VIRUDHUNAGAR S.VELLAICHAMY NADAR POLYTECHNIC COLLEGE

(Affiliated to Directorate of Technical Education, Chennai 600 025)

Virudhunagar - 626 001

MISSION

"Our Mission is to Produce Disciplined and Quality Technocrats through Academic Programme of Noted Excellence to Serve the Society"

VISION

"To be an Institute of Excellence in Technical Education and Training of individuals , Focusing on the needs of the Nation and Society in tune with Technological Developments"

COURSE MATERIAL	
SCHEME	N1
PROGRAMME	BASIC SCIENCE
TERM	II
COURSE	ENGINEERING CHEMISTRY – II
PREPARED BY	❖ M. Selvambigai, Lecturer / Chemistry ❖ K. Nagarajan, Lecturer / Chemistry ❖ S. Nagaraj, Lecturer / Chemistry ❖ S.Sountharya, Lecturer / Chemistry
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DEPARTMENT OF BASIC SCIENCE

ENGINEERING CHEMISTRY – II (N1BE112)

DETAILED SYLLABUS

Contents: Theory

Unit	Name of the Topic	Hours
I	***ENVIRONMENTAL CHEMISTRY***	
	1.1 Air Pollution	4 Hrs.
	Pollution and Air pollution – Definition – Air pollutants (SO_2, H_2S, HF, CO and Dust) – Sources and Harmful effects – smog – Formation of Acid Rain – Harmful effects – Greenhouse Effect – Causes – Global warming – Harmful effects – Ozone Layer – Importance – Causes for Depletion of Ozone Layer (No equations) – Harmful effects of Ozone Layer Depletion – Control of Air Pollution.	
	1.2 Water Pollution	3 Hrs.
	Causes of Water Pollution – Sewage, Effluents, Algae and Microorganisms – Harmful effects – Definition – Sewage – Sewerage – Disposal – Industrial Effluents – Harmful effects of Effluents Treatment of Effluents – Eutrophication – definition – harmful effects.	
	1.3 Solid Waste Management	3 Hrs.
	Solid Waste – Definition – Problems – Types of Solid Waste – Methods of disposal – Land fill and Incineration – Recycling –Definition – Examples – Advantages of Recycling (Basic ideas) Green Chemistry Definition – Goals of Green Chemistry (Basic ideas)	
II	***2.1 Fuels***	4 Hrs.
	Fuel – Definition – Calorific value – calorie – Liquid fuels – liquid hydrogen – power alcohol – uses – Refining of Petroleum – Fractional distillation – Cracking (Concept only) – Gaseous fuels – Preparation, composition and specific uses of Producer gas and Water gas – Composition and uses of CNG and LPG – advantages of gaseous fuels.	
	2.2 Combustion	4 Hrs.
	Definition – Combustion calculation by mass (for solid and liquid fuels) – Stoichiometric calculations – Volume of air required – Definition of Flue gas – Flue gas Analysis – Orsat Apparatus – Simple numerical problems.	
	2.3 Rocket Propellants	2 Hrs.
	Definition – characteristics – Classification of propellants – brief idea of solid and liquid propellants.	

III	***3.1 Polymer*** *Definition – Natural polymer – Rubber – Defects of natural rubber – Compounding of rubber – Ingredients and their functions – Vulcanization – Plastics – types – Thermoplastics and Thermo set plastics – Differences – Mechanical properties of plastics – Polymers in Surgery – Biomaterials – Definition – Biomedical uses of Polyurethane, PVC, Polypropylene and Polyethylene.* ***3.2Abrasives*** *Definition – classification – hardness in Moh's scale – Natural abrasives – Diamond, Corundum, Emery, and Garnet. – Synthetic abrasives – Carborundum – Boron carbide manufacture – properties and uses.* ***3.3Composite Materials*** *Definition – examples – Classification of composites – Advantages over metals and polymers – General application.*	5 Hrs. 3 Hrs. 2 Hrs.
IV	***4.1 Electro Chemistry*** *Electrolysis – Definition – Mechanism – Industrial applications of Electrolysis – Electroplating – Process – Chrome plating – Electrochemical cell – Definition Galvanic cell – Formation of Daniel cell – Electrochemical series – Definition – significance.* ***4.2Energy Sources*** *Primary Battery – Secondary Battery – Definition and example – cell – Construction, Working principle and Uses of Lead – acid Storage battery – Non – conventional Energy Sources – Solar Cell – fuel cell –Definition – working principle.* ***4.3 Chemical Separation Techniques*** *(simple description only) – Filtration – crystallization – simple distillation – fractional distillation – Chromatography – definition and principle – Column chromatography only.*	4 Hrs. 3 Hrs. 3 Hrs.

V	***5.1 Corrosion*** *Definition – types of corrosion – theories of corrosion – galvanic cell formation theory – differential aeration theory – factors influencing rate of corrosion.*	4 Hrs.
	5.2 Methods of Prevention of Corrosion *Galvanization – tinning – anodisation – cathodic protection – sacrificial anode method and impressed voltage method.*	3 Hrs.
	5.3 Organic Coatings *Paint – definition – Components of paints – Varnish – definition –Preparation of oil varnish – differences between paint and varnish – Special Paints – Luminescent paint, fire retardant paint, Aluminum paint and distemper.*	3 Hrs.

Text Book:

1. Engineering Chemistry – I Tamil Nadu Text Book Corporation
2. Engineering Chemistry – Jain & Jain – DhanpatRai& Sons.
3. A Text Book of Engineering Chemistry – S.S. Dara – S. Chand Publication.

Reference Book:

1. Chemistry of Engineering Material – C.V. Agarwal, Andranaidu C. ParameswaraMoorthy – B.S. Publications.
2. Engineering Chemistry – Uppal – Khanna Publishers.
3. A Text Book of Inorganic Chemistry – P.L. Soni – S. Chand Publication
4. Environmental Chemistry – V P Kudesia – Pragati Publishers.
5. A Text Book of Environmental Chemistry and Pollution Control S.S. Dara – S. Chand Publication.

UNIT-1

ENVIRONMENTAL CHEMISTRY

1.1 AIR POLLUTION

INTRODUCTION

In recent days, everyone speaks about pollution. We are all facing huge risks due to pollution. The air we breathe the water we drink and the place where we live and work in may be full of toxic substances. The adverse effects of these pollutants may affect the future generation also.

Pollution

Pollution may be defined as the excessive discharge or addition of unwanted and undesirable foreign matters into the environment that causes huge damage to the life and properties of human, plants and animal.

Environment includes air, water and land. The harmful substances that cause damage are called **pollutants**. They are discharged from various industries, automobiles, microorganism, volcanic eruptions, forests and strong winds.

Causes of pollution

The following are the main causes of pollution.

- Huge increase in population.
- Rapid industrialization.
- Rapid urbanization.
- Uncontrolled exploitation of nature.
- Radioactive substances.
- Volcanic eruptions, etc.

Classification of pollution

To understand the magnitude of pollution problems, it may be classified into three types as follows.

- Air pollution
- Water pollution
- Land pollution

Air pollution

Air Pollution may be defined as the excessive discharge or addition of unwanted and undesirable foreign matters into the atmosphere that causes huge damage to the life and properties of human, plants and animal.

Gaseous pollutants like sulphur dioxide, hydrogen sulphide, hydrogen fluoride, carbon monoxide and dust are the most important primary air pollutants.

Harmful effects of air pollutants

S. No.	Air Pollutants	Source	Harmful effects
1.	Sulphur dioxide (SO_2)	Petroleum industry, thermal power station, manufacture of sulphuric acid etc.	Causes respiratory diseases, eye irritation, throat troubles, damage to agriculture etc.
2.	Hydrogen sulphide (H_2S)	Petroleum industries, paper industries, leather industries etc.	Causes eye irritation, severe throat pain, headache, corrosion of metals etc.
3.	Hydrogen fluoride (HF)	Fertilizer industry, aluminium industry etc.	Causes irritation, respiratory diseases, bone disorders, tooth disorders etc.
4.	Carbon monoxide (CO)	Automobile industry, oil refineries, cigarette, smoke etc.	Causes headache, visual difficulty, paralysis etc.
5.	Dust	Cement industry, mines, glass industry, ceramic industry, agricultural industry etc.	Causes respiratory diseases, affects lungs, accelerates Corrosion etc.

Smog

Smog is a combination of smoke and fog which forms droplets that remain suspended in the air. Smog is a chemical mixture of gases that forms a brownish yellow haze over urban cities. Smog mainly consists of ground level ozone, oxides of nitrogen, volatile organic compounds, SO_2, acidic aerosols and gases, and particulate matter.

There are two types of smog. One is Classical smog caused by coal smoke and fog , second one is photo chemical smog caused by photo chemical oxidants.

Acid rain

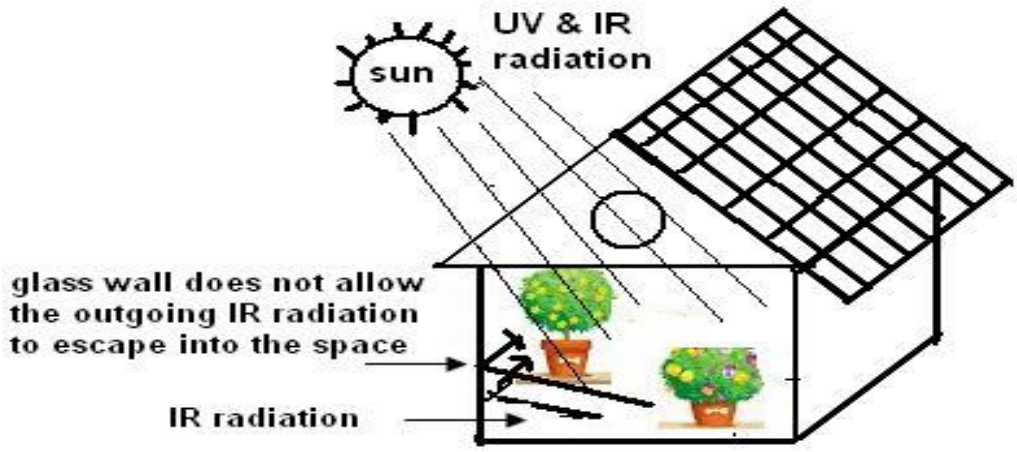
The gases like SO_2 and NO_2 emitted from various industries react with moisture present in the atmosphere to form corresponding acids. It means that rain water contains more acids. The rain water containing the acid is called acid rain. They slowly fall down on the earth as acid rain during snow fall or normal rainfall. This is called as acid rain.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Greenhouse effect

The earth surface gets warmed due to the blanketing effect of pollutants like CO_2 present in the atmosphere. It is known as greenhouse effect.

Several radiations like UV, visible and infra-red rays from the sunlight reaches the earth surface and produce heat energy. Some of the heat that is absorbed by the earth's surface is radiated back into the space. The pollutants like CO_2 and other gases which form a blanket around the earth prevent the heat energy to escape from the surface of earth. Hence the earth gets warmed. It is similar to green glass houses where heat radiation cannot escape from them.



Green House effect

Gases that cause greenhouse effect are mainly CO_2, methane, water vapour and chloro fluoro carbons (CFC). These gases are called greenhouse gases.

IMPACTS OF GREENHOUSE EFFECT:

Global warming

The warming up of the earth's surface due to greenhouse effect is termed as global warming. CO_2 and other greenhouse gases present in the atmosphere trap the infrared radiation from the sun and do not allow the radiations to escape. Hence the earth's surface is warming up more and more.

Harmful effects of global warming caused by Greenhouse effect:

- Evaporation process of surface water is enhanced very much due the increase in temperature of earth's surface which leads to drastic seasonal change. Some region of the world would become dry.
- Sea level is increased due to melting of glaciers. Hence, low lying land areas will be submerged under sea water.
- Food production is mainly affected and it leads to draught.
- The tropical diseases like malarial fever, dengue fever and cholera will spread to the other parts of the world.
- It causes drastic change in seasons. Hence, human beings and animals are mostly affected by climatic change.
- Natural calamities like cyclones, hurricane, typhoons and tsunami may occur frequently and strongly.
- Because of global warming, the normal weather pattern is disrupted. Some parts of the world will face severe water crisis while the other parts will suffer from flooding. Spring arrives earlier in many parts of the world. An early spring may disturb animal migration.
- Biological productivity also decreases due to global warming.

Ozone layer

One of the gifts given by nature is ozone layer. It is present about 20 km above the earth's surface. It forms a layer of about 3mm thickness called ozone layer. Oxygen is converted into ozone by photochemical change as follows.

$$3\,O_{2\,(g)} \xrightarrow{\text{Radiation}} 2\,O_{3\,(g)}$$

The region in which O_3 density high is called ozone layer.

Importance of ozone layer

- Ozone layer covers the earth's surface and prevents the entry of harmful UV radiation. It saves the lives of human beings and animals. If not so, no life is found on earth.
- If the ozone layer is not present in the atmosphere, the harmful UV radiations will enter the earth. This will destroy human and animal life, change the wind pattern, rain fall, climatic change and global temperature.

Causes for depletion of ozone layer

Chlorine plays a vital role in the depletion of ozone layer. Chlorofluoro carbons are released from the supersonic jets, air crafts and jet engines. They get accumulated at high altitude and undergo decomposition in the presence of ultraviolet radiations. Chlorine is the main decomposition product. It reacts with the ozone and converts it into oxygen.

Chlorine converts the ozone molecules into oxygen in the presence of UV radiation as follows.

$$Cl + O_3 \longrightarrow ClO + O_2$$

$$ClO + O \longrightarrow Cl + O_2$$

It is noteworthy that one atom of chlorine may convert huge number of molecules of ozone into oxygen. The main source for chlorine is CFC which is released by aircrafts, jet planes, refrigerators, air-conditioners, etc. **One atom of chlorine can convert about 10^6 molecules of ozone into oxygen**. The other gases which cause ozone layer depletion are NO and NO_2.

Harmful effects of ozone layer depletion

- Due to ozone layer depletion, the harmful UV radiation may enter freely into the earth's surface and affect the lives on earth.
- They affect human beings and cause skin cancer, skin aging, breast cancer, lungs cancer, eye defects and visual defects.
- They reduce the population of aquatic species.
- They affect the growth of plants and vegetables.
- They affect the eco-system very badly.
- The sea food production also decreases due to the depletion of ozone layer.

- Depletion of ozone layer causes the change in earth's climate, wind pattern, rainfall and global warming.

Control of air pollution

"Prevention is better than cure". Similarly, it is better to control the air pollutants at its source itself.

The following are the steps to be taken for controlling air pollution.

- The exhaust gases from automobiles and vehicles should be minimized by the use of catalyst.
- Tall chimneys may be used to reduce the concentration of pollutants at the ground level.
- Smoke may be removed by Cottrell's electrostatic precipitator.
- Dust particles can be removed by the use of bag filters and dust separators.
- The use of coal, wood and traditional fuels should be slowly reduced.
- Solar energy, tidal power, nuclear power and electricity should be used for domestic and industrial purpose.
- Acid and chemical fumes are absorbed in water, concentrated and reduced.
- Growing of trees reduces more pollution as well as the harmful carbon dioxide concentration in the atmosphere. Plants take carbon dioxide during photosynthesis and releases oxygen to environment. Hence, more trees should be planted.

QUESTIONS

PART – A

1. Define pollution.
2. Define air pollution.
3. Give an example for air pollutants.
4. Mention the harmful effects of SO_2.
5. Mention the harmful effects of H_2S.
6. Mention the harmful effects of HF.
7. Mention the harmful effects of CO.
8. Mention the harmful effects of dust.
9. Give an example for gases causing acid rain.
10. Give two examples for greenhouse gases.
11. What is global warming?
12. Mention the name of pollutants responsible for depletion of ozone layer.

PART – B

1. What is acid rain?
2. Mention the harmful effects of acid rain.
3. What is greenhouse effect?
4. Mention the harmful effects of global warming.
5. What are the importance of ozone layer?
6. What is smog?

PART – C

1. What are the major air pollutants? Give their source and harmful effects.
2. What is acid rain? Mention its harmful effects.
3. Write a note on greenhouse effect.
4. What is global warming? List its harmful effects.
5. What are the causes of ozone layer depletion? List the problems caused by ozone layer depletion.
6. Write a note on control of air pollution.

1.2 WATER POLLUTION

INTRODUCTION

Water is more important for all the living things. Water is essential for the plants to grow. If the water is contaminated with any foreign substance, it is harmful to human beings, plants, animals, etc.

Water Pollution:

Water Pollution may be defined as the excessive discharge or addition of unwanted and undesirable foreign matters into the water that causes huge damage to the life and properties of human plants and animal.

Causes of water pollution

The main sources of water pollution are

- Sewage
- Effluents
- Algae and
- Microorganisms

Sewage

Sewage is the liquid waste of the community which includes human wastes, kitchen wastes and street washings.

Harmful effects of sewage

- Hydrogen sulphide gas is produced in the sewage due to the decomposition of organic impurities which gives a bad smell.
- Due to corrosive nature, it affects the pipelines.
- It helps for the growth of harmful bacteria and viruses and cause many diseases like cholera, jaundice, polio etc.
- Inflammable substances like alcohol and ether may cause severe effects and fire accident.
- The enrichment of nutrients like nitrates and phosphates in sewage water which causes the growth of aquatic plants which releases the toxic chemicals .This affects the aquatic lives.
- The solids in it reduce the flow of water and become stagnant.
- The aquatics like fish die due to lack of oxygen in sewage. The biological oxygen demand is reduced.
- It also affects the nature and fertility of the soil and affects the food production.

Sewerage (Treatment of sewage)

Removal of sewage by some treatment methods is called sewerage. It involves the following steps.

- The floating impurities can be removed by mesh screens.
- The suspended impurities can be removed by filtration and coagulation process using Alum.
- Inflammable organic impurities can be removed by oxidation process.
- By neutralization method, the corrosive acids and bases can be removed.
- The bacterial impurities can be removed by chlorination.
- The water left out from the sewage can be treated by suitable purification method and can be used for other purposes.
- By passing oxygen the oxidisable matter is removed.
- It is treated with lime to remove phosphorous as calcium phosphate.

Effluents

The waste water from various industries containing harmful chemicals. This Industrial waste water is known as effluent.

Harmful effects of effluents

- It may cause severe damage to aquatic animals.
- The metals present in the effluent may seriously affect the human organs like kidney, brain, etc.
- It corrodes the pipelines due to acidic nature of effluents.
- The effluents of chemical industries and nuclear power stations may affect the health of human beings and animals.
- The effluents may enrich the acidic nature of the soil and affect the fertility of the land and growth of plants.
- The phosphates and nitrates cause Eutrophication.
- The metallic pollutants like Cu, Pb, Cd present in the effluents affects the health.
- The organic impurities help the growth of disease causing microorganisms like bacteria, virus and protozoa and produces diseases like cholera, jaundice and typhoid.

Treatment of effluents

- Toxic nature of effluents may be removed by chemical methods.
- The acidic nature and basic nature of the effluents may be removed by neutralization.
- The radioactive effluents are carefully stored and buried under the ground.
- The heavy metallic impurities may be removed by special methods.

Harmful effects of heavy metal ions present in effluents

Harmful effects of Lead

- Affects liver and kidney
- Causes nervous disorder
- Produce mental retardation in children
- Produce gastro-intestinal damage
- Causes loss of appetite

Harmful effects of Copper

- Severely affect the digestive system
- Causes vomiting and diarrhea
- Affects blood, bone and teeth
- It is toxic to aquatic life
- Causes cancer and tuberculosis

Harmful effects of Cadmium

- Causes kidney damage
- Affects liver
- Produce anemia and hypertension
- Produce gastro-intestinal damage
- Causes vomiting and diarrhea

Harmful effects of Zinc

- Affects skin
- Causes vomiting and diarrhea
- Causes irritation
- Causes dizziness and itching
- Causes nausea

Harmful effects of algae

- Presence of algae in water produces foul odour and bad taste to water.
- They block the pipelines and filters.
- They affect the aquatic animals due to depletion of oxygen.

Treatment of algae

- The growth of algae can be controlled by using algaecide like copper sulphate.
- The algae can be destroyed by using chemicals like bleaching powder, activated carbon and lime.
- The growth of algae can also be controlled by preventing the sunlight to fall on the surface of water.

Harmful effects and control of microorganisms (Bacteria and viruses)

- They cause diseases like cholera, jaundice, typhoid, etc.
- They are destroyed using disinfectants like bleaching powder and chlorine.

<u>Eutrophication:</u>

The ageing of lake and pond by the enrichment of nutrients is called eutrophication.

Causes of Eutrophication

Eutrophication is due to the mixing of sewage water from agricultural land, domestic detergent wastes, containing nitrogen compounds and phosphates into lake water. It enhances the growth of algae.

Harmful effects of eutrophication

- It enhances the growth of algae in water which leads to depletion of oxygen in water. Algae release the toxic chemicals. It affects the aquatic animals badly.
- When the oxygen level falls to zero, the sulphates are reduced to H_2S.
- It produces bad taste and odour after it decays.
- It blocks the pipelines and filters.
- It admits the growth of bacteria and viruses. It may spread water borne disease like dysentery, cholera, Typhoid, yellow fever which affects human beings.
- It causes an imbalance in eco-system based on water resources.
- Population of aquatic animals is reduced.

- Algal toxin accumulated in shell fish are harmful to human system. They produce paralysis, diarrhea and stomach disorder.
- Algae and other rooted weeds clog the water filters. They also cause damage to hydroelectric engine.

QUESTIONS

PART – A

1. Give two examples for water pollutants.
2. What is sewage?
3. What is sewerage?
4. What are the industrial effluents?
5. Give the problems of lead in water.
6. Give the problems of copper in water.
7. What is eutrophication?

PART – B

1. Mention any three harmful effects of sewage.
2. Write a note on sewage disposal.
3. Mention the harmful effects of effluents.
4. Mention the harmful effects of algae. How it is controlled?
5. Mention the harmful effects of microorganisms. How it is controlled?
6. Mention any three harmful effects of eutrophication.

PART – C

1. What are the major water pollutants? Give their harmful effects.
2. What is sewage? What are its harmful effects? How it is disposed?
3. What are effluents? Explain the problems and treatment of effluents.
4. Mention the harmful effects of metallic pollutants (lead, copper, cadmium and zinc) in water.
5. Define eutrophication. Mention its harmful effect.

1.3 SOLID WASTE MANAGEMENT

INTRODUCTION

Annual municipal waste in India is about 280 million tons per year and is creating huge problems for the country. Hence there is an urgent need to tackle this problem.

Solid waste

Solid waste is a substance which is left of from industries, kitchen or other waste and thus thrown away. They can cause hazard to human health and environment.

Solid waste management is the collection of wastages, transporting, processing, recycling and monitoring of the waste materials to reduce their effect on health and environment.

Types of solid waste

S.No	Types	Examples
1	Commercial Garbage	Bricks, cement, sand etc.,
2	Agricultural waste	Herbicides, pesticides, crop residue, animal and poultry waste etc.,
3	Rural waste	Bagasse, cow dung garbage, rice husk, etc.,
4	Plastic waste	Plastic toys, cosmetics, food packaging, etc.,
5	Medicinal waste	Cotton containing blood, dressing linen, syringes, waste medicines, etc.,
6	Domestic waste & e-waste	Food waste, plastics,computer,TV, broken bottle, ceramic materials, metallic containers, kitchen waste, etc.,
7	Municipal garbage	Food waste, plastics, metals, paper and paper board, etc.,
8	Industrial waste	Products of iron, cadmium, tin, lead, arsenic, mercury, radioactive materials, etc.,

Problems caused by solid waste

- Air becomes unclean with foul smell.
- The biomedical waste causes infectious disease and gives bad smell.
- Human health is affected.
- Pollutes the air, land and ground water.
- Contaminate the environment.
- Affect the climate.

Hence, there is an urgent need for the management of solid waste. Solid waste management is not fully implemented because of

- Lack of education and awareness
- Lack of motivation
- Resistance to change
- Non co-operation from house holds
- Lack of knowledge on benefits of segregation

Methods of disposal of solid waste

The waste management concepts includes 1.Reduce 2.Reuse 3.Recyle

The aim of waste management is to extract maximum benefit from the wastes and to reduce the amount of waste. The final disposal of solid wastes can be carried out by the following methods.

1. Land fill method

In this method, waste is buried underground and covered with soil. Landfills were often established in abandoned areas.

Modern land fill contain a series of three dimensional control cells. The wastes dumped in the appropriate cells can be covered by a layer of soil at the end of each day. Below the wastes dumped in the cell, a double liner system is provided to prevent the lactates from polluting the soil and ground water beneath the site. The upper liner must be a well flexible membrane lining made of plastic or rubber.

A properly designed and well managed land fill can be a hygienic and relatively in expensive method of disposing of waste materials.

Poorly designed landfills can create a number of adverse environment impacts such as wind-blown litter. Harmful gases like methane are given off from land fill sites that cause air pollution and contribute to global warming.

2. <u>Incineration method (Thermal Treatment)</u>

Incineration is a waste treatment process that involves the combustion of solid waste at 1000° C. Waste materials are converted into ash, flue gas and heat. The ash is mostly formed by the inorganic constituents of the waste and gases due to organic waste. The heat generated by incineration can be used to generate electricity. This process reduces the volumes of solid wastes to 20-30 percent of original volume.

Recycling

Recycling is a process of converting used materials (waste) into new useful and valuable products.

This process is carried out to,

1. prevent wastage of potentially useful materials
2. Reduce the consumption of fresh raw materials
3. Reduce energy usage
4. Reduce air pollution and water pollution

Recycling reduces the need for "conventional" waste disposal methods and there by lower greenhouse gas emissions. Recycling is a key component of modern waste reduction and is the third component of the "Reduce, Reuse and Recycle" waste.

Recycling refers to the collection and reuse of waste materials. Materials for recycling may be collected from general waste and reprocessed into new products.

Examples of recycling

- Used paper can be converted into new paper.
- Used foamed polystyrene can be converted into new polystyrene.
- Used aluminium containers can be converted into new containers.
- Kitchen scraps can be used to make compost (Compost is an organic material that adds nutrients to soil).
- Used glass containers can be converted into new glass containers.
- Metal scraps can be converted into new materials.

Advantages of recycling

- It helps in the conservation of natural resources.
- It protects the environment of the area. The recycling is eco-friendly.
- It protects our health.
- It makes the air clean and free from foul smell.
- It reduces the pollution of water bodies.
- It saves lot of energy.
- Forests are saved by recycling the waste paper.
- This minimizes the global warming.

GREEN CHEMISTRY

INTRODUCTION

The chemical industries produce a large number of products that make invaluable contribution in our daily life. It improves the quality of lives and comforts. During the manufacture of such products, the chemical industry releases enormous quantities of environmentally harmful wastes. It results in pollution. Hence, chemistry in particular, has lost some of its glamour in the public eye. One of the most attractive concepts for pollution prevention is green chemistry.

Green chemistry

Green chemistry is defined as the design of environment friendly products and process to minimize or remove hazardous substances. **The chemistry which is used to prevent pollution is called as Green chemistry.**

Natural processes are 'green' while synthetic processes are often 'grey'. Cleaner process and cleaner synthesis will certainly contribute to better environmental protection.

Goals of green chemistry

Some guidelines may be given while designing the products and determining the processes to achieve the goals of green chemistry.

- To prevent the formation of waste material before it is formed.
- It aims to minimize the global warming.
- New methods should be developed to convert almost all the reactants used in the process into the final product.
- To design synthetic methodologies that does not give toxic chemicals.
- To avoid the usage of auxiliary substances (solvents) wherever possible.

- To ensure the conduction of synthetic methods at ambient temperature and pressure.
- To reduce the formation of byproducts which are harmful.
- To make use of renewable materials as raw materials during the process.
- To perform the process in a safe and controlled way.
- To reduce the quantity of highly hazardous chemicals during the process.
- Using the non-conventional energy like solar and wind energy.
- The products should be recyclable.

QUESTIONS

PART – A

1. What are solid waste? Give an example.
2. What are the two methods employed for disposal of solid waste?
3. What is landfill?
4. What is incineration?
5. Define green chemistry.
6. Give any two goals of green chemistry.
7. What is recycling?

PART – B

1. Write a note on land fill.
2. Write a note on incineration.
3. Give any three goals of green chemistry.
4. What is recycling? Give an example.

PART – C

1. List the different types of solid waste. Explain their origination.
2. Mention the problems caused by solid waste.
3. Explain the two methods of disposal of solid waste.
4. Define green chemistry. Give the goals of green chemistry.
5. Explain the advantages of recycling.

UNIT - II

2.1 FUELS

INTRODUCTION

In this present age of rapid industrial development, the power requirement is increasing day-by-day. Heat energy is the main source of power. Burning of carbon, an exothermic reaction produces heat energy. Hence, the carbon compounds have been used as the main source of heat energy.

Fuel

A fuel is a substance, which on proper burning gives large amount of heat energy on combustion. It is used for domestic and industrial purposes. They contain carbon as a main constituent.

Calorific value of a fuel

Calorific value of a fuel is the total quantity of heat liberated when a unit mass or volume of the fuel is completely burnt.

Unit of heat (Calorie)

- Heat energy is measured in terms of calorie or kilocalorie.
- Calorie is the quantity of heat required to raise the temperature of 1 gram of water through 1° Centigrade (1 kcal = 1000 calories)

Classification of fuels

Fuels are classified into natural or primary fuels and artificial or secondary fuels. Each type is further subdivided into solid, liquid and gaseous fuels.

S. No.	State of fuel	Natural	Artificial
1.	Solid	Wood, peat, lignite,coal	Wood charcoal, coke
2.	Liquid	Crude petroleum	Kerosene, petrol, diesel, alcohol
3.	Gaseous	Natural gas	Water gas, producer gas, biogas, coal gas, LPG

Liquid fuels

Liquid hydrogen as a fuel

Hydrogen is a colourless and odourless gas composed of diatomic molecules. It holds greater role as fuel in future.

Liquid hydrogen is a favourable rocket fuel. On combustion, it produces more heat per gram than any other fuel. Further, it produces only water on combustion whereas the fossil fuels produce gases like SO_2, NO_2 and CO_2causing environmental pollution. Hence, hydrogen as a fuel has more advantages than any other fossil fuels.

$$2\ H_2 + O_2 \rightarrow 2\ H_2O$$

Hydrogen is not a primary fuel. It is obtained from other sources of energy. It can be obtained directly from water by decomposing with some energy source. Solar photovoltaic collectors are used to decompose water by electrolysis.

Hydrogen can be liquefied below its temperature of 33.1K. It is a colourless, odourless liquid below 20.2 K. When allowed to expand, it gets heated up above 22 K.

Power Alcohol:

When ethyl alcohol is used as a fuel in internal combustion engine, it is called as power alcohol. Generally ethyl alcohol is used as it 5 – 25% mixture with petrol.

Use of ethyl alcohol in petrol reduces our dependence for petrol on foreign countries & even 5% ethyl alcohol blending in petrol saves our foreign reserves by about Rs. 5000 cores/ annum.

Uses

1. It is used as a fuel in engines.
2. It is also used as a solvent.

Petroleum

Petroleum (Crude oil) is a naturally available liquid fuel. It is dark greenish-brown viscous oil found deep in earth’s crust. It is composed of various hydrocarbons with small amount of other organic compounds as impurities.

Refining of petroleum

The process of purification and separation of various fractions present in petroleum by fractional distillation is called refining of petroleum. Refining is carried out in oil refineries.

Fractional distillation

It is the process of separation of various components of a liquid mixture based on the difference in their boiling points by repeated evaporation and condensation.

Refining of petroleum – Process

- The crude oil is treated with copper oxide to remove sulphur impurities.
- Then it is repeatedly washed with sulphuric acid to remove basic impurities.
- It is then washed with sodium hydroxide to remove acidic impurities.
- Then it is subjected to fractional distillation and various fractions are collected. The various fractions obtained and their uses are given in the table below.

<u>Products of fractional distillation of petroleum and their uses:</u>

S. No.	Fractions	Temperature	Uses
1.	Gases	Below 30°C	Used as industrial and domestic fuel
2.	Petroleum ether	30°C to 80°C	Used as a solvent
3.	Gasoline or petrol	40°C to 180°C	Used as a solvent, fuel and in dry cleaning
4.	Kerosene oil	180°Cto 250°C	Used as illuminant and fuel
5.	Diesel oil or gas oil	250°C to 320°C	Used as fuel for diesel engine
6.	Heavy oil or lubricating oil	320°Cto 400°C	Used for lubrication, cosmetics and in medicines
7.	Residue or asphalt or pitch	Above 400°C	Used for road making and water proofing of roofs

Cracking

Cracking is a process by which the hydrocarbons of high molecular mass are decomposed into hydrocarbons of low molecular mass by heating in the presence or absence of a catalyst.

Generally aluminum silicates are used as catalyst.

$$\underset{\text{n-Decane}}{C_{10}H_{22}} \xrightarrow{\text{Cracking}} \underset{\text{n-Pentane}}{C_5H_{12}} + \underset{\text{Pentene}}{C_5H_{10}}$$

Gaseous fuels

Examples: Producer gas, water gas, CNG and LPG

Producer gas

Producer gas is a mixture of carbon monoxide and nitrogen. It also contains trace of hydrogen and carbon dioxide.

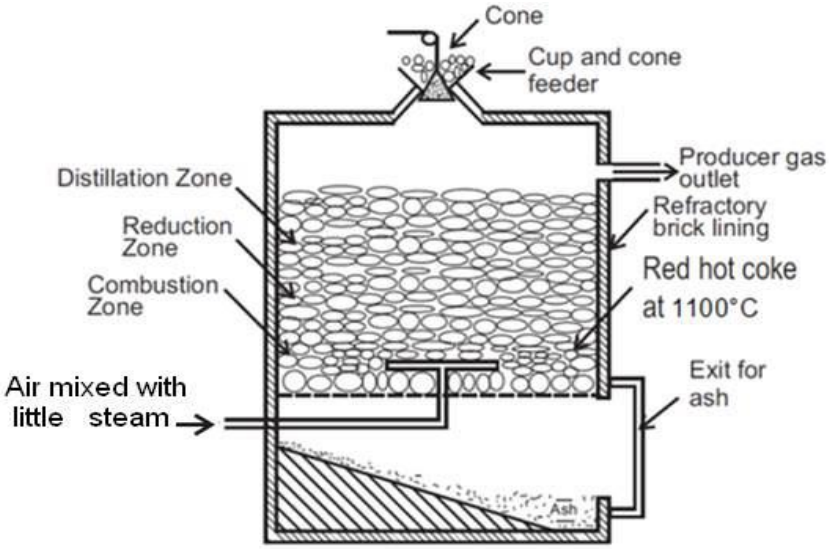
The average composition of producer gas is CO = 22-30%; H_2 = 8-12%; N_2 =52-55% and CO_2 = 3%.Its calorific value is about 1300 kcal/m^3.

Preparation

Producer gas is prepared by passing air over a red hot coke at about 1100°Cin a reactor called gas producer.

$$C + O_2 \rightarrow CO_2$$

$$CO_2 + C \rightarrow 2\ CO$$



Producer gas production

The reactor consists of a steel vessel lined inside with refractory bricks. At the top, it is provided with cup and cone arrangement and an exit for producer gas. At the bottom, it has an inlet for passing air. There is an exit for the as at the base.

Uses

1. It is used as a fuel in the extraction of metal.
2. It is used in the manufacture of glass.
3. It is used as a reducing agent in metallurgy.

Water gas

Water gas is a mixture of carbon monoxide and hydrogen. It also contains trace of carbon dioxide and nitrogen.

The average composition of water gas is CO = 41%; H_2 = 51%; N_2 = 4% and CO_2 = 4%. Its calorific value is 2800 kcal/m^3.

Preparation

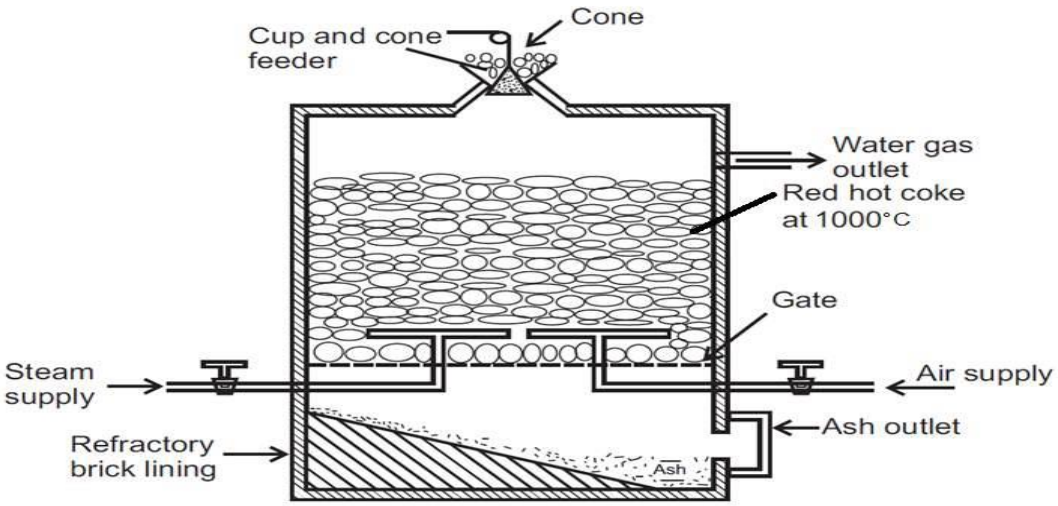
Water gas is prepared by passing steam and little air alternatively over a red hot coke at about 1000°C in a reactor. It is an endothermic reaction. So the temperature of the system decreases.

$$C + H_2O \rightarrow CO + H_2 \text{ (Endothermic reaction)}$$

But, the reaction between carbon and air is exothermic and raises the temperature to about 1000°C

$$C + O_2 \rightarrow CO_2 \text{ (Exothermic reaction)}$$

Thus, the steam and air are sent in alternatively to maintain the temperature at about 1000°C.



Water gas production

The reactor consists of a steel vessel lined inside with refractory bricks. At the top, it has cup and cone feeder and an exit for water gas. At the base, inlet pipes for steam and air are provided. At the bottom, out let for ash is also available.

Uses

1. It is used as a source of hydrogen gas.
2. It is used as an illuminating gas.
3. It is used as a fuel in ceramic industries.

CNG (Compressed natural gas)

1. CNG is a good alternative fossil fuel. It mainly contains methane.
2. CNG is made by compressing natural gas which is found in oil deposits landfills and waste water treatment plants to less than 1% of its volume, it occupies at standard atmospheric pressure.
3. It is stored and distributed in hard containers at a pressure of 2900-3600 psi.

Advantages and uses

1. It is cheaper than petrol or diesel.
2. It emits fewer pollutants like CO_2, CO, etc. In New Delhi, it is used as a fuel for entire city bus fleet, taxis and three wheelers.
3. It is safer than other fuels. In the event of a spill, it disperses quickly in air because, it lighter than air.

LPG (Liquefied petroleum gas)

1. It is a mixture of propane and butane.
2. It is stored in steel cylinder under high pressure.
3. When the cylinder is opened, it comes out in the form of gas.
4. Commercially, it is supplied under various trade names.
5. Its calorific value is 27,800 kcal/m^3.

Uses

1. It is mainly used as a domestic fuel.
2. It is used as a fuel in diesel engines.
3. It is used as a motor fuel.

Advantages of gaseous fuels

- They have high calorific value.
- Very easy storage.
- Very easy transportation.
- They do not product ash.
- They do not produce smoke.
- Very easy to ignite.
- Controlling the flame is very easy.

