

Director of Distance & Continuing Education

Manonmaniam Sundaranar University

Tirunelveli-627012

OPEN LEARNING AND DISTANCE LEARNING (ODL) PROGRAMME

(for those who joined the programmes from the academic year 2025-2026)



B.Sc Chemistry

Course material- Industrial chemistry

Course code- JECH52

Prepared by

Dr. R. SARIKA

Assistant Professor

Department of Chemistry

Manonmaniam Sundaranar University

Tirunelveli-627012

INDUSTRIAL CHEMISTRY – JECHE52

UNIT – I

Survey of Indian Industries and mineral resources in India

Fuel

Fuel is a substance which, when burnt, on contact and react with oxygen or air, produces heat.



This produced heat energy can be used for domestic and industrial purposes. Example-wood, charcoal, coal, petrol, diesel, kerosene, producer gas, etc.

Classification

Fuels may broadly be classified into 2 ways ie.,

1. according to the physical state of existence - solid, liquid and gaseous fuels.
2. according to the mode of their procurement – natural and manufactured fuels

A brief description of natural and manufactured fuels is given in Table 1.

Table 1.1: Natural and Manufactured Fuels

Natural Fuels	Manufactured Fuels
Solid Fuels	
Wood	Bagasse, Straw
Coal	Charcoal
Oil shale	Coke
Liquid Fuels	
Petroleum	Oils from distillation of petroleum
	Coal tar
	Alcohols
Gaseous Fuels	
Natural gas	Coal gas
	Producer G
	Water gas
	Oil gas
	Hydrogen

Solid fuels have the following advantages and disadvantages over liquid and gaseous fuels.

Advantages

- (a) They are easy to transport.
- (b) They are convenient to store without any risk of spontaneous explosion.
- (c) Their cost of production is low.
- (d) They possess moderate ignition temperature.

Disadvantages

- (a) Their ash content is high.
- (b) Their large proportion of heat is wasted.
- (c) They burn with clinker formation.
- (d) Their combustion operation cannot be controlled easily.
- (e) Their cost of handling is high.

Characteristics of fuels

- i) High calorific value
- ii) Moderate ignition temperature
- iii) Low moisture content
- iv) Low non-combustible matter content
- v) Moderate velocity of combustion
- vi) Products of combustion should not be harmful
- vii) Easy to transport
- ix) Combustion should be easily controllable
- x) Should be undergo spontaneous combustion
- xi) Storage cost in bulk should be low
- xii) Should be in air with efficiency, without much smoke

Solid fuels

Classification of coal

Coal is a solid fuel derived from the prehistoric plants. Coal is highly carbonaceous and composed of carbon, hydrogen, nitrogen and oxygen and non-combustible inorganic matter. There exists a number of methods for classifying coal and are based on (1) rank, (2) grade and size and (3) source. The coal is also classified based on the various products of metamorphosis of the original vegetable matter of which the coal is the final product. The coal is thus named as peat, lignite, bituminous, semi-bituminous, semi-anthracite and anthracite.

Anthracite coal → fully transformed coal
 Peat → first stage of this transformation
 Other varieties → intermediate stages of transformation

Some characteristics of peat are as follows:

- fibrous decaying material
- brown in colour
- highly moist
- burn freely

Typical proximate and ultimate analysis of peat is given in Table 1.2

Table 1.2: Proximate and Ultimate analysis value of peat

Proximate analysis		Ultimate analysis	
Content	% composition	Content	% composition
Carbon	58	Volatile matter	5
Oxygen	35	Moisture	90.3
Hydrogen	6	Ash	1.6
Nitrogen	1	Fixed carbon	3

Analysis of Coal

To determine the commercial value of coal certain tests regarding its burning properties are performed before it is commercially marketed. Two commonly used of coal is defined as the quantity of heat given out by burning one unit weight of coal in a calorimeter.

Proximate Analysis of Coal

This analysis of coal gives good indication about heating and burning properties of coal. The test gives the composition of coal in respect of moisture, volatile matter, ash and fixed carbon. The moisture test is performed by heating 1 gm of coal sample at 104oC to 110oC for 1 hour in an oven and finding the loss in weight. The volatile matter is determined by heating 1 gm of coal sample in a covered crucible at 950oC for 7 minutes and determining loss in weight, from which the moisture content as found from moisture test is deducted. Ash content is found by completely burning the sample of coal in a muffled furnace at 700oC to 750oC and weighing the residue. The percentage of fixed carbon is determined by difference when moisture, volatile

matter and ash have been accounted for. The results of proximate analysis of most coals indicate the following broad ranges of various constituents by weight:

Table 1.3: Proximate analysis of few coals and its broad range values

Volatile matter	3-50%
Moisture	3-30%
Ash	2-3%
Fixed carbon	16-92%

The importance of volatile matter in coal is due to the fact that it largely governs the combustion which in turn governs the design of grate and combustions space used. High volatile matter is desirable in gas making, while low volatile matter for manufacturing of metallurgical coke.

Ultimate Analysis of Coal

This analysis of coal is more precise way to find the chemical composition of coal with respect to the elements like carbon, hydrogen, oxygen, nitrogen, sulphur and ash. Since the content of carbon and hydrogen that is already combined with oxygen to form carbon dioxide and water is of no value for combustion, the chemical analysis of coal alone is not enough to predict the suitability of coal for purpose of heating. However, the chemical composition is very useful in combustion calculations and in finding the composition of flue gases. For most purposes the proximate analysis of coal is quite sufficient. The broad range in which the constituents of coal vary by weight as determined by ultimate analysis are given below:

Table 1.4: Ultimate analysis of the constituents of coals and its broad range values

Carbon	50-95%
Hydrogen	2.5-5%
Oxygen	2-4%
Sulphur	0.5-7%
Nitrogen	0.5-3%
Ash	2-30%

Calorific value (heating values) of coals

The efficiency of a fuel (coal) is judged by its calorific value. Heating or calorific value of a fuel is defined as the total quantity of heat liberated by the complete combustion of a unit mass

or volume of the fuel. It is expressed as cal/g or kcal/kg or KJ/kg for solid and liquid fuels. For gaseous fuels, the calorific value is expressed as Kcal/m³. Calorific value of fuel is classified into two types.

i) Gross calorific value (GCV)

ii) Net calorific value (NCV)

i) Gross calorific value or higher calorific value (GCV)

GCV is defined as the total quantity of heat liberated by the complete combustion of a unit mass of the fuel (coal) and the products of combustion are cooled to room temperature. GCV of fuel can be calculated by Dulong formula. Since the calorific value of a fuel is the sum of the calorific value of its constituent elements. The calorific value of C, H and S are 8080, 34500 and 2240 cal/g, respectively. During combustion, Oxygen combined with Hydrogen and forms water vapour (steam). Eight parts by wt. of oxygen are combined with one part by weight of hydrogen. Thus, the H available for combustion will be $(H - \frac{O}{8})$

$$\text{GCV} = \frac{1}{100} [8080C + 34500 (H - \frac{O}{8}) + 2240S] \text{ cal/g}$$

Here C, H, O and S represent the percentage of the elements which can be determined by ultimate analysis of the fuel (coal).

The proximate analysis can also be used to calculate the GCV using Goutel's formula

$$\text{GCV} = [(82XFC) + (\alpha + VM)] \text{ cal/g or}$$

$$\text{GCV} = 4.184 [82XFC) + (\alpha + VM)] \text{ KJ/Kg}$$

Where FC is % of fixed carbon, VM is % of volatile matter, α is a variable that depends on the nature of volatile matter. Its value decreases with increase in VM.

ii) Net calorific value or Lower calorific value (NCV)

NCV is defined as the quantity of heat liberated by the complete combustion of a unit mass of the fuel (coal) and the products of combustion are allowed to escape.

$$\text{NCV} = \text{GCV} - \text{mass of H per unit mass of the fuel burnt} \times 9 \times \text{Liberated latent heat of condensation water vapour produced}$$

[Since, H present in the fuel converted into H₂O (steam) during combustion. One part by wt. of hydrogen produces nine parts by wt. of water.



$$2g + 16g \quad 18g$$

$$1 \quad 8 \quad 9$$

[Latent heat of water is 587 cal/g]

$$\therefore NCV = GCV - \frac{9H}{100} \times 587$$

$$NCV = GCV - 0.09 \times H \times 587 \text{ cal/g}$$

Where H = % of hydrogen

Carbonisation of coal

Coarsely powdered coal taken in a closed retort and heated out of contact with air. Coal decomposes to give water, ammonia, other volatile matters, gases and coke. This process is called as carbonisation of coal or cooking of coal. There are two types of carbonisation process, namely,

i) Low temperature carbonisation (LTC) and ii) High temperature carbonisation (HTC).

i) Low temperature carbonisation (LTC)

In this process, coal is heated at 500°C - 700°C. The yield of coke is 75-80% and it contains 8-12% volatile matter. The coke obtained is not mechanically strong but highly reactive and can be easily ignited to give smokeless flame and used as domestic fuel. Low temperature carbonisation yields a mixture of higher phenols, substituted aromatic hydrocarbons and other N and O containing compounds. The coal gas obtained has calorific value of 6500 kcal/m³ and is richer in hydrocarbons.

ii) High temperature carbonisation (HTC)

It is carried out at 900°C - 1200°C producing coke of good porosity, hardness, purity and strength. It is used in metallurgy. The yield of coke is 65-75% containing 1-3% volatile matter. The coal gas obtained has a low caloric value 4500 kcal/m³.

Liquid Fuels

Characteristics of petroleum

Petroleum is a basic natural fuel. It is a dark greenish brown, viscous mineral oil, found deep in earth's crust. It is mainly composed of various hydrocarbons (like straight chain paraffins, cycloparaffins or naphthenes, olefins, and aromatics) together with small amount of organic compounds containing oxygen nitrogen and sulphur. The average composition of crude petroleum is: C = 79.5 to 87.1%; H = 11.5 to 14.8%; S = 0.1 to 3.5%, N and O = 0.1 to 0.5%.

Petroleum are graded according to the following phsio-chemical properties:

- (a) Specific gravity
- (b) Calorific value
- (c) Fish point or ignition point
- (d) Viscosity
- (e) Sulphur contents
- (f) Moisture and sediment content
- (g) Specific heat and coefficient of expansion

Gasoline aviation petrol (AV gas)

It is a type of gasoline specially designed for use in air craft internal combustion engines. It is a high octane gasoline, having proper combustion and preventing engine knocking. Aviation petrol is manufactured to specific standards by adding additives such as antioxidant and antistatic dissipator to ensure reliability and safety.

Knocking and Anti-Knocking Characteristics of Fuel

In thermal combustion engine, a mixture of gasoline vapours and air is used as a fuel. After the initiation of combustion reaction by spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture, thereby the expanding gas driving the piston down the cylinder. The ratio of gaseous mixture in the solution at the end of the suction- stroke to the volume at the end of compression stroke of the piston is known as the "Compression Ratio". The efficiency of an internal combustion engine increases with the combustion ratio. However, successful high compression ratio is dependent on the nature of constituents present in the gasoline used. In certain circumstances, due to the presence of some constituents in the gasoline used the rate of oxidation becomes so great that the last portion of the fuel- air mixture get

ignited instantaneously producing an explosive violence known as 'Knocking'. Thus, knocking results in loss of efficiency since this ultimately decreases the compression ratio. The most common way of expressing the knocking characteristics of a combustion engine fuel is by octane number or rating. Knocking characteristics of a fuel depends upon the chemical structure of its components present in it. The tendency of fuel to knock is in the following order. Straight-chain paraffins > branched chain paraffin (i.e., iso paraffins) > olefins > cycloparaffins (i.e., napthenes) > aromatics. The olefins of the same carbons chain length possess lesser anti-knock properties than the corresponding paraffin's and so on.

Anti-Knocking agents (octane booster)

These are the substances added to petrol in order to prevent knocking in I.C. Engines.

Ex: Tetra Ethyl led (TEL).

Tetra Methyl led (TML).

Methyl Tertiary Butyl Ether (MTBE).

Leaded Petrol

The petrol containing TEL or TML as anti-knocking agents is called leaded petrol. TEL or TML are the very good anti knocking agents but has some disadvantages as follows.

- a) After combustion lead is deposited as lead oxide on piston and engine walls it leads to mechanical damage.
- b) Lead is a poisonous air pollutant.
- c) It spoils the catalyst used in catalytic converter.

Unleaded petrol

The petrol, which contains anti-knocking agent other than lead, is known as unleaded petrol.

Ex: MTBE is used, as an anti-knocking agent in place of TEL or TML and the petrol is known as unleaded petrol.

Octane Number

Octane number is generally used for gasoline fuel. The rating of a gasoline (or any other internal combustion engine fuel) is the percentage of iso-octane. In a mixture of iso-octane and n-heptane ($\text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$). It has been found that n-heptane

burns very badly and hence its anti-knock value has arbitrarily been given zero. On the other hand, isooctane burns in a very good way, so its anti-knock value has been given as 100.

The octane number (octane rating) is defined as the percentage of isooctane in a mixture of isooctane and n-heptane which matches the knocking property of the gasoline under test. For example, if a sample of petrol matches the knocking property of a mixture of 80% of isooctane and 20% of n-heptane, then its octane number is 80. The octane number of various fuels are listed below.

Third grade gasoline	65
Regular gasoline	74
Premium gasoline	81
Aviation gasoline	100
Triptane (2,2, 3-trimethyl butane)	124

Octane number of a fuel sample is measured by comparing its performance with the performance of various known mixtures of isooctane and n-heptane. For this purpose a standard spark-ignition engine is used.

Significances

- i) Higher the octane number better the fuel (gasoline)
- ii) Fuels with more octane number increase the efficiency of the engine and its lifetime
- iii) Octane number is a measure of fuel performance
- iv) Octane number is important for predicting the knocking of petrol engine.

Cetane Number

Cetane number is generally used for diesel fuel. Cetane number indicates the percentage of hexadecane in a mixture of hexadecane [cetane ($C_{16}H_{34}$)] and 2 methyl naphthalene ($C_{10}H_7CH_3$). The cetane number of cetane is 100 and the cetane number of 2 methyl naphthalene is zero. Higher the cetane number easier the fuel to ignite

Cetane number of a fuel (diesel) is measured by comparing its performance with the performance of various known mixtures of cetane and α -methylnaphthalene. If the given fuel matches in quality with the mixture having 40% of cetane and 60% α -methylnaphthalene, then

its cetane number is 40. Cetane number of diesel can be improved by adding butyl nitrate, carbonates, organometallic compounds

Significances

- i) Higher the cetane number better the diesel fuel
- ii) Fuels with more cetane number increase the efficiency of diesel engine and its life time
- iii) Cetane number is important for predicting the knocking of diesel engine.

Gaseous Fuels

Advantages of gaseous fuel over solid and liquid fuels

Gaseous fuels occur in nature and are manufactured from solid and liquid fuels. The gaseous fuels need very large storage tanks and are highly inflammable, so chances of fire hazards in their use is high. Even then there are several advantages of these fuels when compared with solid and gaseous fuels.

- a) They can be conveyed easily through pipelines
- b) They can be lighted at ease.
- c) They have high heat contents and hence help us in having higher temperatures.
- d) They can be pre-heated by the heat of hot waste gases, thereby affecting economy in heat.
- e) Their combustion can readily be controlled for change in demand like oxidizing or reducing atmosphere, length flame, temperature, etc.
- f) They are clean in use.
- g) They do not require any special burner.
- h) They burn without any shoot, or smoke and ashes.
- i) They are free from impurities found in solid and liquid fuels.
- j) They have high calorific values.

Disadvantages

- (a) Very large storage tanks are needed.
- (b) They are highly inflammable, so chances of fire hazards in their use is high.

Water gas

Water gas is an artificial gaseous fuel and it is essentially a mixture of combustible gases CO and H₂ with a little fraction of non-combustible gases.

Preparation

It is made by passing alternatively steam and little air through a bed of red hot coal or coke maintained at about 900 to 1000°C in a reactor, which consists of a steel vessel about 3 m wide and 4 m in height. It is lined inside with fire-bricks. It has a cup and cone feeder at the top and an opening at the top for the exit of water gas. At the base, it is provided with inlet pipes for passing air and steam.

Reactions

Supplied steam reacts with red hot coke (or coal) at 900-1000°C to form CO and H₂.



Composition

The average composition of water gas is - H₂ = 51%; CO = 41%; N₂ = 4%; CO₂ = 4%. Its calorific value is about 2,800 kcal/m³.

Uses

It is used as a source of hydrogen gas, an illuminating gas, and a fuel gas.

Producer gas

Producer gas is essentially a mixture of combustible gases carbon monoxide and hydrogen associated with non-combustible gases N₂, CO₂, etc.

Preparation

It is prepared by passing air mixed with little steam (about 0.35 kg/kg of coal) over a red hot coal or coke bed maintained at about 1100°C in a special reactor called gas producer. It consists of a steel vessel about 3 m in diameter and 4 m in height. The vessel is lined inside with fire bricks. It is provided with a cup and cone feeder at the top and a side opening for the exit of producer gas. At the base it has an inlet for passing air and steam. The producer at the base is also provided with an exit for the ash formed.

Reactions

The gas production reactions can be divided into four zones:

Ash Zone

The lowest zone consists of mainly of ash, and therefore, it is known as ash zone.

Combustion Zone

The zone next to the ash zone is known as oxidation or combustion zone. Here the carbon burns and forms CO and CO₂. The temperature of this zone is about 1100°C. The following reactions take place.



Reduction Zone

Here carbon dioxide and steam combines with red hot carbon and liberates free hydrogen and carbon monoxide. The reactions are:



All these reduction reactions are endothermic, so, the temperature in the reduction zone falls upto 1000°C.

Distillation Zone

In this zone (400 – 800°C) the incoming coal is heated by outgoing gases by giving sensible heat to the coal. The heat given by the gases and heat radiated from the reduction zone helps to distillate the fuel thereby volatile matter of coal is added to the outgoing gas.

Composition

The average composition of producer gas is CO = 22.3%, H₂ = 8.12%; N₂ = 52.55%; CO₂ = 3%. Its calorific value is about 1,300 kcal/m³.

Uses

It is cheap, clean and easily preparable gas and is used (i) for heating open-hearth furnaces (in steel and glass manufacture), muffle furnaces, retorts (used in coke and coal gas manufacture), etc. and (iii) as a reducing agent in metallurgical operations.

Carburated water gas

It is also an artificial gaseous fuel. It is a fuel gas produced by enriching water gas with gaseous hydrocarbons. The water gas combines with hydrocarbons to increase the calorific value. Water gas is passed through a heated retort in which oil containing gaseous hydrocarbons is sprayed.

Uses: Carburated water gas is used i) heating, ii) for lighting, iii) as a fuel for internal combustion engines.

Natural gas

LPG (Liquefied Petroleum Gas)

-LPG is available in the market in two forms- one is propane and the other is butane. Propane is popular alternative fuel because of its infrastructure of pipe lines, processing facilities and storage for its efficient distribution and also it produces fewer emissions. Propane is produced as a byproduct of natural gas processing and crude oil refining

-Natural gas contains LPG, water vapour and other impurities and about 55% of the LPG is compressed from natural gas purification. LPG is a simple mixture of hydrocarbon mainly propane/propylene (C_3S) and butane/ butylene (C_4S)

-Propane is an odourless, non-poisonous gas which has lowest flammability range.

Advantages

- i) Emission is much reduced by the use of LPG.
- ii) LPG mixes with air at all temperatures.
- iii) Uniform mixture can be supplied to all cylinders of multi-cylinder engine.
- iv) Engine with high compression ratio (10:1) can use propane.
- v) There is cost saving of about 50% and longer life with LPG running engine.

Disadvantages

- (i) A good cooling system is necessary because LPG vaporizer uses engine coolant to provide the heat to convert the liquid LPG to gas.
- (ii) The weight of vehicle is increased due to the use of heavy pressure cylinder for storing LPG.
- (iii) A special fuel feed system is required for LPG.
- (iv) Requirement of safety device to prevent accident due to explosion of gas cylinders or leakage in the gas pipes.

Applications

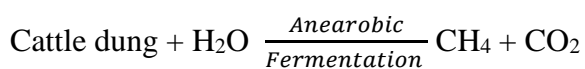
-LPG is used as a fuel in heating appliances and vehicles. It is increasingly used as an aerosol propellant and a refrigerant, replacing chlorofluorocarbons in an effort to reduce damage to the ozone layer.

-In Europe, LPG is used as an alternative to electricity and heating oil (kerosene). It can also be used as power source for combined heat and power technologies (CHP). CHP is the process of generating both electrical power and useful heat from a single fuel source. This technology has allowed LPG to be used not just as fuel for heating and cooking, but also for de-centralized generation of electricity.

-LPG has higher potential as an alternate fuel for IC engine.

Gobar gas

Gobar gas is the biogas produced from cow dung.



The produced gas is the composition of methane 50-70 % and carbon-dioxide 25-50%. Residual amounts of N₂, H₂ and O₂. Traces of H₂S, H₂O and NH₃.

Gobar gas is produced through anaerobic digestion of cow dung. This involves four stages.

- i) Hydrolysis: Bacteria convert complex carbohydrates proteins and fats into sugars, amino acids and fatty acids
- ii) Acidogenesis: Acidogenic bacteria produce volatile fatty acids, alcohols and gases
- iii) Acetogenesis: Acids and alcohols become acetic acid, hydrogen, CO₂ and other gases.

iv) Methanogenesis: Breakdown of acids and alcohols into methane. Each kilogram cow dung can produce 15-30 liters of gobar gas/day.

Uses

- i) Gobar gas production uses raw materials which otherwise pollute soil and water
- ii) It is a renewable energy source
- iii) Its production is eco-friendly and does not damage ecosystems
- iv) It is a useful conversion of a waste into a fuel gas
- v) It is very cheap

Propellants

Propellant is the chemical mixture burnt to produce thrust (sudden movement) in rockets. The mixture consists of a fuel and an oxidizer. Fuel is a substance that burns when combined with oxidiser for propulsion. The oxidiser is an agent that releases oxygen for combination with a fuel. The ratio of oxidiser to fuel is called the mixture ratio. The rocket fuel used in the Chandrayaan-2 mission is UDMH (Unsymmetrical Dimethyl Hydrazine). The oxidiser used is nitrogen tetroxide. Propellants are classified according to their state as liquid, solid, or hybrid.

Examples:

Solid Propellant: Nitrocellulose and additives, HTPB (Hydroxyl-terminated polybutadiene)
NC = Nitrocellulose

Liquid propellants: Cryogenic propellants contain liquid hydrogen as the fuel and liquid oxygen as the oxidiser.

UNIT – II

Cosmetics, Soaps and Detergents

Cosmetic word is originated from Greek word “Kosmetikos” means adorn and preparation. The study of cosmetics is known as “cosmetology”. Cosmetic are external preparation meant for to apply on external part of the body i.e., nails, skin, hair for colouring, covering, softening, cleaning, nourishing, waving, setting, preservation, removal and protection” etc. The important techniques of skin care are;

1. Cleansing
2. Application of toners and freshners
3. Moisturising

1. Cleansing

It is used to remove all the impurities accumulated in the pores of the skin, removing any residual make up and sweat. Cleansing lotion/cream or milk can be used for deep cleansing.

2. Application of toners and skin freshners

Toner is applied to refresh and cool the skin. Freshener provides the soothing effect on the skin.

3. Moisturing

Moisturisers are cosmetic emulsions used to keep the skin soft, moist and without cracks. These are made up of NMF (Normalising Moisturising Factor) ingredients. The moisturisers delay the formation of wrinkles.

Powders

i) Face powder

A face powder is basically a cosmetic product, which has as its prime functions the ability to complement skin color by imparting velvet like finish. It enhances the appearance of the skin by masking the shine due to the secretion of sebaceous and sweats glands. It consists of various constituents, which imparts essential characteristics of a good product.

Table 2.1: Main ingredients of face powder

Ingredients	Ingredients
Talk (slip character)	Gum Arabic (binder) 0.5 %
Zinc stearate (slip character) 2.5%	Water 47 %
Kaolin (covering material) 9 %	Preservative – trace
TiO ₂ (covering material) 4 %	Colourant – trace
Glycerol (emulsion binder) 2.5	Perfume - Trace

ii) Compact powder

Compact powder is a type of face powder compressed in to a cake and applied with a powder puff. It is more popular because of its ease in application, storage and convenience. It has larger particle size than normal face powder and more adherences to the skin. It contains basic face powder ingredients like covering power agents, slipping agents, bloom and peach finish agent, absorbent, adherent, colouring agent and binding agent with preservatives.

There are varieties of binding agents like dry binder, oil binder, water soluble or water repellent and emulsion binders are mostly used in compact. Because of the presence of binder, which are mostly susceptible to microbial attack, so most useful preservatives like p-hydroxy benzoate is used in formulation. Compacts are manufactured by various methods, such as wet method, dry method and damp method. Most commercially useful method is damp method.

Creams and Lotion

Creams are semisolid dosage forms containing more than 20% water or volatile components and typically less than 50% hydrocarbons, waxes, as vehicles. They may also contain one or more drug Substances dissolved or dispersed in a suitable cream base.

Types of Cream

1. Cleansing cream
2. Moisturizing cream
3. Vanishing cream
4. Cold cream

i). Cleansing cream

Cleansing cream is necessary to effectively remove oil, water, oil-soluble filth, and surface grime, particularly from the face and throat, as well as makeup from the face.

Characteristics of a good cleansing cream:-

- Be able to effectively remove oil-soluble & water-soluble soil, and surface oil from skin.
- Should be stable & have good appearance.
- Should melt or soften on application to the skin
- Should spread easily without too much of drag
- Its physical action on skin & pore openings should be that of flushing rather than Absorption.

Marketed preparation: - Nivea, ponds, Noxzema, etc

ii). *Moisturizing cream*

A moisturizer, or emollient, is a cosmetic preparation used for protecting, moisturizing, and lubricating the skin. These functions are normally performed by sebum produced by healthy skin.

Moisturizers improve skin hydration and increase the water content of the stratum corneum by supplying water directly to the skin from its aqueous phase and increasing occlusion to reduce transepidermal water loss. It also covers small skin cracks, forms a soothing protective film, and protects the skin from friction.

Benifites of moisturizer: • Prevent dryness • Slow the digns of aging • Help fight acne • Protection from the sun

Marketed preparation: - Boroplus, Dove, Vaseline, Lakme, Ponds, Lotus, etc.

iii). *Vanishing cream*

They get their name because they seem to disappear when applied to the skin. A large amount of stearic acid is used as an oil phase. This gives an oil phase that melts above body temperature and crystallizes in a suitable form, making it invisible when used and forming a greasy film.

Benefits of vanishing cream:

- Use adhesive for makeup powder.
- Reduces loss of moisture from dry skin.

- Smoothen the skin & keep it soft.
- Prevent skin from roughening & chapping.

Marketed preparation: - nivea, plum, ponds, vicco, turmeric, cuticura, etc

iv). *Cold cream*

Cold cream is an emulsion of water and certain fats, usually, beeswax and various fragrances, designed to smooth the skin and remove make-up. Cold cream is a water-in-oil emulsion (an emulsion of a small amount of water in a large amount of oil).

Benefits of cold cream:

- The primary use of the cream for skin treatment.
- Mineral ingredients in the cream, work as a moisturizer.
- Generally useful for dry skin.
- It can also be used as an alternative to lip balm if you have very dry, chapped lips.
- It can be used as a makeup remover and cleanser.
- Sometimes it is applied to the face before putting on any makeup.
- It can be used as an alternative to shaving cream,
- With a hot washcloth it can help exfoliate the skin.

Marketed preparation: - nivea, garnier, lacto, etc

Shaving cream

Cosmetic cream which is spread over the face or another part of the body before shaving is called shaving cream. It consists of oil and water based emulsion with surfactant or soap.

Sunscreen

Sunscreen protects the skin by absorbing or reflecting the UV (UVA and UVB) radiation from the sunlight. It is commonly

Make up preparations

Skin creams and lotions are common ingredients in makeup preparation. Following steps are used for makeup preparations.

i) *Deep cleanse*: Before make up, the skin surface (face) is cleaned to remove dirt, dust and dead skin cells.

ii) *Toning*: After cleaning the skin surface, apply toner using a cotton pad and swipe across the skin surface or face gently. The toner helps to fix the make up on the skin surface.

iii) *Serum*: After toning, apply serum on the skin surface. Serum is a moisturising agent that boost hydration level in the skin surface.

iv) *Eye mark*: Then apply eyemark or eye cream to reduce fine lines around the skin surrounding the eyes.

v) *Moisturise and protect*: Then apply moisturiser which helps the skin surface as soft, moist and healthy appearance.

vi) *Primer*: The next step is to boost the skin surface with a primer. The primer makes the skin surface ready to apply makeup.

Dental care

Toothpastes

Toothpastes are the preparation intended for use with a toothbrush for the purpose of cleaning the accessible surface of the teeth. It enhance personal appearance by maintaining cleaner teeth, brushing with it reduce the tooth decay, helps to maintain healthy gingival and reduces the intensity of mouth odours. Therapeutic purpose like chlorophyll toothpaste to prevent gingival disease and carries; anti-enzyme tooth paste for preventing dental carries; fluoride tooth paste for giving hardness and lasting quality to tooth structure and as anti-dental carries and cleaning purpose like ammoniated toothpaste loose the dental plaque by chemical reaction and make them susceptible to removal by tooth brushing. The general formulation of toothpaste contains various ingredients for their special properties are as follows: -

1. *Abrasives*: It removes debris; residual stains from teeth and polishing agent. The agents uses for this purpose are calcium carbonate, dibasic calcium phosphate dehydrate, tricalcium phosphate, insoluble sodium metaphosphate, hydrated alumnae and calcium pyrophosphate etc.

2. *Surface-active agents*: These agents lower surface tension to improving cleaning and also for foaming characteristics, e.g., sodium lauryl sulphate, sodium coconut monoglyceride sulfanate and sodium N-lauryl sarcosinate etc.

3. *Humectants*: It is used to retain moisture or prevent paste from hardening of paste when it expose to air, e.g., glycerol, sorbitol and propylene glycol etc.

4. *Binders*: These are used to prevent separation of liquid phase from solid, particularly during storage, e.g., glycerite of starch, natural tree exudates, seaweed colloids etc.

5. *Flavors*: These are used to impart taste of paste. Most command flavours used in pastes are spearmint, peppermint, wintergreen and cinnamon-mint etc.

6. *Miscellaneous*: Therapeutics Ingredients like chlorophyll, fluorides, anti-enzymes agent and antibiotic etc.

Haircare

Shampoos

Shampoo can be defined as a preparation of a surfactant in suitable form liquid, solid or powder. Which when used under the condition specified will remove surface grease, dirt and skin debris from hair shaft and scalp without affecting adversely the hair, scalp or health of the user. Shampoo leave the hair fragrant soft, lustrous and manageable. The formulation of a shampoo should have special capabilities like minimizing eye sting, controlling dandruff or imparting appealing fragrance to gain more favourable acceptance from particular segments of the population.

Types

There are variety of forms and types of shampoos are available in the market due to its unusual compensate and their combination such as;

(i) Children's and infants shampoo.

(ii) Shampoo for dry, oily and normal hairs.

(iii) Shampoo for men etc.

The most common form of the shampoo is cream and gel shampoos because of its high stability during storage and good efficiency. There are varieties of forms are available in the market like liquid, cream, gel, powder and aerosol etc. The major component of the shampoo is surfactant (soaps and synthetic detergent) with other additions like conditioners, sequestering agents, rinsing components (acids), foam builders, opacifying agents, clarifying agents (e.g. EDTA)

anti-dandruff agent, thickening agent, preservatives, stability additives and other cosmetic additions (e.g. perfume and dyes).

(a) *Acid Balanced Shampoo*: As the term “acid balanced shampoo” called the balance of acidic nature of fatty acids of oils used in shampoo to maintain the “acid mantle of skin”. This is achieved by optimum concentration of alkaline compounds in shampoo.

(b) *Egg Shampoo*: The Egg Shampoo is a type of special shampoo where shampoo is used as base and egg is for its special material to contact with the hair. Egg shampoo is used for its conditioning, nourishing as well as cheer effect to the hairs.

The most common ingredients of shampoo are:

1. Sodium lauroyl sulphate (Surfactant)
2. Ammonium lauroyl sulphate (Surfactant)
3. Cocamidopropyl betaine (Produce lather)
4. Zinc Pyrrolidine Carboxylic Acid
5. Poly Ethylene Glycol
6. Disodium EDTA
7. Polysorbate – 20
8. Coal tar
9. Citric acid
10. Euxyl
11. Perfume/colourant
12. Deionised water

Conditioners

A hair care product that helps to improve the appearance, feel, volume, or shine of the hair is a hair conditioner. In general, conditioners make hair more manageable by reducing friction between hair strands and ease the process of combing the hair. It also strengthens the hair, reduces frizz, and makes them anti-static.

Types

Several conditioners are available in the market, but it is essential to have an understanding of different types of ingredients used for various purposes while planning to formulate one.

1. *Rinse-out Conditioner*: These are the most common type and also known as "instant conditioner." These are meant to be used daily, applied for a shorter time after shampoo, and treats hair cuticle from outside, making the hair smooth.

2. *Deep Conditioner*: These conditioners are designed specifically for dry and damaged hair and are denser than regular conditioners. These conditioners do not produce significant effects on normal to oily hairs and can make them look oily and can weigh hairs down. Deep conditioners contain a significant quantity of fatty acids, oils, esters as well as proteins and amino acids. Deep conditioners are left in the hair for 30 minutes and then rinsed off.

3. *Leave-in Conditioners*: These conditioners are formulated for thin, oily, or curly hairs and are very light, thin, and less viscous. These can be sprayed after washing hair and makes a thin layer over hair, and assist in detangling the hair strands and making hairs smooth

The most common ingredients of hair conditioners are:

1. Isopropyl lauroyl sarcosinate
2. Lauroyl glutamate
3. Lauroyl lysine
4. Grape seed oil
5. Lauroyl arginine
6. Xanthan gum
7. Hyaluronic acid
8. Sodium Pyrrolidine Carboxylic Acid
9. Sodium stearyl glutamate
10. Phenoxy ethanol
11. Citric acid
12. Deionised water

Perfumes

Perfumes derived from natural plant sources utilize various parts of the plant, including flowers, leaves, stems, bark, roots, seeds, and resins. The chief constituents are typically essential oils, which are complex mixtures of volatile organic compounds like linalool, limonene and eugenol,

Classification

Perfumes are a mixture of fragrant essential oils, aroma compounds, and solvents. They are designed to give a pleasant smell to the human body, objects, or living spaces. But not all perfumes are created equally. Based on their composition, perfumes are categorized into different types.

1. Based on Fragrance Concentration
2. Based on Fragrance Notes
3. Based on Fragrance Families

Perfumes of plant origin (Natural)

Essential oil, floral extract and plant-based aromas have characteristics flavour and fragrances properties, possess biological activities and are widely applied in aromatherapy and healthcare in addition to several industries such as cosmetics, flavouring and fragrances, spices, pesticides, as well as herbal beverages.

Table 2.2: Various parts of the plants used in food, beverage, baking, perfume industries cosmetic industries and house – hold products

Name	Family	Fragrance	Parts Of The Plant
Cardamom	Zingiberaceae	1,8-cineole, α -terpinyl acetate, sabinene, and β -linalool	Whole dried fruits or seed pods
Cinnamon	Lauraceae	Cinnamaldehyde	Dried inner bark
Mustard	Brassicaceae	Alkyl isothiocyanate	Seed
Clove	Myrtaceae	Eugenol	Flower buds
Mango	Anacardiaceae	Ethyl butanote	Fruits and their extract
Tea	Theaceae	Geraniol	Leaves
Jasmine	Oleaceae	Eugenol, geraniol	Flower
Sandalwood	Santalaceae	Santalol	Wood
Citrus	Rutaceae	Linalool, pinene	Leaf
Vetiver	Poaceae	Vetisinol, khusimol	Roots
Rosewood	Leguminosea	Linalool	Bark
Bergamot	Rutaceae	Limonene, linalool	Peel

Aloevera	Lilaceae	Lignin	Leave
Capsicum	Solanaceae	Capsaicin	Pericalps
Saffron	Iridaceae	Crocin, Safranol	Stigma
Curry leaf	Rutaceae	Linalool, elemol	Leave

Perfumes of animal origin

Perfumes of animal origin

i) Ambergris from sperm whale

Ambergris is a solid waxy material produced in the digestive system of sperm whale. It is used as a fixative in perfume industry. Its smell is almost similar to isopropyl alcohol. The three chief constituents of ambergris are;

- i) triterpenoid - ambrein
- ii) sterol - epicoprostanol and
- iii) steroid lactone – coprostanone

Ambrein has only a mild smell. But its oxidation products ambroxide and ambrinol are the main components responsible for the odour of ambergris.

ii) Civetone from civet cat

Civet oil is a glandular secretion produced by both sexes of civet cat. The chief constituent of civet oil is civetone (4%). It also contains cyclopentadecanone, cyclohexadecanone and cycloheptadecanone.

Civetone is used as flavour and perfumery. It has a strong odour. It is pleasant on extreme dilution.

iii) Musk from musk deer

Musk is a substance obtained from a gland of the male musk deer. This gland is situated in its back or rectal area. Musk or Kasthanur is a strong smelling substance used as perfumes and as a traditional medicine and to treat inflammation, cardiovascular and neurodisorder.

Synthetic perfumes

Synthetic perfumes are chemically manufactured compounds which give the smell similar to natural fragrant.

Exmples: i) Benzyl acetate - Jasmine flavour

ii) Methyl benzoate - Fruity smell

Classification of synthetic perfumes

Synthetic perfumes are classified into different types on the basis of their functional group. The five important classes of compounds in most synthetic fragrances are

i) Alcohols, ii) Aldehydes, iii) Ketones and iv) Esters

Table 2.3: Synthetic perfumes containing alcohol, aldhyde, ketone and ester groups and their corresponding flavour

perfumes	Flavours
Synthetic alcohol	
Geraniol	Rose-like aroma
Vetiverol	Vetiver smell
Citronellol	Rose-like aroma
Santanol	Sandal-like perfume
Nerol	orange smell
Terpeneol	Lilac smell
Synthetic aldehyde	
Citral	Sweet lemon flavour
Vanillin	Vanilla flavour
Cuminaldehyde	Cumin flavour
Synthetic ketone	
Civetone	Strong musky odour
Muscone	Musky odour
Jasmone	Jasmine flavour
3-Penten-2-one	Fruit and spicy aroma
Chromone derivatives	oud-attar smell
Benzoin	Benzoin smell

Vetivone	Vetiver smell
Synthetic ester perfumes	
Ethyl benzoate	Fruity smell
Linolyl acetate	Lavender smell
Benzyl acetate	Sweet aroma of jasmine

Soaps and Detergents

Soaps and detergents are cleansing agents that, when dissolved in water, can remove dirt from surfaces. Soap is made through the saponification reaction of fats or oils with an alkali, while detergents are synthetic, water-soluble compounds chemically different from soaps.

Soaps

Till 18th century soap was believed to be a mechanical mixture of fat and alkali. But the concept of saponification. Soaps are alkali metal salts of higher fatty acids. They are represented by general formula RCOOM , where RCO^- is the acetyl ion of higher fatty acid and M^+ is alkali metal ion (Na^+ or K^+). Soap is produced by reacting fatty acid with alkali or hydrolysing the glycerides with alkali.

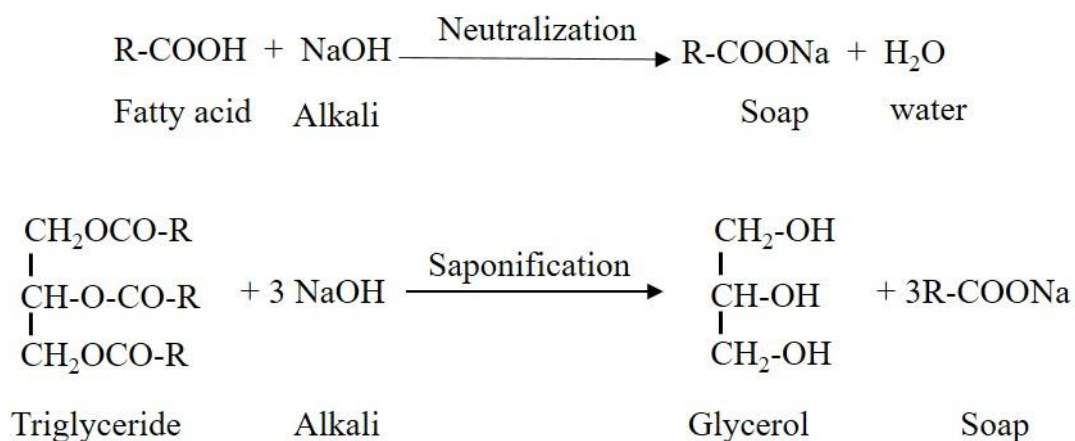


Figure 2.1: Preparation of soap

Properties of soaps

- i) Solubility in water: Soaps are freely soluble in soft water but sparingly soluble in hard water.

ii) Cleansing action: Soap is an emulsifying agent. Soap contains hydrophilic (water attracting) end and a hydrophobic (oil attracting) end. Both ends of soap allow it to emulsify oils and dirt, making them easier to wash away with water.

iii) Interaction with mineral salts: Soaps react with mineral salt in hardwater, forming a precipitate called scum, which can reduce their effectiveness.

iv) Surfactant properties: Soaps act as surfactant. They reduce the surface tension between water and other substances (dirt). This helps the mixing of water and dirt and clean the dirt more effectively.

Manufacture of Soap

Step 1 - Oil preparation

The oils used most commonly are, as in the Colgate-Palmolive process, tallow and coconut oil. These are blended together and dried in a vacuum chamber. Once the oils are dry, bleaching earth is sucked by the vacuum into the chamber to remove any coloured impurities. The spent earth is landfilled and the oils stored ready for saponification.

Step 2 - Saponification

The mixture of bleached oils is mixed with spent lye from the washing stage (see below) and a caustic soda solution. The mix is heated and then left to settle into two layers. The neutral lye (which is now rich in glycerine) is pumped off and the mixture of soap and unreacted oils which has risen to the top is left in the pan. More caustic liquor is added to this and the mix reheated to saponify the remaining free oils.

Step 3 - Washing

The crude soap is then pumped to a divided pan unit (DPU) where it is washed by a countercurrent of lye. This lye is a mixture of fresh brine solution and nigre lye (see below). The washed soap comes out the far end of the DPU and is sent to the fitting pans, while the lye comes out the near end and is pumped back into one of the saponification pans.

Step 4 - Fitting

Here the remaining unwanted glycerine is removed from the soap by reboiling with water, NaCl and a small amount of NaOH solution. The electrolyte concentration in the water is such that the soap and water to separate out into two layers. The top layer is 'neat' wet soap, which

is pumped off to be dried. The bottom layer is known as the 'nigre' layer, and consists of a solution of soap, glycerine and NaCl. This is left in the pan, re-boiled with further salt and left to stand, forming a soap crust over a lower layer of salt and glycerine (nigre lye). This soap is left in the pan and is mixed with the next intake of washed soap, while the nigre lye is pumped back to the DPUs to wash the next batch of crude soap.

Step 5 - Drying

Moisture is flashed off under vacuum in the same manner as was described above for the Colgate-Palmolive process.

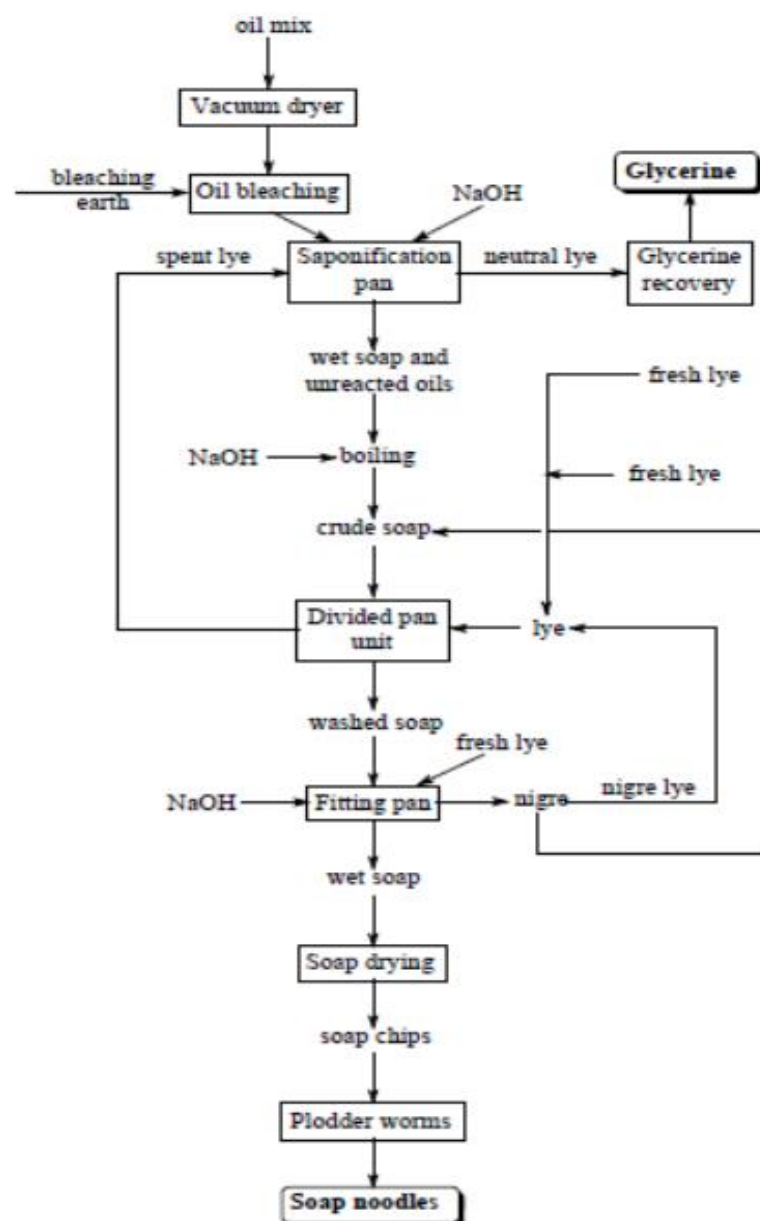


Figure 2.2: Manufacturing of soap by batch process

Types of Soap

Transparent Soap

- ✓ Transparent soap undergoes a chemical reactions as any other soaps, but it has added solvents that dissolve the soap (salt) crystals into such tiny particles that light can pass through it.
- ✓ The main ingredients of transparent soap are glycerine, sugar syrup and Isopropyl alcohol 99%. The addition of glycerine makes the soap mild and conditioning on the skin.
- ✓ Use of distilled water is the key to achieving a highly transparent bar of soap. This soap gives a smooth creamy lather, rather than large bubbles as we do not add any strong lather boosting agents.
- ✓ The mild coconut based surfactant that we use gives excellent wetting properties to the soap with a mild cleansing foam suitable for dry or sensitive skin.
- ✓ Examples: Pears, Medimix transparent soap.

Toilet Soap (Bath Soap)

- ✓ They are made from best quality selected materials and usually contain only 10-15 % moisture and some quantity of glycerol.
- ✓ Pure alkali (caustic potash) is added in right proportion avoiding any excess alkali, as it may harm the skin.
- ✓ It also contain expensive perfumes and no fillers are used.
- ✓ Transparent soaps are prepared from best quality coconut oil, castor oil and caustic potash.
- ✓ Examples: Cinthol, Hamam, Mysore sandal saop etc.,

Powder Soap (Washing Soap)

- ✓ These soaps are used for sanitation purpose like washing clothes, cleaning utensils, floors etc.

- ✓ They are prepared from oils or fats using sodium hydroxide. They contain alkali, fillers like Na_2CO_3 , silicate, clays, optical whiteners etc.
- ✓ Typical soap contains 20% soap, 40% soda ash (Na_2CO_3) and 40% water as water of crystallization. Jelly soaps prepared from coconut oil and caustic potash.
- ✓ Examples: Tide, Surexcel, Ariel, Rin, etc.,

Liquid soap

- ✓ Liquid soap is a cleaning agent in the liquid form used for the washing hands or body.
- ✓ Basically, liquid soap lasts half as long as other soap bars, and its cost increases due to the raw materials (mainly plastic) necessary for its packaging.
- ✓ Duration is another negative point of liquid soap, in fact, it lasts less than other solid soap and its properties are diluted in water and, therefore, less effective.
- ✓ Major ingredients of liquid soaps are sodium Lauryl sulphate, Essential oil or coconut oil, Sodium benzoate, Sandal wood.
- ✓ Examples: Dettol liquid hand wash, Savlon hand wash etc.,

Detergents

Amphipathic molecules that contain charged hydrophilic or polar groups at the end of long lipophilic hydrocarbon groups are called detergents. The charged hydrophilic group is also called the head and the long lipophilic hydrocarbon group is called the tail. Detergents are also known as surfactants as they have the ability to decrease the surface tension of water. Examples – Sodium lauryl sulphate, