pressure steam, plant marine, pumps, water fillings etc.

Q.6.b.i) Mention the advantages of composite materials (3 M)

Ans:

The composite materials find variety of applications in all these areas where, high mechanical strength, dimension stability, thermal stability, corrosion, resistance, abrasion resistance etc. is desirable. They find application in following industries.

a) Construction.
b) Electrical and electronics and telecommunication
c) Transportation
d) Agriculture
e) Sport goods
f) Automobile
g) Aviation industry
h) Mobiles

Composites, in short are extremely useful and more research work is going on to develop newer materials to cater to various industries.

Q.6.b.ii) Distinguish between anodic and cathodic coating (2 M)

Ans:

Anodic coating	Cathodic Coating
1. This type of coating protect base metal sacrificially.	1. This type of coating protect the base metal because of high corrosion resistance and noble behaviour
2. The coating metal is at lower electrode potential than base metal.	2. The coating metal is at higher electrode potential than base metal.
3. Corrosion of base metal does not enhance even on breaking "anodic coating" as it heals its film	Corrosion of base metal enhances, if there is a small cut in coating
4. Eg. Galvanising i.e. Zn coating on iron/steel	Eg. Tinning i.e. tin coating on iron/steel/copper/brass.

Q.6.c) What is biodiesel? Discuss the method to obtain biodiesel. What are the advantages of biodiesel? (4 M)

Ans:

1. Chemically biodiesel is the methyl esters of long chain carboxylic acids.
   Method to obtain biodiesel are:
   1. Filter cheap or waste vegetable oil/fat/
   2. Heat it at 110^0C with stirring to remove any water from it.
   3. Prepare sodium methoxide from sodium metal and methanol. Add the sodium methoxide about 2% by weight to the vegetable oil or fat.
   4. Add methanol about 20% by volume to the, mixture.
   5. Heat the mixture with stirring for 30 minutes.
   6. Cool and mix sufficient water, stir well. The glycerol and soap dissolve in water phase.
   7. Separate the water insoluble phase from water phase
   8. Add antioxidants to biodiesel to avoid it to become gummy due to oxidation and polymorphism.

   Advantages:

   1. Biodiesel is cheaper
   2. It has high cetane numbers 46 to 54 and high c.v. of about 40 kJ/m.
   3. It is regenerative and environment friendly.
   4. It does not give out particulate and co-pollutants.
   5. It has certain extent of lubricity.
   6. It use provides good market to vegetable oils and reduces over dependence for diesel on foreign countries, saving currency.
   7. It is clean to use biodiesel in diesel engines.