QUESTIONS

PART – A

1. Define fuel.

2. Define fossil fuel.

3. Define calorific value of a fuel.

4. How are fuels classified?

5. Give two examples for liquid fuels.

7. Give two examples for gaseous fuels.

8. What is petroleum?

10. What is meant by cracking?

11. What is producer gas?

12. Give the composition of producer gas.

13. What is water gas?

14. Give the composition of water gas.

15. What are the components present in CNG?

16. Mention the uses of CNG.

17. What are the components present in LPG?

18. Mention the uses of LPG.

19. What is power alcohol?

PART – B

1. What is refining of petroleum?

2. Write a note on liquid hydrogen as fuel.

3. Give the composition and uses of producer gas.

4. Give the composition and uses of water gas.

5. Give the composition and uses of CNG.

6. Give the composition and uses of LPG.

PART – C

1. Write a note on solid fuels.
2. Explain the fractional distillation of petroleum.
3. Describe the manufacture of producer gas. List its uses.
4. Describe the manufacture of water gas. List its uses.
5. Write a note on CNG.
6. Write a note on LPG.
7. What are the relative advantages of gaseous fuels?

2.2 COMBUSTION

INTRODUCTION

Combustion is an exothermic chemical reaction accompanied by heat and light. To ensure complete combustion, substance should be brought to its ignition temperature. Most of the combustible substances are enriched with carbon, hydrogen and sulphur.

During combustion they undergo thermal decomposition and oxidation to give products like CO_2, H_2O and SO_2 etc. Hence for an efficient combustion it is essential that the fuel must contact with sufficient quantity of air. The air contains oxygen which is used for combustion. But the non-combustible constituents like N_2, CO_2 and H_2O do not take any oxygen from air.

Incomplete combustion occurs only when there is too little air or oxygen is supplied. During incomplete combustion the carbon monoxide is formed instead of CO_2.

Ignition temperature:

The minimum temperature at which a fuel catches fire and burns is called ignition temperature.

Definition:

The chemical reaction of a fuel with oxygen (oxidising agent) which produces heat and light energy is called combustion of a fuel.

Example: Combustion of carbon

$$C + O_2 \rightarrow CO_2\,(g) + 97\ \text{kcal}$$

The gaseous products of combustion are mainly CO, CO_2, N_2, SO_2, O_2 and H_2O which are known as flue gases.

The main elements present in most of the fuels are carbon (C), hydrogen (H), oxygen (O) and sulphur (S).

Air contains 23% by mass of oxygen and 21% by volume of oxygen.

Combustion calculation by mass (for solids and liquids):

Stoichiometric or minimum quantity of air required for the complete combustion of solid and liquid fuels.

Substances always combine in definite proportions which are determined by the molecular masses of the substances involved and the products formed.

1. Combustion of Carbon

$C(s) + O_2(g) \rightarrow CO_2(g)$

12 32 44

12 Kg of carbon requires32 Kg of oxygen for complete combustion

The given carbon in the fuel requires oxygen for complete combustion = 32 / 12 × C Kg

For C Kg of carbon in the fuel requires oxygen for complete combustion = 8 / 3 × C Kg

2. Combustion of Hydrogen

$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(l)$

4 32 36

4 Kg of hydrogen requires 32 Kg of oxygen for complete combustion.

The given hydrogen in the fuel requires oxygen for complete combustion = 32 / 4 × H Kg

For H Kg of hydrogen in the fuel requires oxygen for complete combustion = 8 × H Kg

= 8 H Kg

Combined hydrogen in fuel present as moisture (H_2O) does not undergo combustion. The rest of hydrogen only takes part in the combustion reaction.

3. Combustion of Sulphur

$S(s) + O 2 (g) \rightarrow SO 2 (g)$

32 32 64

32 Kg of sulphur requires 32 Kg of oxygen for complete combustion = S Kg

The given sulphur in the fuel requires oxygen for complete combustion = 32 / 32 × S Kg

= S Kg

On combining the above three equations,

Let us assume that 1 Kg of fuel contains' C' Kg of carbon, H Kg of hydrogen and S Kg of sulphur. Then the total mass of oxygen required for the complete combustion of 1 Kg of fuel is given below:

The theoretical oxygen required for combustion of 1 Kg of fuel

= (8 / 3 × C + 8H + S)

C = Wt. of carbon; H = Wt. of hydrogen; S = Wt.of sulphur

Minimum mass of oxygen is calculated on the basis of complete combustion.

Note: If the fuel already has some amount of oxygen, then that amount of oxygen has to be deducted from the total mass.

Minimum mass of oxygen required = (Theoretical O_2 required) – O_2 present in fuel

The total mass of oxygen required per Kg of fuel = $(8 / 3 \times C + 8H + S) - O_2$

(O_2 = Mass of oxygen)

<u>Mass percentage of oxygen</u>

The mass percentage of oxygen in air=23%

23% of Oxygen is supplied by 100 % Mass of air supply

That is to supply 23 Kg of oxygen = 100 Kg of air required

Hence, one Kg of oxygen is supplied by = 100 / 23 Kg of air

Hence the mass of air that is required for combustion of 1 Kg of fuel is

Minimum mass of air required for combustion of 1 Kg of fuel

$= (8 / 3 \times C + 8H + S) - O_2 \times 100 / 23$ Kg

Where C, H, O and S are the respective masses of carbon, hydrogen, oxygen and sulphur present in 1 Kg of the fuel.

Examples:

Example 1

A fuel contains 90% carbon, 3.5% hydrogen, 3% oxygen and 0.5% sulphur Determine stoichiometric mass of air required to completely burn 1 Kg of this fuel.

C = 90% = 0.9 Kg H = 3.5% = 0.035 Kg

O = 3% = 0.03 Kg S = 0.5% = 0.005 Kg

<u>1. Combustion of carbon</u>

For C Kg of carbon in the fuel requires oxygen for complete combustion = $8 / 3 \times C$ Kg

For 0.9 Kg of C requires oxygen for complete combustion = $8 / 3 \times 0.9$

= 2.4 Kg

<u>2. Combustion of hydrogen</u>

For H Kg of hydrogen in fuel requires oxygen for complete combustion = $8 \times H$ Kg

0.035 Kg of hydrogen requires oxygen for complete combustion = 8 H

= 8 x 0.35

= 0.28 Kg

3. Combustion of Sulphur

The given sulphur in the fuel requires oxygen for complete combustion = 32 / 32 × S Kg

= S Kg

0.005 Kg of sulphur requires oxygen for complete combustion = 32 / 32 x 0.005

= 0.005 Kg

Minimum mass of oxygen required for complete combustion of 1 Kg of the fuel

= 2.4 + 0.28 + 0.005

(Theoretical O_2 required) = 2.685 Kg

Minimum mass of oxygen required = (Theoretical O_2 required) – O_2 present in fuel

= 2.685 – 0.03

= 2.655 Kg

Minimum mass of air required for complete combustion of 1 Kg of the fuel

= 100 / 23 × 2.655

= 11.54Kg

Example 2:

Calculate the minimum mass of air required for complete combustion of 1 Kg of a fuel having the composition C = 92%, H 2 = 4%, O 2 = 2% and ash = 2% by weight.

C = 92% = 0.92 Kg H 2 = 4% = 0.04 Kg O 2 = 02% = 0.02 Kg

1. Combustion of carbon

For C Kg of carbon in the fuel requires

oxygen for complete combustion = 8 / 3 × C Kg

0.92 Kg of C requires oxygen for complete combustion = 8 / 3 × C Kg

= 8 / 3 × 0.92 Kg

= 2.45 Kg

2. Combustion of hydrogen

For H Kg of hydrogen in the fuel requires oxygen for complete combustion = 8 × H Kg

For 0.04 Kg of hydrogen requires oxygen for complete combustion = 8 × 0.04

= 0.32 Kg

Minimum mass of oxygen required for complete combustion of 1 Kg of the fuel = 2.45 + 0.32

(Theoretical O_2 required)

= 2.77 Kg

Minimum mass of oxygen required = (Theoretical O_2 required) – O_2 present in fuel

= 2.77 – 0.02

= 2.75 Kg

Minimum mass of air required for complete combustion of 1 Kg of the fuel = 100 / 23 × 2.75

= 11.96 Kg

Example 3:

Calculate the minimum amount of air by mass required for complete combustion of 2 Kg of coke assuming 100% carbon.

For C Kg of carbon in the fuel requires oxygen for complete combustion = 8 / 3 × C Kg

Mass of O 2 required for combustion of 2 Kg of coke = 8 / 3 × 2 Kg

= 5.33 Kg

Minimum mass of air required for complete combustion of 2 Kg of the fuel = 100 / 23 × 5.33

= 23.17 Kg

Excess air

During combustion, there is an incomplete combustion, when stoichiometric air is supplied. In practice, excess amount of air is supplied to get complete combustion. To avoid cooling effect, about 25% to 50% preheated air is supplied.

Total mass of air/Kg of fuel = Stoichiometric mass of air + Excess mass of air

Let the theoretical minimum air supplied = Y Kg

Let the air supplied in excess is = 50 %

Excess air supplied = 150 / 100

Then the actual amount of air supplied per Kg of fuel including the excess air

= Y × (100 + 50 / 100)

Minimum mass of air required for complete combustion of 1 Kg of the fuel

=Y × (150 / 100)

= Y × 1.5 Kg of air

Example 4

Calculate the mass of air to be supplied for the combustion of 1 Kg of a fuel containing 75% carbon, 8% hydrogen and 3% oxygen, if 40% excess air is supplied.

C = 75% = 0.75 Kg H = 8% = 0.08 Kg O = 3% = 0.03 Kg

1. Combustion of carbon

For C Kg of carbon in the fuel requires oxygen for complete combustion = 8 / 3 × C Kg

0.75 Kg of C requires oxygen for complete combustion = 8 / 3 × 0.75 Kg

= 2 Kg

2. Combustion of hydrogen

For H Kg of hydrogen in the fuel requires oxygen for complete combustion = 8 × H Kg

0.08 Kg of hydrogen requires oxygen for complete combustion = 8 × H Kg

= 8 x 0.8

= 0.64 Kg

Minimum mass of oxygen required for complete combustion of 1 Kg of the fuel

= 2 + 0.64

(Theoretical O_2 required)

= 2.64 Kg

Minimum mass of oxygen required = (Theoretical O_2 required) – O_2 present in fuel

= 2.64 – 0.03 = 2.61 Kg

Minimum mass of air required for complete combustion of 1 Kg of the fuel

= 100 / 23 × 2.61

= 11.35Kg

Excess air supplied = 40%

Minimum mass of air required for complete combustion of 1 Kg of the fuel

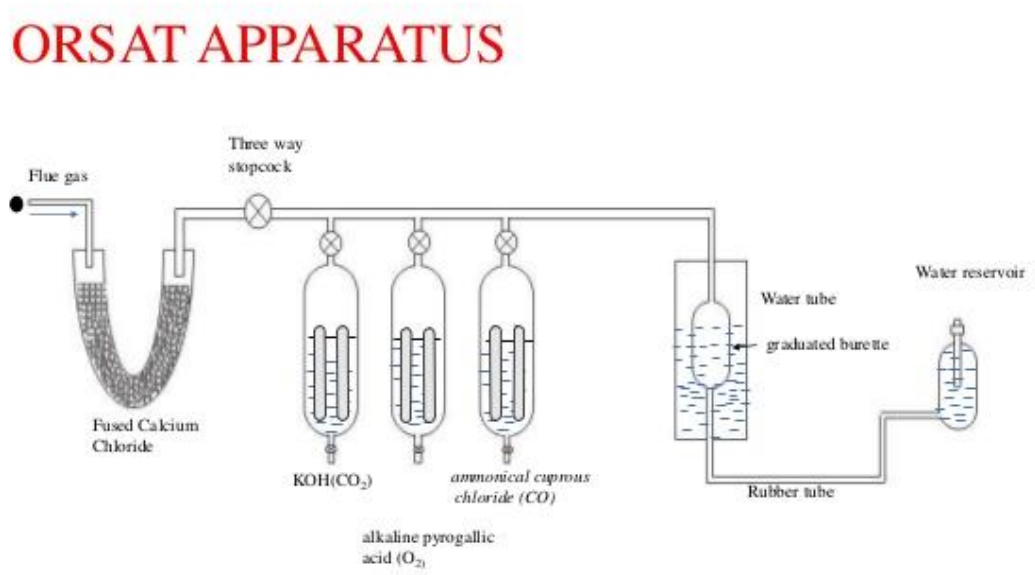
= 11.35 × 140 / 100

= 15.89 Kg

Flue gas

Flue gas is a mixture of gases produced from the products of combustion of a fuel. Its major constituents are CO, CO_2, O_2 and N_2.

The efficiency of combustion can be understood by quantitative analysis of flue gas. Usually, excess oxygen in the flue gas suggests that excess of air is supplied for combustion. More carbon monoxide content, suggests, incomplete combustion process. Based on flue gas analysis, improvement in the design of internal combustion engines, combustion chamber, furnace, etc., can be done.



Flue gas analysis by Orsat's apparatus

Mainly, the flue gases CO, CO_2 and O_2 are quantitatively analysed by Orsat's apparatus. The apparatus consists of a graduated burette (100 ml) surrounded by water, for maintaining constant temperature. One end of burette is connected to a leveling bottle through a rubber tube. The leveling bottles contain saturated NaCl solution which does not absorb any flue gases. By raising and lowering the leveling bottle, the volume of gases present in it are made to overflow and have close contact with three absorption pipette solutions.

The absorption pipettes have solution for absorption of CO_2, O_2 and CO respectively. The first pipette is filled upto the mark with standard KOH solution to absorb CO_2. The second pipette is filled with standard alkaline pyrogallol solution. This solution absorbs CO_2 and O_2. The third pipette is filled with standard ammonical cuprous chloride. This solution absorbs CO_2, O_2 and CO. Hence, it is necessary to pass the flue gas first through standard KOH solution and then through standard alkaline pyrogallol solution and finally through standard ammonical $CuCl_2$ solution.

To flush out the air in the apparatus, the three way stop clock is opened to the flue gas supply after closing the entries of absorption pipettes. By lowering the leveling bottle, the flue gas is admitted in the burette and the three way stop clock is opened to the flue gas supply after closing the absorption pipettes. Now, the leveling bottle is raised and the gas-air mixture is pushed out into the atmosphere. The procedure is repeated until the pure flue gas occupies the apparatus. Then adjust the leveling bottle and exactly permit 100 ml of the flue

gas as noted in the burette and close the three way stop clock completely. First, the stopper of the first absorption pipette having KOH solution is opened and the flue gas in the burette is forced into pipette solution by raising the leveling bottle. By repeatedly raising and lowering the leveling bottle, the gas is brought into intimate contact with the pipette KOH solution which absorbs the

CO_2 gas completely.

Then, the residual gases are taken into the burette and the levels of the KOH solution is made to stand in fixed mark. By adjusting the leveling bottle, the volume of residual gases after the removal of CO_2 by the absorption pipette is measured in the burette. The decrease in volume gives the volume of CO_2in 100 ml of the sample flue gas. The same procedure is then repeated with the alkaline pyrogallol solution.

After the absorption of O_2 in the absorption pipette, the pipette level is fixed and entry closed. After that the burette reading is noted by leveling with the leveling bottle. The further decrease in volume gives the volume of O_2 in 100ml.of the flue gas.

Finally, the third absorption pipette is opened and by adjusting the leveling bottle up and down, the remaining flue gas is forced to pass through the ammonical cuprous chloride solution of the absorption pipette. This is done to have complete absorption of the remaining CO gas in the absorption pipette.

After this, the level of pipette is made fixed and entry closed. The residual gas finally present in the burette is then measured by using the leveling bottle. The decrease in value from the last noted value gives the volume of CO present in 100 ml. of the flue gas. The percentage of nitrogen is obtained by the difference.

QUESTIONS

PART – A

1. Define combustion.
2. Write the complete equation for the combustion of methane present in a fuel.
3. What is flue gas?

PART – B

1. Mention the use of flue gas analysis.
2. Name the reagents used for the absorption of CO_2, O_2 and CO in flue gas analysis.

PART – C

1. Explain flue gas analysis by Orsat apparatus.
2. Calculate the mass of oxygen required for the combustion of 1 Kg of a carbon, hydrogen and sulphur.
3. A sample of hydrocarbon contains 18.18% hydrogen and 81.82% of carbon by weight. Find the mass of air required for the complete combustion of 1 Kg of the fuel.
4. A sample of coal was found to have the following composition.C = 75%, H_2 = 5.2%, O_2 = 12.1%, N_2 = 3.2% and ash = 4.5% by mass.
   i. Calculate the amount of air required for complete combustion of 1 Kg of coal.
   ii. Calculate the amount of air required for complete combustion of 1 Kg of coal if 40% excess air is used.

5. A fuel is found to contain C = 90%, H = 6%, S = 2.5%, O2 = 1% and ash= 0.2% by mass.
   i. Calculate the amount of air required for complete combustion of 1 Kg of fuel.
   ii. Calculate the amount of air required for complete combustion of 1 Kg of fuel if 25% excess air is used.

2.3 ROCKET PROPELLANTS

Rocket propellants

Rocket propellants are either high oxygen containing fuels or a mixture of fuels and oxidants which produce large volume of gases on combustion.

These gases are allowed to escape through a small opening. Now a thrust is developed and the rocket is pushed in the opposite direction.

Eg. Nitrocellulose, nitroglycerine, hydrazine, hydrogen peroxide are the common examples for rocket propellants.

Characteristics of rocket propellants

- They should produce huge volume of gases on combustion.
- They should produce low molecular weight products like H_2, N_2, CO on combustion.
- They should burn at a slow and controlled rate.
- They should be stable over wide range of temperature.
- They should be safe to handle and store.
- They should not produce any toxic products.
- They should not leave any solid residue.
- They should produce high temperature on combustion.

Classification of propellants

Rocket propellants are classified into two types.

1. Solid propellants
2. Liquid propellants

Solid propellants

Solid propellants are classified into homogeneous propellants and heterogeneous propellants.

Homogeneous propellants

A single solid propellants or a mixture of solid propellants thoroughly mixed in a colloidal state is called a homogeneous solid propellants.

Examples

1. Nitrocellulose or gun-cotton
2. A mixture of nitrocellulose and nitroglycerine(ballistae)
3. A mixture of nitrocellulose and nitroglycerine and petroleum jelly(cordite)

Heterogeneous propellants

A heterogeneous solid propellants contains an oxidizing dispersed in a fuel.

Examples

1. A mixture of potassium perchlorate,asphalt oil.
2. A mixture of ammonium perchlorate, resin binder.
3. A mixture of ammonium picrate,sodium nitrate and plastic resin.

Liquid propellants

Liquid propellants are classified in to two types.

1. Monopropellants
2. Bipropellants

Monopropellants

A monopropellants has fuel and oxidant in the same molecule or in solution containing the fuel and oxidant.

Examples

H_2O_2, nitromethane, ethylene oxide, hydrazine and a mixture of methanol.

Bipropellants

The liquid fuel and oxidant are kept separately. Mixing takes place in the combustion chamber by injection them separately into the combustion chamber.

Common fuels : Liquid hydrogen, hydrazine, ethyl alcohol, kerosene

Common oxidant : Liquid oxygen, ozone, liquid fluorine, hydrogen peroxide.

QUESTIONS

PART – A

1. Define Rocket propellants.
2. Name the classification of Rocket propellants.
3. What are the types of solid propellants?

PART – B

1. Give three examples of homogeneous propellants.
2. Define mono propellants. Give an example.

PART – C

1. Explain the charactertics of rocket propellants.
2. Define solid propellants. How are they classified? Give an example.

UNIT – III

3.1 POLYMER

Natural rubber

Rubber is a natural elastic polymer of isoprene (C_5H_8). It is obtained from the milk of rubber called 'Latex'.

Defects of natural rubber

The natural rubber obtained from latex cannot be used in industries because it has the following defects.

- It becomes soft and sticky during summer.
- It becomes hard and brittle during winter.
- It swells up in oils.
- It flows plastically due to prolonged stress.
- Chemicals easily affect natural rubber.

Compounding of rubber

Natural rubber is compounded with certain substances to increase the **quality of rubber.**

1. Reinforcing agents or hardeners

They are compounded with natural rubber to give strength to the rubber.

Example: Carbon powder, zinc oxide, calcium carbonate etc.

2. Softeners

They are added to make the rubber more soft and elastic.

Example: Vegetable oils, stearic acid, paraffin oil, etc.

3. Anti-oxidants

They are added to prevent destruction of rubber due to aerial oxidation.

Example: β-naphthol, phenol.

4. Vulcanization

Vulcanization is process of heating the natural rubber with sulphur at 140°C in CO_2 atmosphere. By vulcanization, the hardness of rubber is improved.

Example: sulphur.

5. Pigments (Colouring matter)

They are added to give different colours to rubber.

Example:

Zinc oxide - White

Lead chromate - Yellow

Chromium oxide – Green

6**. Accelerators**

They are added to speed up the vulcanization reaction of rubber.

Example: Benzothiozole

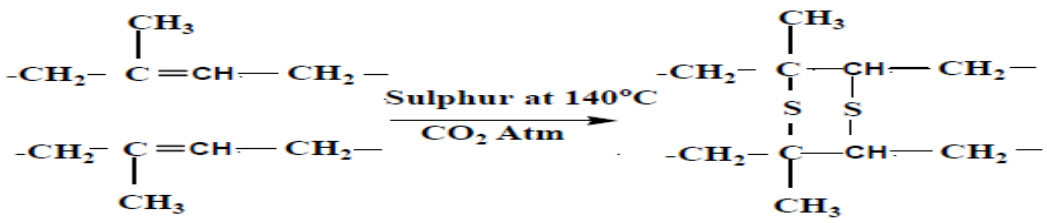
7. Fillers

Fillers are added to increase the quantity without affecting the quality. The production cost is reduced.

Example: Textile wastes, asbestos, mica, gypsum, talc, etc.

Vulcanization of rubber

- Vulcanization is compounding of rubber with sulphur.
- Vulcanization is process of heating the natural rubber with sulphur at 140°Cin CO_2 atmosphere.
- The double bonds present in rubber chain opened and cross linked through sulphur atoms. Hence the vulcanized rubber becomes very hard.
- The hardness of rubber increases as the percentage of sulphur increases.2 to 4% sulphur addition gives soft elastic rubber. When sulphur content is more than 30%, hard rubber called 'Ebonite' is obtained.



PLASTICS

The name plastics or plastic materials in general is given to organic materials of high molecular mass, which can be moulded into any desired form when subjected to heat and pressure in presence of catalysts. Polymer resin is the basic binding material, which forms the major part of plastics. In the recent years, plastics have attained greater importance in every walk of life due to their unique properties. Now plastics substitute all engineering materials like wood, metal, glass, etc. because of their special advantages over other conventional materials.

Plastics

Plastics are organic polymer materials of high molecular mass, which can be moulded into different shapes by using heat and pressure.

Types of plastics

Plastics are classified into two types.

1. Thermoplastics
2. Thermosetting plastics

1. Thermoplastics

They are the resins which soften on heating and set on cooling. Thus, they can be remoulded any number of times and used.

Example: Polythene, PVC, nylon, etc.

2. Thermosetting plastics

They are the resins which set on heating and cannot be resoftened. Hence, their scrap cannot be reused.

Example: Bakelite (Phenol-formaldehyde resin), urea-formaldehyde resin, etc.

Differences between thermoplastics and thermosetting plastics

The differences between the two types of plastics arise mainly due to the difference in their chemical structure.

S.No	Property	Thermo plastics	Thermo setting plastics
1.	Action of heat	They soften on heating and set on cooling every time	They set on cooling and cannot be resoftened
2.	Types of bonding between adjacent polymer chains.	The polymer chains are held together by weak force called Vander wall's force of attraction	The polymer chains are linked by strong chemical bonds (covalent bonds)
3.	Solubility	They are soluble in organic solvents.	They are insoluble in Organic solvents.
4.	Expansion due to heating	They expand very much on heating	Their expansion is only marginally on heating
5.	Types of polymerisation	They are formed by addition polymerisation	They are formed by condensation polymerisation
6.	Types of moulding	They are proceeded by injection moulding	They are proceeded by compressing moulding
7.	Scrap recovery	Scrap can be reused	Scrap cannot be reused
8.	Example	Polythene, PVC, nylon	Bakelite

Mechanical properties of plastics

1. **Creep or cold flow**

   Creep is a time dependent continuous deformation of plastics under load. Plastics undergo a change in shape when a load is applied continuously. Creep is due to the displacement of molecules in a polymer structure. Because of this property, plastics cannot be used as load bearing materials.

2. **Strength to weight ratio**

   The stress to strain ratio of a plastic is higher than that of the lightest metals namely Al or Mg. Plastics have good strength when compared to the light weight metals like aluminium, magnesium, etc. Hence, they replace metals like aluminium and magnesium in many fields. Therefore plastics are mainly used for rocket and space ship constructions.

3. **Thermal stability**

   Plastics either degrade or soften at high temperatures. Hence, they cannot be used at high temperatures.

4. Softening temperature

Softening temperature refers to the particular temperature at which a plastic changes from elastic stage to fluid stage. Temperature below which a polymer is hard and above which it is soft is known as 'Glass transition temperature (T_g).

5. Optical properties

Some of the plastics are transparent like glass. Hence, they can be substituted for glass in optical instruments.

6. Electrical properties

Plastics are good insulators as they are poor conductors of electricity. So they are mainly used for electrical insulation purposes.

7. Hardness

Hardness is defined as the resistance of the plastics to penetration, scratching etc. Hardness of plastics can be determined by penetration tests. Thermosetting plastics are hard in nature when compared to thermoplastics.

8. **Impact strength**

When subjected to suddenly applied load or stress, plastics undergo rupture at a particular load or stress. Impact strength of plastics is measured by tests in which a pendulum is allowed to attack the specimen. Plastics have better impact strength when compared to glass. Hence, they are replacing glasses in many places.

9. **Tear resistance**

The resistance to tearing is an important property when plastic films are used as packing material. It is measured by using a falling pendulum with a striking edge. Plastics have poor tear resistance

Biomaterials (Polymers in medicine and surgery)

Biomaterials are the materials that can be implanted in the body to provide special prosthetic functions and used in diagnostic, surgical and therapeutic applications without causing adverse effect on blood and other tissues.

Use of polymers as biomaterials is increasing day-by-day, since, many polymers have diverse properties which are more similar to the certain organs of the body. Their appeal and acceptability is mainly due to their versatility and the fact that they are tailor-made or modified at will, suits specific body functions.

Biomedical uses of polymers

The mostly used polymers in medical applications are silicone rubber and polyurethane. Polymers used in specific medical applications in medicine are given below.

S.No.	Polymer	Applications
1.	Polyurethane	Heart valves, blood filters, artificial hearts, vascular tubes, etc.
2.	Polyvinyl chloride (PVC)	Disposable syringes, etc.
3.	Polypropylene	Heart valves, blood filters, etc.
4.	Polyethylene	Disposable syringes, etc.

QUESTIONS

PART – A

1. What is rubber?
2. What is Latex?
3. What is compounding of rubber?
4. What is vulcanization?
5. Give any two defects of natural rubber.
6. Define plastic.
7. What are the types of plastics?
8. What are biomaterials?

PART – B

1. Give any three defects of natural rubber.
2. What are thermoplastics? Give an example.
3. What are thermosetting plastics? Give an example.

PART – C

1. Give any three defects of natural rubber. What is compounding of rubber? Mention the ingredients and their functions.
2. Explain vulcanization of rubber.
3. How natural rubber is obtained from Latex? Explain.
4. List the differences between thermoplastics and thermosetting plastics.
5. Explain the mechanical properties of plastics.
6. What are biomaterials? Mention its uses.

3.2 ABRASIVES

INTRODUCTION

We have observed different hard and soft substances used for the cutting, grinding and polishing surfaces in day-to-day life.

Hard silicon carbide discs are used in workshops in shaping machines. Emery sheets are used to clean the metal surfaces before painting them. Discs are used for sharpening knives and other cutting tools.

Fine metal powders are used for mosaic polishing.

Abrasives

Abrasives are a hard substance which is used for cutting, grinding and polishing the surface of other materials.

Hardness of an abrasive

Hardness is the main property of an abrasive. It is defined as the capacity of an abrasive to grind another substance. Harder the abrasive, better will be its capacity to grind the surface of other substances.

Moh's scale

Hardness of abrasives is measured in a scale called Moh's scale. In Moh's scale, the hardness of Diamond, which is the hardest among all the substances, is taken as 10. The hardness of Talc, which is the softest substance, is taken as 1. Thus, the hardness of other substances in Moh's scale lies in between 1 and 10.

Hardness of abrasive materials

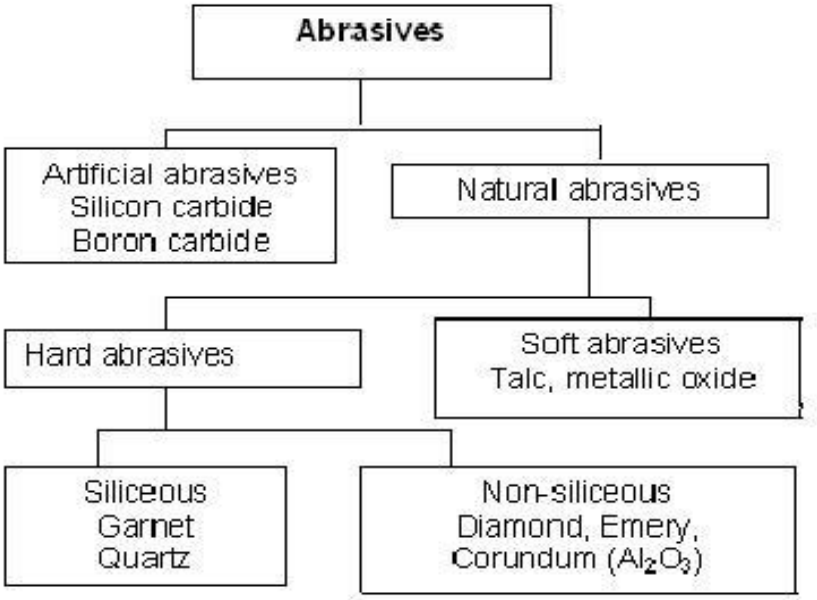
Material	Hardness (Moh's scale)
Talc	1
Gypsum	2
Calcite	3
Fluorite	4
Appatite	5
Feldspar	6
Quartz	7
Topaz	8
Corundum	9
Diamond	10

Generally, hardness of abrasives is measured by piercing a needle through it using some pressure. Hardness is measured in terms of the distance pierced by the needle in the abrasive material and comparing the same with a standard substance of known hardness

The other important property of an abrasive is toughness. Abrasive material should be brittle so that it can function effectively. The other important character of an abrasive is its ability to withstand high temperature (Refractoriness).

Classification

Abrasives are classified as natural and artificial abrasives. They are further classified as follows.



Important natural abrasives

Diamond

- It is a natural, hard, non-siliceous abrasive.
- It is the hardest substance in the world.
- It is an **allotrope** of carbon.
- It is the purest form of carbon.
- Its hardness in Moh's scale is 10.
- The impure varieties called Bort and carbanado are used as abrasives.

Uses

- It is used for cutting, grinding and polishing purposes.
- It is mainly used in rock drilling.

Corundum

- It is a natural, hard, non-siliceous abrasive.
- It is fused aluminium oxide (Al_2O_3).
- It is obtained by fusing the ore of aluminium called Bauxite.
- Its hardness in Moh's scale is 9.

Uses

- It is mainly used in grinding wheels.
- It is specially used for grinding paper pulp.

Emery

- It is a natural, hard, non-siliceous abrasive.
- It is a mixture of corundum (Al_2O_3) and magnetite (Fe_3O_4).
- The presence of magnetite decreases the hardness of corundum.
- Its hardness in Moh's scale is 7 to 9.

Uses

- It is mainly used for scratching and rubbing surfaces.
- It is used for making abrasive paper and cloth.

Types of emery

Depending on the percentage of alumina, emery is classified into the following three types.

S.No	Types of emery	% of alumina	Uses
1.	Grecian emery	85%	In grinding wheels
2.	Turkish emery	75%	Grinding and polishing the glass
3.	American emery	60%	Used in mental and wood polishing work

Garnet

- It is a natural, hard, siliceous abrasive.
- It consists of tri silicates of alumina, magnesia and ferrous oxide.
- Its hardness in Moh's scale is 6.5.

Uses

- It is used for grinding glass.
- It is used for making abrasive paper and cloth.

Important synthetic abrasive

Silicon carbide (SiC)-carborundum:

It is also known as carborundum. It is a siliceous artificial abrasive. In hardness, it is almost equivalent to diamond 9.3.

Preparation

Silicon carbide is prepared by fusing a mixture of silica (sand) and carbon (coke) with some salt and saw dust in an electric arc furnace at 3000°C.

$$\underset{\text{(Sand)}}{SiO_2} + \underset{\text{(Coke)}}{3\,C} \xrightarrow{3000°C} SiC + 2\,CO$$

Salt and saw dust is added to infuse air into the product so that it can be broken into pieces easily.

The product obtained is first washed with strong acid followed by strong base to remove basic and acidic impurities respectively. Finally, it is washed with water.

Properties

- It is very hard and chemically inert.
- Its hardness in Moh's scale is 9.8.
- It can stand at very high temperature

Uses

- It is used for making grinding wheels, cast iron and bronze.
- It is used for cutting and grinding glass.
- It is used for grinding granite. It is used for grinding carbides.

Boron carbide (B_4C)

It is also known as norbide. It is also an artificial siliceous abrasive. It is harder than silicon carbide. It's hardness varies from 9.5 to 9.7 on Moh's scale.

Preparation

Boron carbide is prepared by heating a mixture of boron oxide (B_2O_3) and carbon (coke) in an electric arc furnace at 2500°C.

$$2B_2O_3 + 7C \xrightarrow{2500°C} B_4C + 6CO\uparrow$$

The product obtained is first washed with strong acid followed by strong base to remove basic and acidic impurities respectively. Finally, it is washed with water.

Properties

- It is chemically inert.
- It is harder than silicon carbide.
- Its hardness in Moh's scale is 9.5 to 9.7.

Uses

- It is used for cutting steel.
- It is used for cutting tungsten carbide.
- It is used for grinding other hard materials.

QUESTIONS

PART – A

1. What are abrasives?
2. What is Moh's scale?
3. Give two examples for natural abrasives.
4. Give two examples for synthetic abrasives.
5. What is carborundum?
6. What is norbide?

PART – B

1. How are abrasives classified? Give an example.
2. List the uses of diamond.
3. List the uses of corundum.
4. List the uses of emery.
5. List the uses of garnet.
6. List the uses of silicon carbide.
7. List the uses of boron carbide.
8. How is carborundum prepared?
9. How is norbide prepared?

PART – C

1. What are abrasives? How are they classified? Give an examples.
2. Write a note on the following natural abrasives.

   a. Diamond b. Corundum c. Emery d. Garnet
3. How is silicon carbide prepared? Explain. Give its properties and uses.
4. How is boron carbide prepared? Explain. Give its properties and uses.

3.3 COMPOSITE MATERIALS

INTRODUCTION

Each class of basic engineering materials like metals, high polymers and ceramics has its own outstanding and distinct characteristics as well as laminates. However very stringent requirements of supersonic aircraft, gas turbines and high temperature reactors have forced to develop a new class of materials called “composites”.

The composite materials are generally made by placing the dissimilar materials together in such a manner that they work as a single mechanical unit. The properties of new materials so produced are different in kind and scale from those of any constituents.

Thus, it has become possible to incorporate or alter properties, more than that introduces a combination of properties like high strength and stiffness at elevated temperatures. Metals for instance, lose their strength at elevated temperatures. High polymeric materials in general can withstand still lower temperatures.

Ceramics, due to their brittleness are unsatisfactory structural materials. This led to the exploration of combination of metals and polymers with ceramics resulting in composites having required properties which seems to be the hope for the future.

Composite material

A composite material contains two phases namely

1. Matrix phase
2. Dispersed phase.

Matrix phase:

A continuous body constituent which encloses the composite and gives a bulk form is called matrix phase. The matrix acts as a medium which protects and binds the dispersed phase.

The matrix phase may be metals, ceramics or polymers.

Dispersed phase:

The substance which is dispersed in the matrix phase is called the dispersed phase. It constitutes the internal structure of the composite.

Definition:

A multiphase material consisting of a mixture of two (or) more substances with different properties which are mutually insoluble is called as Composite material.

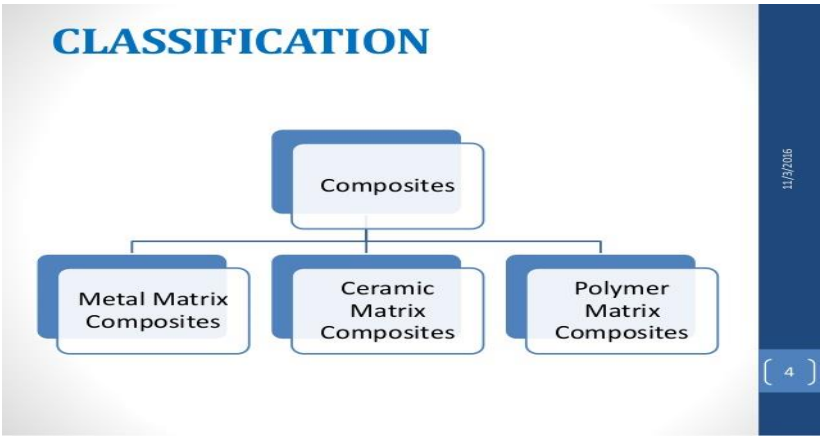
Concrete is the best example for composite.

Thus, using composites it is possible to have such combination of properties like high strength and stiffness, corrosion resistance and ability to with stand extreme high temperature conditions.

Examples

1. Wood (A composite of cellulose fibers and lignin cementing materials)
2. Rain proof cloth (A cloth impregnated with water-proof material)
3. Bone (A composite of soft callogen and brittle and hard material apatite)

Classification of composites



Advantageous properties of composite materials over metals and polymers

The important advantages of composite materials over metals and polymers are given below.

- Higher specific strength.
- Lower specific gravity.
- Higher specific stiffness.
- Lower electrical conductivity.
- Better corrosion and oxidation resistance.
- Good impact and thermal shock resistance
- Can be fabricated easily.

General applications of composite materials

- In fabrication of roof and floors.
- In aeronautical applications like components of rockets, aircrafts, helicopters, etc.
- In valves, pump parts, spray nozzles, etc.
- In communication antennae, electronic circuit boards, etc.
- In marine applications like propellers, shaft, hulls and other ship parts.
- In automobile industries, turbine engines, etc.

QUESTIONS

PART – A

1. What are composite materials?
2. Give an example for composite materials.

PART – B

1. Write any three advantages of composite materials over metals and polymers.
2. Mention any three applications of composite materials.

PART – C

1. Write a note on advantages of composite materials over metals and polymers.
2. Mention the applications of composite materials.

UNIT-IV

4.1 ELECTROCHEMISTRY

INTRODUCTION

Electrochemistry is a branch of chemistry which deals with the relationship between electrical energy and chemical energy. It deals the chemical reactions brought by electric current and chemical reaction producing electrical current.

Electrochemical reactions find applications in many industries. Electrochemistry broadly discusses about electrical effects on passing electricity through a solution.

Electrolysis comes under this category and finds applications in

i) Metallurgy

ii) Electroplating

Iii) Chemical manufacturing processes including medicines.

Chemical effects producing electricity

Electrochemical cells including Dry cells, Daniel cells, Leclanchecells, rechargeable batteries are used in day to day life in torchlight, transistors, wall clocks, automobiles and cell phones.

The basics of electrolysis and its applications in electroplating are discussed in the following sections.

Electrolyte

An electrolyte is a substance, which conducts electricity both in solution and in fused state.

Example: Sodium chloride, hydrochloric acid, copper sulphate solution, etc.

Non-electrolytes

A non-electrolyte is a substance which does not conduct electricity either in solution or in fused state.

Example: Sugar solution, urea solution, alcohol, etc.

Strong electrolytes

The electrolytes, which ionize completely in solution, are called strong electrolytes.

Example: Sodium hydroxide, potassium chloride, sodium chloride solutions etc.

Weak electrolytes

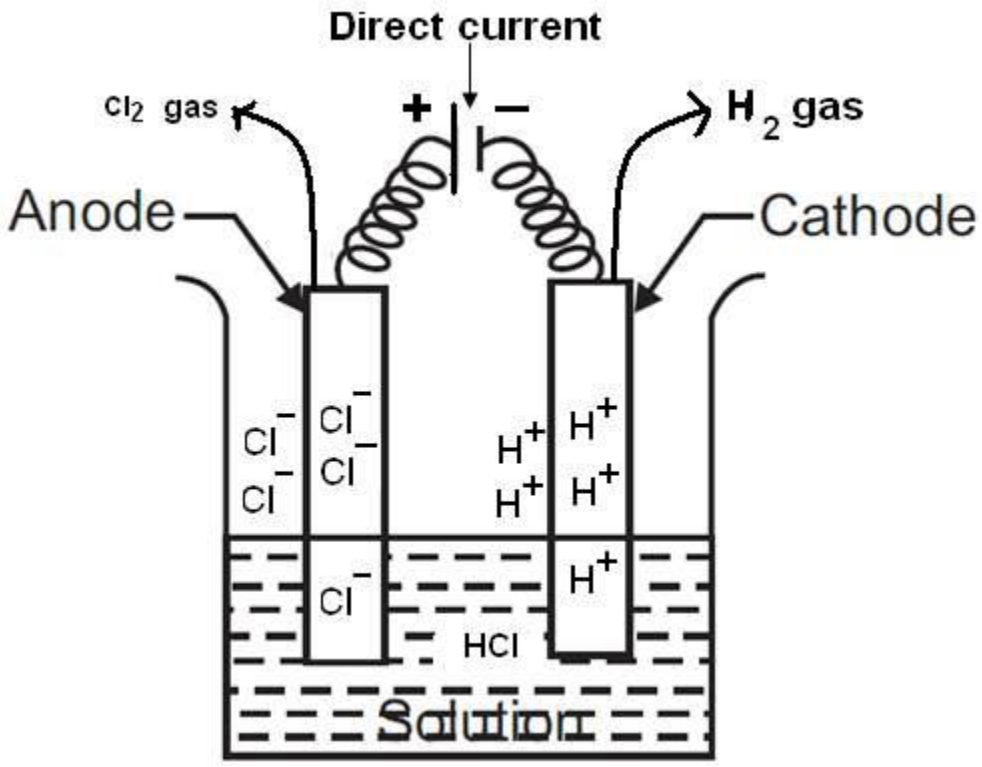
Electrolytes which do not ionize completely in solution are called weak electrolytes.

Example: Acetic acid, oxalic acid, etc.

Electrolysis

Decomposition of an electrolyte by passing electric current is called electrolysis. During electrolysis, electrical energy is converted into chemical energy.

Example: Electrolysis of hydrochloric acid.



Mechanism of electrolysis

Hydrochloric acid contains H^+ ions and Cl^- ions. During electrolysis, H^+ions move towards the cathode (-ve electrode). So, H^+ ions are called cations. Similarly Cl^- ions move towards the anode (+ve electrode). So, Cl^- ions are called anions.

Anodic reaction:

At the anode, Cl^- ions get oxidized to chlorine atoms by loss of electrons.

$Cl^- \rightarrow Cl + e^-$ (oxidation)

$2Cl \rightarrow Cl_2$ (gas)

Chlorine gas is liberated at the anode.

Cathodic reaction:

At the cathode, H+ ions get reduced to hydrogen atoms by gain of electrons.

$H^+ + e^- \rightarrow H$ (reduction)

$2H \rightarrow H_2$ (gas)

Hydrogen gas is liberated at the cathode.

Thus, hydrochloric acid decomposes into hydrogen and chlorine.

Electrolysis depends on the following factors:

- Nature of electrodes used
- Physical nature of electrolytes used.

Industrial Applications of Electrolysis

Electrolysis is applied in

(i) Electroplating

(ii) Anodisation of Aluminium

(iii) Electrolytic refining of metals.

Electroplating

Electroplating is the coating of a more noble metal over a less noble metal by electrolysis.

Electroplating is done for the following purpose.

(a) To make the surface corrosion resistant.

(b) To improve the surface appearance.

In electroplating,

The metal which is to be electroplated (base metal) is taken as cathode; the metal to be coated on (coat metal) is taken as anode. A salt solution of coat metal is taken as electrolyte.

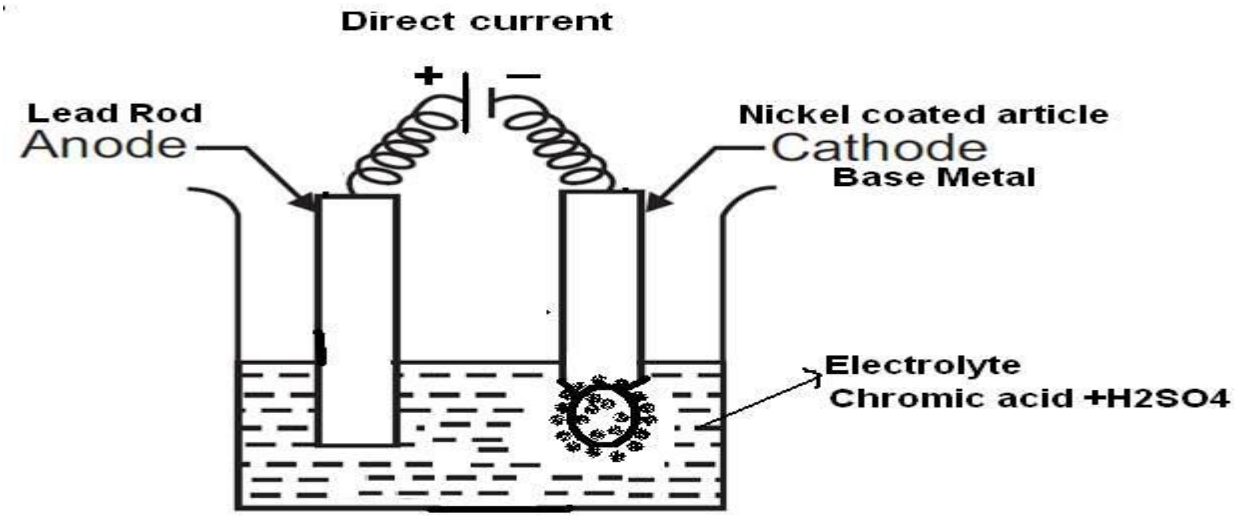
Example: Chrome plating, silver plating, copper plating, gold plating etc.

Chrome plating

Coating of chromium over nickel or copper coated mild steel is called chrome plating.

<u>Process:</u>

The nickel or copper coated iron article (base metal) is placed at the cathode.



- A lead-antimony rod is used as the anode.
- A solution of chromic acid and sulphuric acid (100:1) is used as the electrolyte.
- Temperature of the electrolytic solution is maintained at 40^0C to 50^0C.
- A current density of 100 – 200 mA/cm^2 is used.
- Sulphate ions act as catalyst for coating.

When electric current is passed, electrolysis takes place and chromium is deposited over the base metal.

ELECTROCHEMICAL CELL

INTRODUCTION

A system in which two electrodes are in contact with an electrolyte is called as cell. There are two types of cells.

i) Electrolytic Cell

ii) Electrochemical cell.

Electrolytic cell is a device which produces chemical change when an electrical energy from outside source is supplied. Here, electrical energy is converted into chemical energy.

Electrochemical Cell

Electrochemical cell is a device in which chemical energy from a redox reaction is utilized to get electrical energy. Here, chemical energy is converted into electrical energy.

Example: Daniel cell.

Galvanic Cell

Galvanic cells are electrochemical cells in which the electrons transferred due to redox reaction, are converted into electrical energy. A galvanic cell consists of two half cells with each half-cell contains an electrode. The electrode at which oxidation takes place is called anode and the electrode at which reduction occurs is called cathode. The electrons liberated to the electrolyte from the anode leaves the metal ions at anode. The electrons from the solution are accepted by metal ions at the cathode to become metal.

Representation of cell:

Galvanic cell is generally represented as follows.

$M1 / M1^{+} || M2^{+} / M2$ (or) M1 / (Salt of M1) || (Salt of M2) / M2

Where, M1 & M2 are Anode and Cathode respectively and $M1^{+}$& $M2^{+}$are the metal ions in respective electrolyte.

The symbol || denotes salt bridge. The above representation of galvanic cell is known as galvanic cell diagram.

Example: The typical example for galvanic cell is Daniel cell.

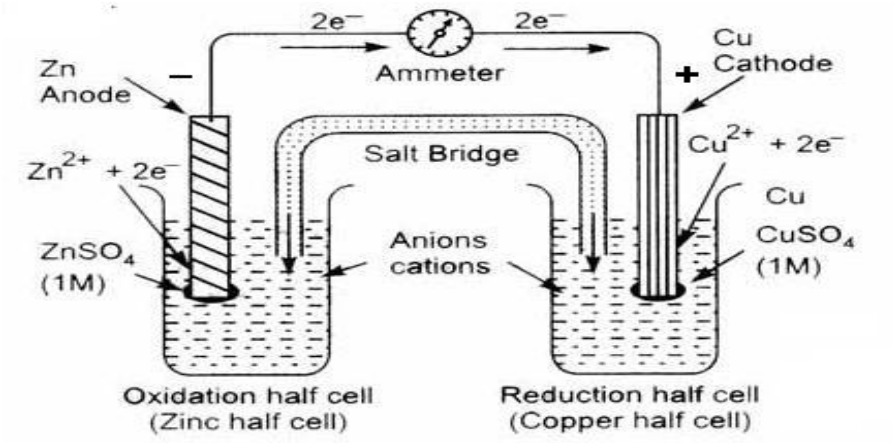
Single electrode potential

The measure of tendency of a metallic electrode to lose or gain electrons when in contact with a solution of its own salt in a half cell of an electrochemical cell is called as single electrode potential. The tendency of an electrode to lose electrons is called oxidation potential while the tendency of an electrode to gain electrons is called reduction potential.

Formation of Daniel Cell

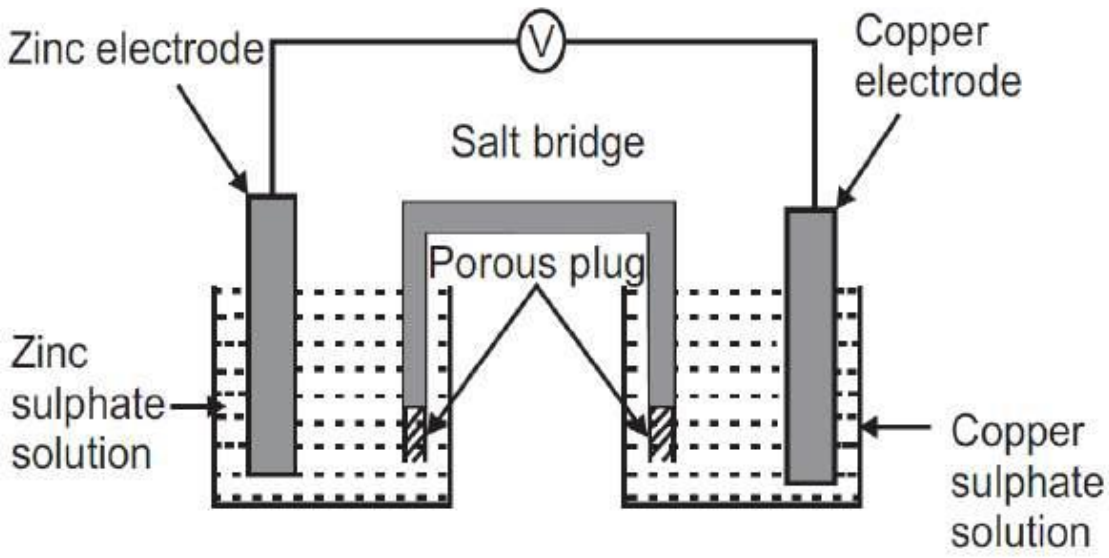
This cell consists of a zinc rod as anode dipped in zinc sulphate solution (electrolyte) in a glass tank and copper rod as cathode dipped in copper sulphate (electrolyte) in another glass tank. Each electrode is known as half-cell. The two half cells are interconnected by a salt bridge and zinc and copper electrodes are connected by a wire through voltmeter. The salt bridge contains saturated solution of KCl in agar-agar gel. The cell diagram of Daniel cell is

$Zn / Zn^{2+} || Cu^{2+} / Cu$ or $Zn / ZnSO_4 || Cu / CuSO_4$



Daniell cell

<u>The other simple diagram of Daniel cell</u>



<u>Redox reaction occurs at the electrodes of the Daniel cell:</u>

<u>At anode</u>

$Zn \rightarrow Zn^{2+} + 2e^{-}$ (Oxidation)

<u>At cathode</u>

$Cu^{2+} + 2e^{-} \rightarrow Cu$ (Reduction)

<u>Overall Cell reaction</u>

$Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$

Electrochemical series:

When various metals as electrodes are arranged in the order of their increasing values of standard reduction potential on the hydrogen scale, then the arrangement is called electrochemical series.

Electrode	Electrode Reaction	Reduction Potential (E^0) Volts	Nature
Li^+ / Li	$Li^+ + e^- \rightarrow Li$	**-3.01**	Anode
Mg^{2+} / Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	**-2.37**	Anode
Pb^{2+} / Pb	$Pb^{2+} + 2e^- \rightarrow Pb$	**-1.12**	Anode
Zn^{2+} / Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	**-0.76**	Anode
Fe^{2+} / Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	**-0.44**	Anode
Sn^{2+} / Sn	$Sn^{2+} + 2e^- \rightarrow Sn$	**-0.13**	Anode
H^+ / H	$H^+ + e^- \rightarrow H$	**0.00**	Pt – reference
Cu^{2+} / Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	**+0.34**	Cathode
Ag^+ / Ag	$Ag^+ + e^- \rightarrow Ag$	**+0.80**	Cathode
Au^+ / Au	$Au^+ + e^- \rightarrow Au$	**+1.50**	Cathode

Significance and applications of electrochemical series

i) Calculation of standard EMF of a cells

Standard electrode potential of any cell can be calculated using this series.

ii)Relative ease of oxidation and reduction

Higher the value of standard reduction potential (+ve value) greater is the tendency to get reduced. Thus, metals on the top having more negative(–ve) values are more easily ionized (oxidized).

iii) Displacement of one element by other

Metals which lie higher in the series can displace those elements which liebelow them in the series.

iv) Determination of equilibrium constant for the reaction

The equilibrium constant for the cell can be calculated from the standard electrode potential.

v)Hydrogen displacement behaviour

Metals having more negative potential in the series will displace hydrogen from acid solutions.

vi) Predicting spontaneity of redox reactions

Spontaneity of redox reaction can be predicted from the standard electrode Potential values of complete cell reaction.

QUESTIONS

PART – A

1. What is an electrochemical cell?
2. Give two examples for electrochemical cell.
3. Define single electrode potential.
4. What is galvanic cell?
5. Write an example for a galvanic cell.
6. What is Daniel cell?

PART-B

1. How will you write a short representation of a Daniel cell?
2. Define electrochemical series.
3. Write any three applications of electrochemical series.

PART - C

1. Explain electrochemical cell with example.
2. Explain the construction and working of Daniel cell.
3. Describe the galvanic cell with cell reactions.
4. What are the applications of electrochemical series?

4.2. ENERGY RESOURCES

INTRODUCTION:

Battery is a device that stores chemical energy and releases it as electrical energy. Hence a device which converts chemical energy into electrical energy is called battery, cell, or storage battery.

A battery is an electrochemical cell which is often connected in series in electrical devices as a source of direct electric current at a constant voltage.

A cell contains one anode and one cathode. The emf of a single cell is around 2 volt. A battery contains several anode and cathode. The emf of a battery which contains six anodes and six cathodes is around 12 v.

Definition:

Battery is a device that stores chemical energy and releases it as electrical energy. Hence a device which converts chemical energy into electrical energy is called battery or cell.

Batteries are classified as follows,

i) Primary battery

ii) Secondary battery

iii) Fuel battery or Flow battery

Primary battery

Primary battery is a cell in which the cell reaction is not reversible. Thus, once the chemical reaction takes place to release the electrical energy, the cell gets exhausted. They are use and throw type.

Example: Dry cell, Leclanche cell etc.

Secondary battery

Secondary battery is a cell in which the cell reaction is reversible. They are rechargeable cells. Once the battery gets exhausted, it can be recharged.

Example: Nickel-Cadmium cell, Lead-acid cell (storage cell), etc.

Lead – acid storage cell:

The typical example for storage cell is Lead-acid storage cell. A secondary battery can operate as a voltaic cell and as an electrolytic cell. When it acts as a voltaic cell, it supplies electrical energy and becomes run down. When it is recharged, the cell operates as an electrochemical cell.

Construction and Working:

A lead – acid storage cell consists of a number of voltaic cells (3 to 6) connected in series to get 6 to 12 V battery. In each cell, a number of Pb plates, used as anodes are connected in parallel and a number of PbO_2 plates, used as cathodes are connected in parallel. The plates are separated by insulators like rubber or glass fibre. The entire combination is immersed in20% dil.H_2SO_4.

The cell is represented as

$$\mathbf{Pb \mid PbSO_4 \mid\mid H_2SO_4 \mid\mid PbSO_4 \mid PbO_2 \mid Pb}$$

When the lead-acid storage battery operates, the following cell reactions occur.

Anodic reaction:

Oxidation reaction takes place at anode. The electrons are released from anode. Hence the anode is called as negative anode and is represented as (-).

Lead is oxidized to Pb^{2+} ions and gives two electrons, which further combines with $SO_4^{2-}$to form insoluble $PbSO_4$.

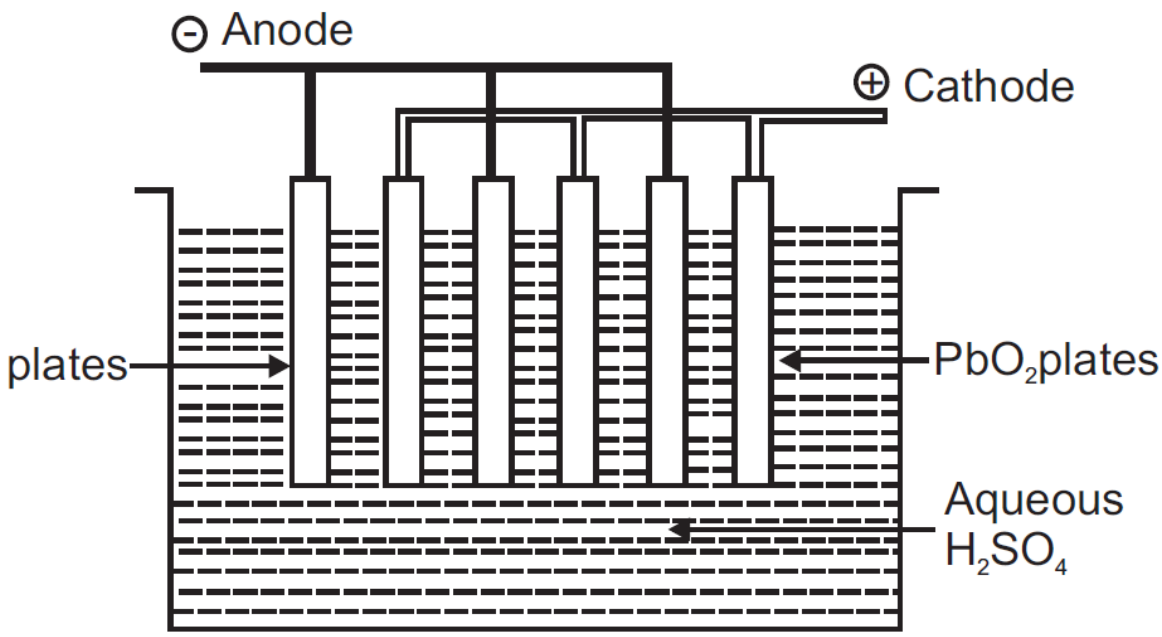
$$Pb\ (s) + SO_4^{2-} \rightarrow PbSO_4\ (s) + 2e^-$$

Cathodic reaction:

Reduction takes place at cathode. Hence the cathode is called as positive cathode and is represented as (+).

PbO_2 is reduced to Pb^{2+} ions, which further combines with SO_4^{2-} to form insoluble $PbSO_4$.

$$PbO_2\ (s) + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4\ (s) + 2H_2O$$



Overall cell reaction during discharging:

$$Pb\,(s) + PbO_2\,(s) + 2H_2SO_4\,(aq) \xrightarrow{\text{discharging}} PbSO_4\,(s) + 2H_2O + \text{Energy}$$

From the above cell reactions, it is clear that $PbSO_4$ is precipitated at both the electrodes and the concentration of H_2SO_4 decreases. So, the battery needs recharging.

Overall cell reaction during recharging:

The cell can be recharged by passing electric current in the opposite direction. The electrode reaction gets reversed. As a result, Pb is deposited on anode and PbO_2 on the cathode. The concentration of H_2SO_4 also increases.

$2PbSO_4\,(s) + 2H_2O + \text{Energy} \rightarrow Pb\,(s) + PbO_2\,(s) + 2H_2SO_4\,(aq)$

Advantages of Lead – acid batteries:

1. It is made easily.
2. It produces very high current.
3. The self-discharging rate is low.
4. It works effectively even at low temperatures.

Uses:

1. Lead – acid batteries are used in cars, buses, trucks etc.
2. It is used in gas engine ignition, telephone exchanges, and power stations hospitals.
3. IT industry, educational institutions, laboratories etc.

Non-conventional Energy Sources

Energy received from the sun is the best example for non-conventional energy resources.

Example: Solar cell

Solar cell

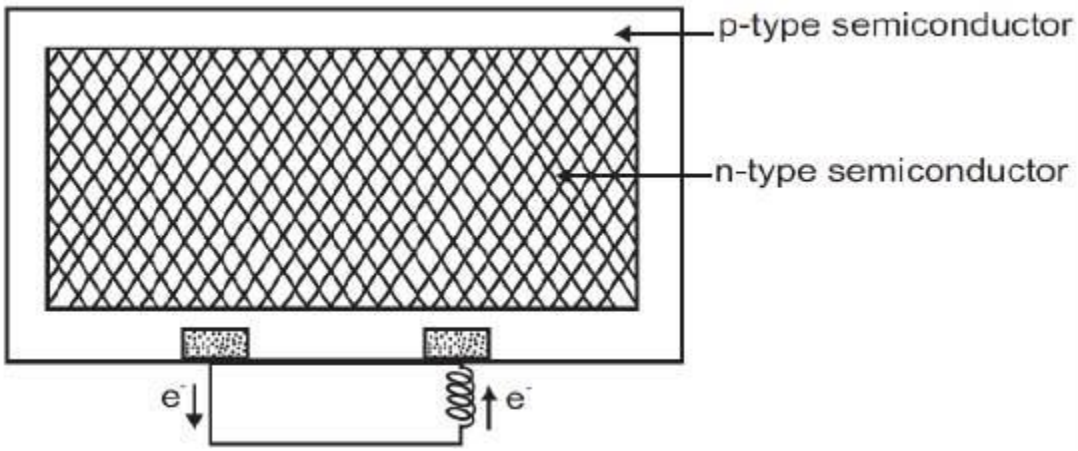
A device which converts the solar energy (energy obtained from the sun) directly into electrical energy is called 'Solar cell'. This is also called as 'Photovoltaic cell'.

Principle:

The basic principle involved in the solar cells is based on the photovoltaic (PV) effect. When sun rays fall on the two layers of semiconductor devices, potential difference between the two layers is produced. This potential difference causes flow of electrons and thus produces electricity.

Example: Silicon solar cell

Construction:



Solar cell consists of a p-type (such as Si doped with boron) and a n-type (such as Si doped with phosphorous) semiconductor plates. They are in close contact with each other.

Working:

When the solar rays fall on the top layer of p-type semiconductor, the electrons from the valence band get promoted to the conduction band and cross the p-n junction into n-type semiconductor. Thereby potential difference between two layers is created, which causes flow of electrons (i.e. electric current). The potential difference and hence current increases as more solar rays falls on the surface of the top layer. Thus, when this p- and n- layers are connected to an external circuit, electrons flow from n-layer to p-layer and hence current is generated.

Applications of solar cell:

1. Solar cells are used in street lights.
2. Water pumps are operated by using solar batteries.
3. They are used in calculators, watches, radios and TVs.
4. They are used for eco-friendly driving vehicles.
5. Silicon Solar cells are used as power source in space crafts and satellites.
6. Solar cells can even be used in remote places and in forests to get electrical energy without affecting the atmosphere.

Fuel Cell

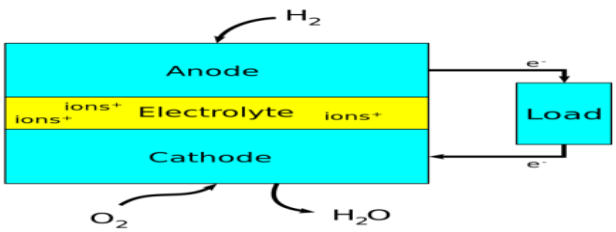
A fuel cell is an electrochemical cell that converts the chemical energy of a **fuel** (often hydrogen) and an oxidizing agent (often oxygen) into electricity through a pair of redox reactions. **Fuel cells** can produce electricity continuously for as long as **fuel** and oxygen are supplied.

Principle:

A fuel cell is a device that converts chemical potential energy into electrical energy.

H_2O_2 Fuel cell (Green Fuel Cell)

In a H_2O_2 fuel cell Graphite impregnated with platinum or palladium alloy is used as a electrodes. Aqueous KOH or H_2SO_4 or ion exchange membrane is used as the electrolyte. Fuel (H_2) is pumped in at the anode and oxidant (O_2) is pumped in at the cathode. The electrodes of the cell are porous to allow the passage of fuel oxidant.



Anodic reaction:

Hydrogen reacts with the ions the electrolyte producing water and electrons.

$2\ H_2(g) + 4OH^-\ (aq) \rightarrow 4H_2O\ (l) + e-$

Cathodic reaction

$O_2\ (g) + 2H_2O(l) + 4e- \rightarrow 4OH^-$

Net reaction: $2H_2\ (g) + O_2\ (g) \rightarrow 2H_2O$

QUESTIONS

PART - A

1. Define a storage battery.
2. What is a primary battery? Give an example.
3. What is a secondary battery? Give an example.
4. Define a fuel cell.

PART-B

1. What is dry cell? Give an example.
2. Write a short representation of lead - acid storage cell.
3. Give any three uses of lead – acid battery.
4. What is a solar cell?
5. Give any three applications of solar cell.

PART - C

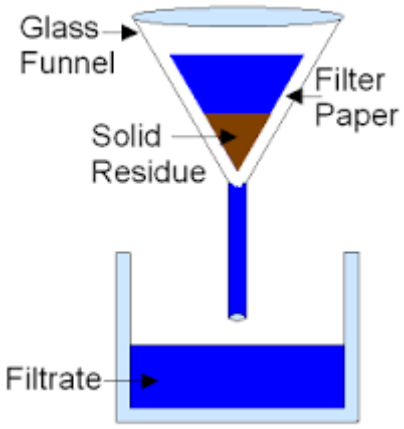
1. Explain the construction and working of lead – acid battery.
2. Write a note on solar cell.
3. Explain the uses of solar cells.
4. Explain construction and working of fuel cell with example.

4.3 Chemical Separation Techniques:

Filtration:

Filtration is the process of separating suspended solid matter from a liquid, by causing the latter to pass through the pores of some substance, called a filter. The liquid which has passed through the filter is called the filtrate.

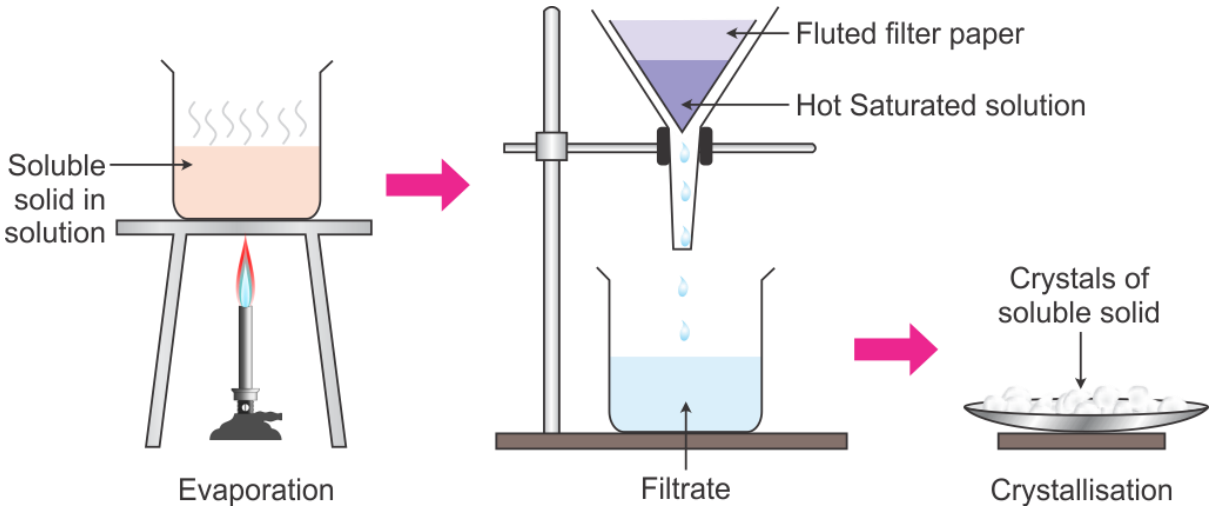
It is a method for separating an insoluble solid from a liquid. When a mixture of sand and water is filtered: the sand stays behind in the filter paper (it becomes the residue) the water passes through the filter paper (it becomes the filtrate)



Crystallization:

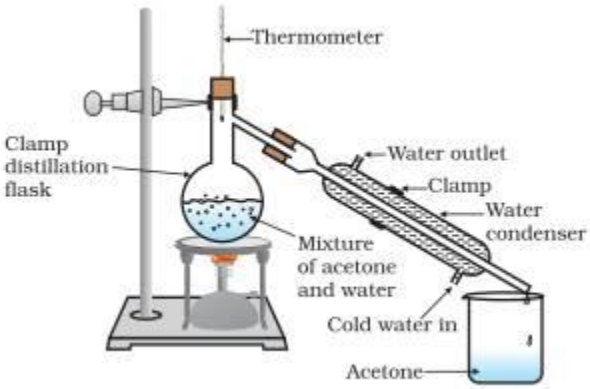
Crystallization is the solidification of atoms or molecules into a highly structured form called a crystal. **Crystallization** can also refer to the solid-liquid separation and purification technique in which mass transfer occurs from the liquid solution to a pure solid crystalline phase.

It is one of the separation methods which is used to obtain pure copper sulphate from an impure sample. Crystallization: The process of cooling a hot, concentrated solution of a substance to obtain crystals is called **crystallization**.



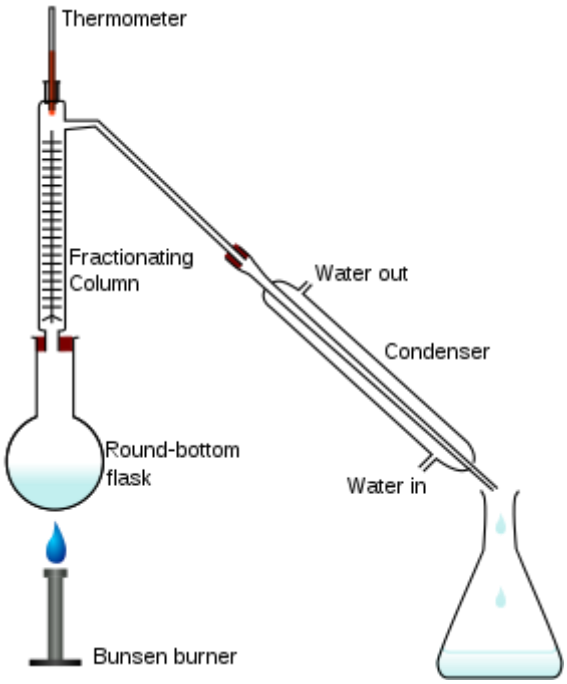
Distillation:

This method is to purify liquids from non-volatile impurities, and used for separating the constituents of a liquid mixture which differ in their boiling points. There are various methods of distillation depending upon the difference in the boiling points of the constituents. The methods are (i) simple distillation (ii) fractional distillation and (iii) steam distillation. The process of distillation involves the impure liquid when boiled gives out vapour and the vapour so formed is collected and condensed to give back the pure liquid in the receiver. This method is called simple distillation. Liquids with large difference in boiling point (about 40k) and do not decompose under ordinary pressure can be purified by simply distillation eg. The mixture of $C_6H_5NO_2$(b.p 484k) &C_6H_6(354k) and mixture of diethyl ether (b.p 308k) and ethyl alcohol (b.p 351k)



Fractional distillation:

This is one method to purify and separate liquids present in the mixture having their boiling point close to each other. In the fractional distillation, a fractionating column is fitted with distillation flask and a condenser. A thermometer is fitted in the fractionating column near the mouth of the condenser. This will enable to record the temperature of vapour passing over the condenser. The process of separation of the components in a liquid mixture at their respective boiling points in the form of vapour and the subsequent condensation of those vapour is called fractional distillation. The process of fractional distillation is repeated, if necessary. This method finds a remarkable application in distillation of petroleum, coal-tar and crude oil.



Chromatography:

The most valuable method for the separation and purification of small quantity of mixtures. As name implies chroma-colour and graphed writing it was first applied to separation of different colored constituents of chlorophyll in 1906 by M.S Tswett, a Russian botanist. He achieved it by passing a petroleum ether solution of chlorophyll present in leaves through a column of $CaCO_3$ firmly packed into a narrow glass tube. Different components of the pigments got separated into land or zones of different colors and now this technique is equally well applied to separation of colorless substances.

Principle: chromatography is selective distribution of the mixture of organic substances between two phases – a stationary phase and a moving phase. The stationary phase can be a solid or liquid, while the moving phase is a liquid or a gas. When the stationary phase is a solid, the moving phase is a liquid or a gas. If the stationary phase is solid, the basis is adsorption, and when it is a liquid, the basis is partition.

Definition: Chromatography is defined as a technique for the separation of a mixture brought about by differential movement of the individual compound through porous medium under the influence of moving solvent. The various methods of chromatography are

1. Column chromatography (CC)

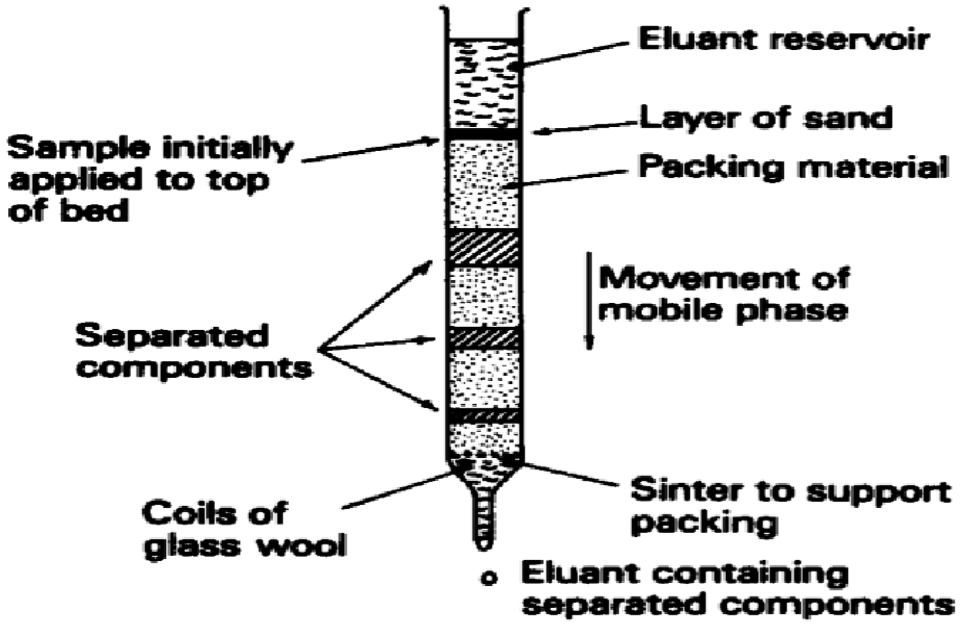
2. Thin layer chromatography (TLC)

3. Paper chromatography (PC)

4. Gas-liquid chromatography (GLC)

5. Ion–exchange chromatography.

Column chromatography:



This is the simplest chromatographic method carried out in long glass column having a stop cock near the lower end. This method involves separation of a mixture over a column of adsorbent (Stationary phase) packed in a column. In the column a plug of cotton or glass wool is placed at the lower end of the column to support the adsorbent powder. The tube is uniformly packed with suitable absorbent constitute the stationary phase. (Activated aluminum oxides (alumina), Magnesium oxide, starch are also used as absorbents).The mixture to be separated is placed on the top of the adsorbent column. Eluent which is a liquid or a mixture of liquids is allowed to flow down the column slowly. Different components depending upon the degree to which the components are adsorbed and complete separation takes place. The most readily adsorbed substances are retained near the top and others come down to various distances in the column.

QUESTIONS

PART - A

1. What is chromatography?
2. What is filtration?
3. Define crystallization.
4. What is fractional distillation?

PART-B

1. Write a short note on distillation.
2. What are the various methods of chromatography?

PART - C

1. Explain column chromatography.
2. Explain the chemical separation techniques of fractional distillation.

UNIT -V

5.1CORROSION

INTRODUCTION

Corrosion is a 'billion' dollar thief'. Even though it is a natural phenomenon in which the gases, moisture and other chemicals present in the atmosphere react chemically with metals to convert them into their salts, it results in loss of material and money. We know very well that metals have a strong crystalline structure and when they are converted into their salts they lose the metallic strength resulting in the damage to machineries in which they are used. Thus corrosion causes damage to metals and thereby to the society. The estimate of loss due to corrosion is approximately 2.5 billion dollars per annum all over the world. Hence it is necessary to understand the mechanism of corrosion.

In this lesson we are going to study about the causes and the mechanism of Corrosion so that we can find ways to prevent this social enemy.

Corrosion is defined as the slow and continuous destruction of metal or alloy by the environment.

Due to corrosion the useful properties of a metal like malleability, ductility, electrical conductivity and also the surface appearance are lost.

The most familiar example of corrosion is rusting of iron when exposed to atmospheric conditions. Another example is the formation of green film or basic Carbonate [$CuCO_3$+$Cu(OH)_2$] on the surface of copper when exposed to moist air containing CO_2 and oxygen.

Definition

Corrosion is defined as the slow and continuous destruction of metal or alloy due to the chemical or electrochemical reaction with its environment.

It may be due to chemical or electrochemical reaction of the metals with the environment.

Example: Rusting of iron.

Causes of corrosion:

Metal occur in nature in two different forms. They are

1. Native state
2. Combined state.

1. Native state:

The metals occur in native, free, uncombined states or **pure metal are highly stable and non-reactive with the environment.** They do not combine with other elements. They are noble metals exist as such in the earth crust. They have very good corrosion resistance.

Eg. Au, Pt, Ag, Pd, Cu , etc.

2. Combined state

Except noble metal, all other metals are reactive and form stable compounds as their oxides, sulphides, chloride and carbonates. They exist in the form of stable compounds called ores or mineral.

Ex.FeO_2.ZnO, PbS,$CaCO_3$ etc.,

Except noble metal, the other metals in the pure state are thermodynamically **unstable** as they are considered in excited state ie., higher energy state. Therefore, as soon as the metals are extracted from their ores, the reverse process begins and form stable **metallic compounds**, which are thermodynamically stable, i.e., lower energy state.

The properties such as electrical conductivity, ductility, malleability etc., are lost due to corrosion.

Types of Corrosion:

Corrosion is of two types.

1. Chemical Corrosion or Dry Corrosion
2. Electrochemical Corrosion or Wet Corrosion

1. Chemical Corrosion or Dry Corrosion

The direct chemical action of atmospheric gases like oxygen, halogens, **H_2S** etc., in a dry environment on metals is known as chemical Corrosion. Due to this, a dry layer of the Corrosion product is formed on the surface of the metal.

Example:

When magnesium is exposed to atmosphere, magnesium oxide is formed over the surface.

$2Mg+O_2 \rightarrow 2MgO$

A solid film of the corrosion product is formed on the surface of the metal which protects the metal from further corrosion. If a soluble or volatile corrosion product is formed, then the metal is exposed to further attack.

For example, chlorine attack silver generating a protective film of silver halide on the surface which prevents the further corrosion.

$2Ag+Cl_2 \rightarrow 2AgCl$

On the other hand, stannic chloride formed on tin is volatile and so corrosion is not prevented.

2. Electro Chemical Corrosion or wet corrosion

Wet corrosion

Wet corrosion occurs due to the electrochemical action of moisture and oxygen on metals. Corrosion of iron takes place due to electrochemical attack.

There are two theories to explain the rusting of iron.

1. Galvanic cell formation theory
2. Differential aeration theory.

1. Galvanic cell formation theory

Definition:

"When a metal with impurities (or two dissimilar metals (Fe and Cu) are in contact with each other) is exposed to atmosphere in presence of an electrolyte or moisture, a mini galvanic cell is formed. The more anodic metal undergoes corrosion. This type of corrosion is known as galvanic corrosion".

Example: Rusting of iron

Corrosion is an oxidation process. Oxidation is a process which involves loss of electron. Oxidation takes place at **anode**. When iron metal with small amount impurities (Cu) is placed in the environment is exposed to the environment (moisture), it undergoes corrosion. Hence it acts as anode and under goes Oxidation. Iron metal loses its two electrons and becomes Fe+2ion. Hence the iron metal undergoes oxidation when it is corroded. The impurities present in the metal act as **cathode** and undergo reduction. The electron released at anode is absorbed at cathode to form either Hydrogen or water or hydroxide ion depending on the environment. The moisture in the environment behaves like **electrolyte**. **Hence a galvanic cell is formed.**

Rusting of iron is explained as below.

<u>Anodic reaction (oxidation)</u>

The metal at the anode is oxidized into ferrous ions.

$Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation-loss of electron)

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3 \rightarrow Fe_2O_3$

Fe^{2+} ions combine with OH^-in the environment forming ferrous hydroxide $Fe(OH)_2$, which under goes further oxidation to give ferric hydroxide $Fe(OH)_3$ the ferric hydroxide undergoes decomposition to give ferric oxideFe_2O_3(Rust).

Thus rust formed is explained based on the theory of Galvanic cell formation.

Electrolyte

The moisture (H_2O) in the environment act as electrolyte. It dissociates to give H^+ and OH^- ions**.**

$$H_2O \rightarrow H^+ + OH^-$$

<u>Cathodic reaction (Reduction)</u>

The electrons released at anode are taken up by the H+ ion in the environment.

(i) In acidic medium (reduction-gain of electron)

$2H^+ + 2e^- \rightarrow H_2$ (gas) ↑

(ii) In neutral solution with oxygen

$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$

The ferric oxide formed (Fe_2O_3) over iron is called as Rusting of iron.

Examples:

1. Corrosion of soldered metal around copper wire.
2. Corrosion of steel shaft in bronze bearing.
3. Corrosion of steel pipe connected to copper plumbing.

<u>Control</u>

Galvanic corrosion can be avoided by selecting two dissimilar metals which are very close in the electrochemical series.

It can also be avoided by connecting two dissimilar metals through insulating material.

By making cathodic area smaller and anodic area larger.

<u>Differential aeration theory or concentration cell formation theory:</u>

According to this theory, when a metal is exposed to varying concentrations of air (oxygen) or an electrolyte, concentration cell is formed. The metallic area which is exposed to less amount of oxygen act as anode undergoes corrosion.

The metallic area which is exposed to greater amount of oxygen act as cathode. Corrosion of metal occurs due to difference in concentration of air or electrolyte. **Hence this theory is called as Differential aeration theory or concentration cell formation theory.**

Examples:

1. Corrosion on wire fence

In an iron fence the point where wires cross is less exposed to oxygen and becomes anode. Therefore corrosion takes place at the point of contact where the wire crosses.

2. Metal partially immersed in water, the immersed portion is less exposed to oxygen and becomes anode. Therefore corrosion takes place.

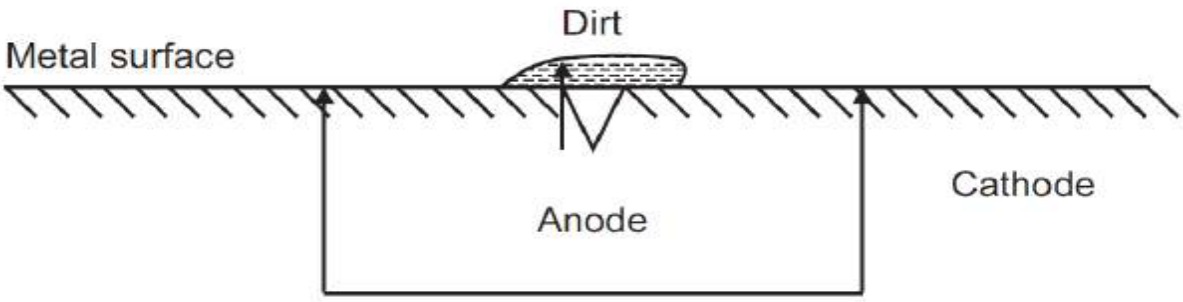
3. Metal area covered by drop of water, sand or dust.

The less oxygenated area acts as Anode (gets corroded)

The more oxygenated area acts as the Cathode (Protected from Corrosion).

Reaction At anode- (less oxygenated area)-oxidation-loss of electron corrosion takes place.

$Fe \rightarrow Fe^{2+} + 2e^{-}$ (oxidation or corrosion)



At cathode (more oxygenated area)

$\frac{1}{2} O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-}$ (Reduction)

$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2$

Which is further oxidized to $Fe(OH)_3$ .Since the anodic area is small and the cathodic area is large, corrosion is more concentrated at the anode. Thus, a small hole is formed on the surface of the metal. This type of intense localized corrosion is called pitting.

Factors influencing the rate of corrosion:

The factors that affect the rate of corrosion are

1) Nature of the metal and its surface

2) Nature of the atmosphere

3) Nature of the corrosion product.

Factors connected with the metal:

1) **The position of the metal in the Electrochemical Series**

The type of impurity present in it and its electropositive nature decides the corrosion of a metal. For example, when iron has impurities like copper, tin, etc. iron corrodes since iron is more electropositive than metals like copper and tin. On the other hand when iron is coupled with zinc, zinc corrodes since zinc is more electropositive than iron.

2) **Purity of the metal.**

Generally pure metal does not corrode, as there is no cathode spot available to induce corrosion.

3) **Surface of the metal.**

A rough surface corrodes readily as it collects more dirt and provides more cathode spot for corrosion. A polished surface does not corrode easily.

4) **Stress corrosion.**

Stress in a metal surface is produced by mechanical workings such as quenching, pressing, bending, and riveting improper heat treatment etc. The portion subjected to more stress acts as anode and other portion act as cathode. This leads to the formation of stress corrosion. Stress corrosion is noted in fabricated articles of certain alloys like high zinc brasses and nickel brasses. Caustic embrittlement noted in boilers is a typical example for stress corrosion, which is due the attack of alkali present in water on stressed boiler metal.

5) **Anode to cathode area ratio.**

When a bigger cathode area covers a smaller anode area, severe corrosion is noted in the anodes pot. This is called erosion. It is frequently encountered in piping agitators, condenser tubes etc. where turbulent flow of gases and vapors remove the coated surfaces resulting in differential cells. Removal of surface coatings can also be caused by rubbing or striking activities of solids

on the coated surfaces.

6) Physical state of a metal.

The rate of corrosion is influenced by grain size, orientation of crystals, stress etc. The smaller the grains size of the metal greater the rate of corrosion.

Factors connected with the Nature of the atmosphere

1. Temperature of the atmosphere:

   The rate corrosion increases with increase of temperature.

2. pH of the atmosphere:

   Lower the pH greater is the corrosion.

3. Amount of moisture in the atmosphere:

   Increase of moisture in the environment increases the rate of corrosion.

4. Amount of oxygen in the atmosphere:

   In some cases oxygen enhances the corrosion and in another it passivates the metal.

5. Amount of chemical fumes in the atmosphere:

Industrial fumes like HCl, H_2SO_4 produces electrolytes which are acidic

in nature and increases the rate of corrosion.

Examples

1. Buried pipelines and cables passing from one type of soil to another suffer corrosion due to differential aeration.

2. Lead pipe line passing through clay get corroded because it is less aerated than sand.

Factors connected with the corrosion product

In some cases the corroded product sticks to the surface and absorbs more moisture. This induces further corrosion. Examples:

a) In Rusting of iron, as rust formed over iron absorbs more moisture, rate of rusting of iron increases.

b) In some cases the corroded product acts as the protective coating which prevents further corrosion.

c) Aluminium oxide formed over the surface of aluminium prevents further corrosion and act as a protective coating. This is the basic principle of anodisation.

d) In some other cases the corroded product falls out of position exposing the fresh metal surface for further corrosion.

E.g. Magnesium Oxide formed over the surface of Magnesium falls out of position exposing a fresh surface for further corrosion

Questions:

Part A

1. What is corrosion?
2. What is dry corrosion?
3. What is wet Corrosion?
4. What are the types of corrosion takes place in a metal when anode is small `and cathode is large? Why?

Part B

1. Write a note on galvanic cell formation theory.

2. Write a note on differential aeration theory.
3. What are the factors influencing the rate of corrosion?

PART-C

1. Explain the mechanism of Galvanic corrosion.
2. Explain the differential aeration theory with suitable examples.

5.2 METHODS OF PREVENTION OF CORROSION

INTRODUCTION

Corrosion can be prevented by the following methods:

1. Control of environment
2. Alloying
3. Surface coating
4. Cathodic protection

Control of environment:

The corrosion rate can be reduced by modifying the environment. The environment can be modified by the following:

1. Deaeration: **Removal of dissolved oxygen and other gases in water by mechanical agitation is called deaeration**.The presence of increased amounts of oxygen is harmful since it increases the corrosion rate. Deaeration aims at the removal of dissolved oxygen.

Dissolved oxygen can be removed by deaeration or by adding some chemical substance like Na_2SO_3.

2. Dehumidification: **Removal of moisture content present in air is called as dehumidification.** This can be achieved by adding silica gel which can absorb moisture preferentially on its surface.

3. Inhibitors: In this method, some chemical substance known as inhibitors are added to the corrosive environment in small quantities. These inhibitors substantially reduce the rate of corrosion.

Alloying:

Both corrosion resistance and strength of many metals can be improved by alloying. eg . Stainless steels containing chromium produce a coherent oxide film which protects the steel from further attack.

Surface Coating:

Surface coating the method of coating of one metal over the other metal (metal to be protected from corrosion). Corrosion of metal surfaces is a common phenomenon. To protect a metal surface from corrosion, the contact between the metal and the corrosive

environment (air, moisture, corrosive gases, etc.) is to be cut off. This is done by coating the surface of the metal with a continuous, non-porous material. Such a coating is referred to as surface coating or protective coating. In addition to protective action, such coatings also give a decorative effect and reduces wear and tear.

Objectives of Coating Surfaces

1. To prevent corrosion
2. To enhance wear and scratch resistance
3. To increase hardness
4. To insulate electrically
5. To insulate thermally
6. To impart decorative colour.

Metallic Coating:

Surfacing coatings made up of metals are known as metallic coatings. These coatings separate the base metal from the corrosive environment and also function as an effective barrier for the protection of base metals. The metal which is coated upon is known as the base metal.

The metal applied as coating is referred to as coat metal.

The different methods used for metal coating are.

1. Hot dipping
   (a) Galvanization
   (b) Tinning
2. Metal spraying.
3. Cladding.
4. Cementation
   (a) Sheardizing – Cementation with Zinc powder is called Shearding.
   (b) Chromizing - Cementation with 55% Chromium powder & 45% Alumina is called Chromizing.
   (c) Calorizing – Cementation with Aluminium and Alumina powder is called Calorizing
5. Electroplating or electrodeposition.

Hot dipping:

In the process of hot dipping, the metal to be coated is dipped in the molten bath of the coating metal. Such hot dip coatings are generally nonuniform. The common examples of hot dip coatings are galvanizing and tinning.

1. **Galvanization**: **The process of coating a layer of zinc over iron is called galvanization.** The steel article is first pickled with dilute sulphuric acid to remove traces of rust, dust, etc. at 60-90^{0}C for about 15 -20 minutes. Then this metal is dipped in a molten zinc bath maintained at 430^{0}C.When zinc is coated over iron, zinc and iron forms a galvanic cell. The electropositive zinc forms the anode and undergoes corrosion. Hence iron is protected from corrosion by sacrificial protection method. The surface of the bath is covered with ammonium chloride flux to prevent oxide formation on the surface of molten zinc. The coated base metal is then passed through rollers to correct the thickness of the film. It is used to protect roofing sheets, wires, pipes, tanks, nails, screws, etc.

2. **Tinning:**

The coating of tin over iron is called tin plating or tinning. Tinning is done to protect iron, steel and copper from corrosion. It is also called tinplating. Since tin is non-toxic, it is mainly used in food industry for coating food containers. Tin-coated utensils are used for storing foodstuffs, pickles, oils, etc.

Tin is nobler metal (more cathodic) than iron. It is more resistant to atmospheric corrosion. Thus, uniform layer of tin protects iron from corrosion. Tinning the base metal is first pickled with dilute sulphuric acid to remove surface impurities. Then it is passed through molten tin covered with zinc chloride flux.

The tin coated article is passed through a series of rollers immersed in a palm oil bath to remove the excess tin. Galvanizing is preferred to tinning because tin is Cathodic to iron, whereas zinc is anodic to iron. So, if the protective layer of the tin coating has any cracks, iron will corrode.

If the protective layer of the zinc coating has any cracks, iron being Cathodic and is not corroded. The corrosion products fill up the cracks, thus preventing corrosion.

Differences between Galvanizing and Tinning:

Galvanizing	Tinning
1. A process of covering iron or steel with a thin coat of 'Zinc' to prevent it from rusting.	A process of covering iron or steel with a thin coat of 'Tin' to prevent it from corrosion.
2. Zinc protects the iron sacrificially. (Zinc undergo corrosion)	Tin protects the base metal without undergo any corrosion (non- sacrificially)
3. Zinc continuously protects the base metal even if broken at some places.	If any break, in coating causes rapid corrosion of base metal.
4. Galvanized containers cannot be used for storing acidic food stuffs as Zinc becomes toxic in acidic medium.	Tin is non-toxic in nature of any medium.

Electroplating (Refer Electrochemistry)

Electroplating is process in which the coat metal is deposited on the base metal by passing a direct current through an electrolytic solution by means of electrolysis.

Objectives of Electroplating:

1. To increase corrosion resistance.
2. To get better appearance.
3. To increase the hardness.
4. To change the surface properties of metals and nonmetals.

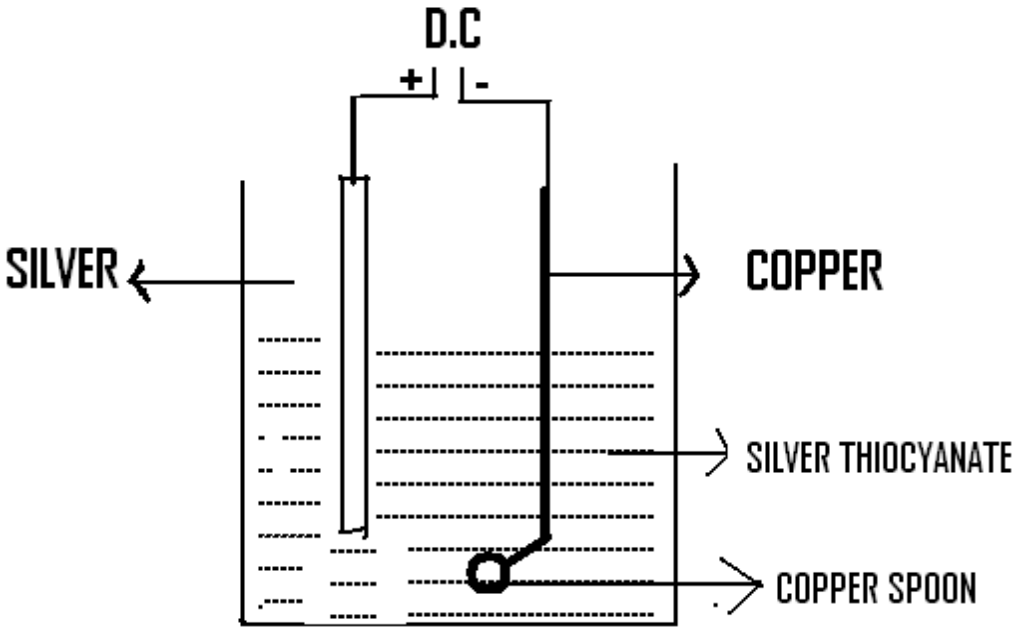
Process

In electroplating, the cleaned base metal is made as the cathode and the coat metal is taken as the anode. A solution of the coat metal salt is taken as the electrolyte. The electrodes are connected to the battery and DC current is passed. Now electrolysis takes place and the coat metal is deposited over the base metal.

The nature of coating depends on 1) the current density 2) time 3) temperature and 4) the concentration of the electrolyte. For example, to electroplate a spoon made of copper with silver, the copper spoon is taken as the cathode. A silver plate is taken as the anode.

Silverthiocyanate solution is the electrolyte. When the electrodes are connected to a DC source of electricity, silver is deposited over the copper spoon.

Electroplating Diagram:



The following electrolytes are used for coating other metals.

Copper sulphate – Copper

Nickel sulphate – Nickel

Chromic acid – Chromium

Factors affecting electroplating

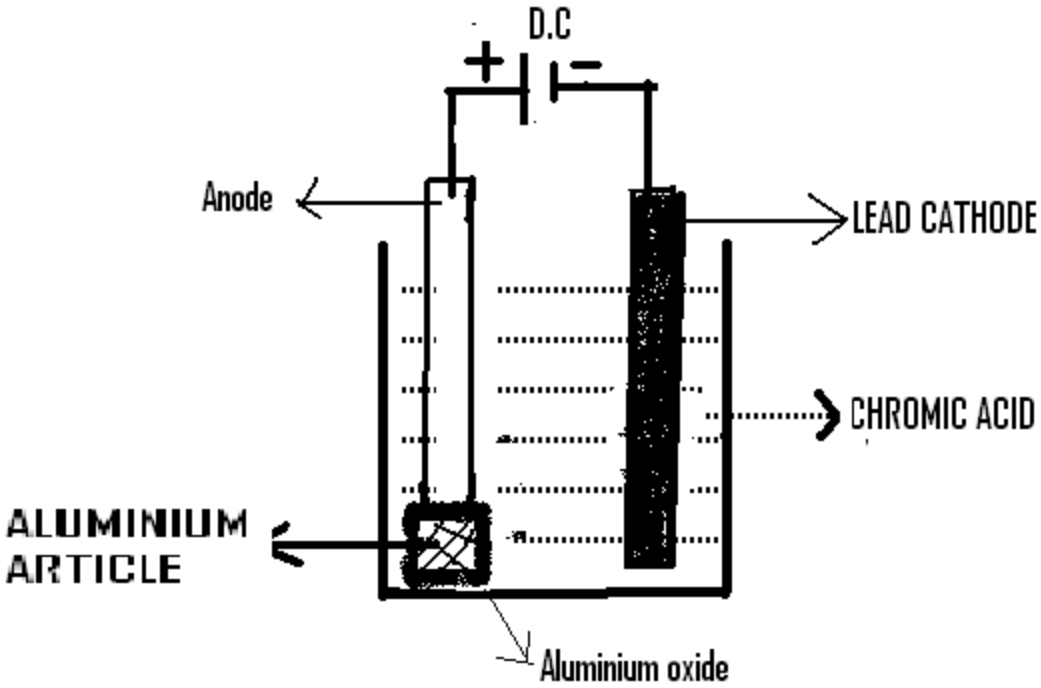
The following are the factors affecting electroplating:

1. Cleaning of the article is essential for a strong adherent electroplating.
2. Concentration of the electrolyte is a major factor in electroplating.
3. Low concentration of metal ions will produce uniform coherent metal deposition.
4. Thickness of the deposit should be minimized in order to get a strong adherent coating.
5. Additives such as glue and boric acid should be added to the electrolytic bath to get a strong adherent and smooth coating.
6. The electrolyte selected should be highly soluble and should not undergo any chemical reaction.
7. The pH of the electrolytic bath must be properly maintained to get the deposition effectively.

INORGANIC COATING

Anodising:

Anodising is the process of coating aluminium oxide on the surface of aluminium or its alloy.



This type of coating is produced on nonferrous metals like Al, Zn, Mg and their alloys, by anodic oxidation process, by passing direct electric current though a bath in which the metal is suspended from anode. Here the base metal behaves as an anode. For anodizing 8% sulphuric acid is used as the electrolyte. Since it is a good oxidising agent, it oxides aluminium (at the anode) into aluminium oxide. The electrolytes are sulphonic, chromic, phosphoric, oxalic or boric acid. Anodized coatings have more corrosion resistance due to thicker coating.

'Aluminium oxide coatings" are formed by the oxidation taking place on the aluminium surface at moderate temperatures (35 to 400°C) and moderate current densities. The formed oxide film is initially thin and gain thickness by the continuous oxidation of aluminium anode. The surface of oxide film contains pores, which may cause corrosion. The pores can be sealed by exposing to boiling water, when the oxide is converted into monohydrate ($Al_2O_3.H_2O$). This process is called sealing process.

The anodized aluminium and its alloy are used in: 1.aircrafts 2.window frames 3.machine parts 4.fancy article and 5.Refrigerator, etc.

Cathodic Protection:

The principle involved in cathodic protection is to force the metal behave like a cathode. Since there will not be any anodic area on the metal, corrosion does not occur. There are two types of cathodic protection.

(a) Sacrificial anodic protection.

(b) Impressed current cathodic protection.

(a) Sacrificial anodic protection:

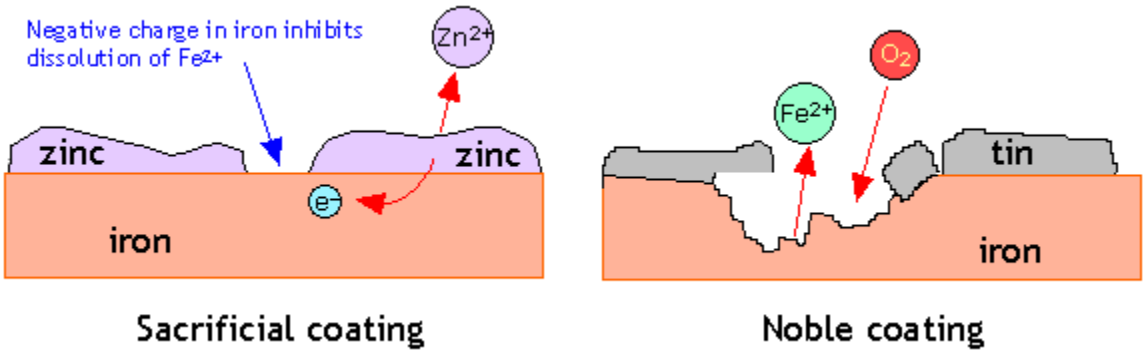
In this technique, a more active metal is connected to the metal structure to be protected so that all the corrosion is concentrated at the more active metal and thus saving the metal structure from corrosion. This method is used for the protection of sea going vessels such as ships and boats.

Sheets of zinc or magnesium are hung around the hull of the ship. Zinc and magnesium being anodic to iron get corroded. Since they are sacrificed in the process of saving iron (anode), they are called sacrificial anodes. The corroded sacrificial anode is replaced by a fresh one, when consumed completely.

Important applications of sacrificial anodic protection are as follows:

(i) Protection from soil corrosion of underground cables and pipelines.

(ii) Magnesium sheets are inserted into domestic water boilers to prevent the formation of rust.



(b)Impressed current cathodic protection:

In this method, an impresses current is applied in an opposite direction to nullify the corrosion current and converting the corroding metal from anode to cathode. This can be accomplished by applying sufficient amount of direct current from a battery to an anode buried in the soil and connected to the corroding metal structure which is to be protected.

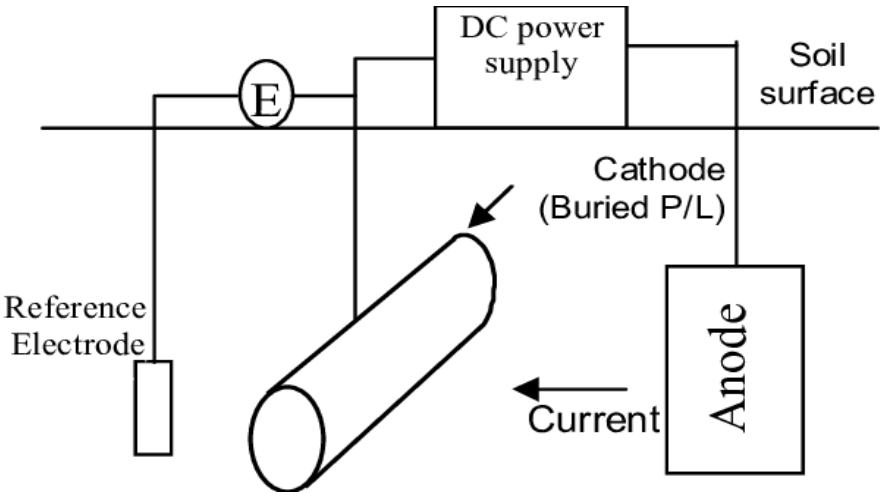


FIGURE: IMPRESSED CATHODIC PROTECTION

The anode is in a backfill (composed of gypsum) so as to increase the electrical contact with the soil. Since in this method current from an external source is impressed on the system, this is called impressed current method. This type of protection is given in the case of buried structures such as tanks and pipelines.

Questions:

PART -A

1. What is Galvanization?
2. What is anodising?
3. What is base metal?
4. What is coat metal?
5. Galvanizing is preferred to tinning. Why?
6. What is Sherardizing?

PART -B

1. What is a sacrificial anode? How does it function?
2. Differentiate between galvanizing and tinning.
3. What is anodizing? How it is carried out? What are its applications?
4. What is tinning? What are its merits & demerits?

PART-C

1. Explain the various methods of prevention of corrosion.
2. Explain briefly about cathodic protection.
3. Explain briefly about electroplating.

5.3 ORGANIC COATINGS

INTRODUCTION

Organic coating includes paints and varnishes. In this lesson, we are going to study about paint and its components. A little introduction to special paints used is also discussed. Further we are going to study about varnish its types and their preparation.

PAINT

DEFINITION

Paint is a dispersion of pigment in drying oil.

Paint coating is given to both metallic and wooden articles to protect them from corrosion and to give better surface appearance. Paint covers the manufacturing defects in the articles. When paint is applied to a metal surface, the thinner evaporates while the drying oil slowly oxidizes forming of pigmented film.

Components of paint and their functions

The important constituents of paint are as follows.

1. Pigments
2. Vehicle or drying oils or medium
3. Thinners
4. Driers
5. Fillers or extenders
6. Plasticizers
7. Anti skinning agents

1. Pigment:

A pigment is a solid and colour-producing substance which gives desired colour to the paint.

Example:

White pigments -- Titanium oxide, Zinc oxide.

Black pigments -- Graphite, Carbon black.

Red pigments -- Red Lead, Indian red (Fe_2O_3).

Functions:

The following are the functions of the pigment:

(a) A pigment gives opacity and colour to the film.

(b) It covers the manufacturing defects.

(c) A pigment gives strength to the film.

(d) It protects the film by reflecting the destructive ultraviolet rays.

2. Vehicle or drying oils or medium:

The liquid portion in which the pigment is dispersed is called a medium or vehicle.

Example:

Linseed oil, dehydrated castor oil, soybean oil and fish oil.

Functions:

(a) Vehicles hold the pigment particles together on the metal surface.

(b) They form the protective film by evaporation or by oxidation and polymerization of the unsaturated constituents of the oil.

(c) Vehicles give better adhesion to the metal surface.

(d) They impart water repellency, durability and toughness to the film.

3. Thinner:

Thinners are added to paints to reduce the viscosity of the paints in order to make it easy to apply on the metal surface.

Example:

Turpentine, kerosene and petroleum sprit.

Functions:

1. Thinners reduce the viscosity of the paint to render it easy to handle and apply to the metal surface.
2. They dissolve the oil; pigments etc. and produce a homogeneous mixture.
3. Thinners evaporate rapidly and help the drying of the film.
4. They increase the elasticity of the film.

4. Driers:

Driers are used to speed up the drying process and accelerate the drying of the oil film by oxidation, polymerization and condensation.

Example:

Naphthentates and Resinates of lead, cobalt and manganese.

Functions:

Driers act as oxygen carrier catalysts which help the absorption of oxygen and catalyze the drying of the oil film by oxidation, polymerization and condensation.

5. Fillers or extenders:

Fillers are used to increase the volume of the paint and to reduce the cost. It increases the durability of the paint.

Example:

Asbestos, talc, china clay, calcium sulphate and calcium carbonate.

Functions:

(a) Fillers serve to fill the voids in the film.

(b) They reduce the cracking of the paint .

(c) Fillers increase the durability of the paint.

(d) They reduce the cost of the paint.

6. Plasticizers:

Plasticizers are chemicals added to increase elasticity of the film and to prevent cracking of the film.

Example

Tertiary amyl alcohol, triphenylphosphate,triglyceryl phosphate.

7. Anti-skinning agents:

They are chemicals added to the paint to prevent skinning of the paint.

Example:

Polyhydroxy phenols, guaiacol, etc.

VARNISH

Definition

Varnish is a homogenous colloidal dispersion of natural or synthetic resin in oil or spirit medium.

If the medium is oil it is known as oil varnish.

If the medium is spirit it is known as spirit varnish.

It is used as a protective and decorative coating to the wooden surfaces. It provides a hard, transparent, glossy appearance and durable film to the coated surface.

There are two main types of varnish

1. Oil Varnish
2. Spirit Varnish

1. Oil Varnish

Preparation

Oil varnishes are more difficult to manufacture. Resins that are used in the preparation of oil varnishes are high molecular weight substances and are not easily soluble in oil. The resin is taken in an aluminium vessel and heated over a fire pit or in a small furnace. When resin melts , the temperature is slowly increased to about 300^0C. This process is known as **gum running**. Some cracking or depolymerization of the resin takes place and about 25 per cent of the resin is lost in the form of fumes.

The required quantity (about 25 per cent of the weight of the resin) of boiled oil or linseed oil along with driers is separately heated to 200^0 to 250^0C and is slowly added to the heated resin with constant stirring until thorough combination has taken place. This operation is known as **cooking**. Over heating must be avoided as it causes discoloration of the varnish.

The kettle is removed from the furnace and allowed to cool, white spirit is then added (which is a petroleum fraction, boiling between 150^0C and 200^0C). It is the most common thinner.

The varnish is stored in tanks for some days for maturing. Foreign matter and particles of resin, which have not dissolved, settle during this period. During maturing, the colour of the varnish also improves and it becomes more homogenous. The varnish is filtered and packed for marketing.

2. SPIRIT VARNISH

A Spirit varnish is a dispersion of resin in spirit.

Preparation

The resin and spirit are placed in a cylindrical drum. plasticizer and other components are added. The resin is dissolved by agitating the mixture or by rotating the drum. It is then filtered and used. The final product is called spirit varnish.

Differences between paint and varnish:

S. No	Paint	Varnish
1.	Paint has pigment	There is no pigment in the Varnish
2.	It can be applied to both metals & wooden articles	It can be applied only to the wooden articles
3.	It is Opaque	It is transparent

Special paints

In addition to the normal ingredients some special chemicals are in corporated to paints for some specific purposes. They are commonly known as special paints.

1. Luminous paint:

Luminous paints are visible in the dark. Since it contains luminophor pigments (like CdS, ZnS) that are used for visibility in the dark .They absorb light radiations and emit them in the dark. The active components in luminous paint are specially prepared phosphorescent materials like CdS, ZnS, etc. For colour effect in luminous paints, certain chemicals like copper salts (green), silver salts (blue), cerium and uranium salts (yellow), etc. are added

Uses:

They find application in inks, advertising signboards, road marks, road traffic signs, number plates of vehicles, watch dials, map, chart, etc.

2. Fire-retardant paint:

The paints which retard the fire are called as fire-retardant. This paint contains the chemicals PVC, Chlorinated rubber, urea formaldehyde and carbonate pigments which are fire-resistant in nature. These substances at higher temperatures breakdown to give the non-inflammable gases like CO_2 ,NH_3 ,HCl and HBr. These gases are non-combustible and do not support combustion. Thus the fire is retarded.

Uses:

Mainly used in defense, industrial, commercial, education and residential complexes.

The most frequent source of a fire in any hotel, restaurant or residence. The walls, doors and even kitchen counters should be protected against the spread of fire.

False ceiling, Lift, Equipment Rooms, Aircraft Safe deposit vaults, lockers, Computer Server rooms, Power plants Chemical Plants, Storage Tanks, structures in Sugar Mills, Textile Mills and Floorings.

3. Aluminium Paint:

The base material in aluminium paint is a fine powder of aluminium. The ground fine powder of aluminium is suspended in either spirit varnish or an oil-varnish depending on the requirement. When paints are applied, the thinner evaporates and oil, if any, undergoes oxidation and polymerization. A bright adhering film of aluminium is obtained on the painted surface.

Uses:

Wooden and metallic article for interior and exterior decoration.

Advantages of aluminium paint:

1. It possesses a good covering power.
2. It imparts very attractive appearance to the surface.
3. It has fairly good heat-resistance.
4. It has very good electrical resistance
5. The painted film is waterproof.
6. The electrical surface is visible even darkness.
7. Corrosion protection for iron and steel surface is better than all other paints.

4. Distempers

Distempers are water paints. They contain chalk powder, glue and pigment dissolved in water. They are very cheap and can be easily applied on walls. They are durable and give pleasing finish to walls. The ingredients of distemper are

1. Whiting agent or chalk powder (the base)
2. Glue or casein (the binder)
3. Colouring pigment and
4. Water (the solvent or thinner).

Advantages:

1. Distempers are cheaper than paints and varnishes
2. They can be applied easily on plasters and wall surfaces in the interior of the buildings.
3. They are durable.
4. They give smooth and pleasing finish to walls.

QUESTIONS

PART -A

1. Define paint.
2. What is Varnish?
3. What is distemper?

PART-B

1. Write a short note on luminous paint.
2. Write a note on Aluminium paint.
3. Explain about Fire retardant paint.
4. What are the differences between paint and varnish?

PART-C

1. What are the components present in the paint? Explain their functions.
2. How is oil varnish preferred?
3. Explain briefly about special paints.

MODEL QUESTION PAPER-I

ENGINEERING CHEMISTRY-II (N1BE112)

(Time: Three Hours)

(Maximum Marks: 75)

N.B **1. Answer any five questions in each of PART-A and PART-B**

2. Answer any two divisions of each question in PART-C.

3. Each question carries 2(two) Marks in PART-A, 3(three) Marks in PART-B and 5(five) Marks for each division in PART-C.

PART-A (5 × 2=10 Marks)

1. Which gases are responsible for greenhouse effect?
2. Define - Sewerage.
3. Define - CNG.
4. What are Rocket propellants?
5. Define – Hardness of abrasives in Moh's scale.
6. What is chrome plating?
7. What are the types of corrosion?
8. Define - Galvanization.

PART-B (5 × 3=15 Marks)

9. Write short note on acid rain.
10. Write short note on landfill method.
11. What is cracking?
12. Write a short note on vulcanization.
13. What are the advantages of composites over metal polymers?
14. What is primary battery? Give an example.
15. Write a short note on crystallization.
16. What are the differences between paints and varnishes?

PART - C **(5 × 2 × 5=50 Marks)**

17. (a) What are the harmful effects of some important air pollutants?

    (b) What is the eutrophication? Mention their harmful effects.

    (c) What are the goals of green chemistry?

18. (a) What are the advantages of gaseous fuels?

    (b) Describe flue gas analysis by Orsat's apparatus.

    (c) What are the characteristics of rocket propellant?

19. (a) What are the differences between thermoplastics and thermosetting plastics?

    (b) Give the preparation, properties and uses of silicon carbide.

    (c) What are the applications of composite materials?

20. (a) Explain the construction and working of Daniel cell.

    (b) Explain the construction and working of lead- acid storage battery.

    (c) Write a note on chemical separation technique of fractional distillation.

21. (a) Explain the Galvanic cell formation theory for corrosion.

    (b) Explain the cathodic protection method of prevention of corrosion.

    (c) Write notes on components of paint.

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MODEL QUESTION PAPER-II

ENGINEERING CHEMISTRY-II (N1BE112)

(Time: Three Hours)

(Maximum Marks: 75)

N.B **1. Answer any five questions in each of PART-A and PART-B**

2. Answer any two divisions of each question in PART-C.

3. Each question carries 2(two) Marks in PART-A, 3(three) Marks in PART-B and 5(five) Marks for each division in PART-C.

PART-A (5 × 2=10 Marks)

1. What is global warming?
2. Define - Sewage.
3. What is the calorific value of a fuel?
4. What are Rocket propellants?
5. What are the defects of natural rubber?
6. What is secondary battery?
7. What is corrosion?
8. Define - Tinning.

PART-B (5 × 3=15 Marks)

9. Write short note on acid rain.
10. Write short note on incineration method.
11. What is cracking?
12. What is bio material? Give an example.
13. What is emery?
14. What is electrochemical series?
15. What is chromatography?
16. What is a fire retardant paint?

PART - C **(5 × 2 × 5=50 Marks)**

17. (a) What are the harmful effects of ozone layer depletion?

    (b) How is sewage water disposed?

    (c) What are the goals of green chemistry?

18. (a) Give the preparation and uses of producer gas.

    (b) Describe flue gas analysis by Orsat's apparatus.

    (c) What are the characteristics of rocket propellants?

19. (a) What are the mechanical properties of a plastics?

    (b) Give the preparation, properties and uses of boron carbide.

    (c) What are the advantages of composite materials over metals and polymers?

20. (a) Explain electrolysis with an example.

    (b) Explain the construction and working of lead- acid storage battery.

    (c) Write note on chemical separation technique of fractional distillation.

21. (a) Explain the differential aeration theory for corrosion.

    (b) Explain the cathodic protection method of prevention of corrosion.

    (c) Write note on components of paint.

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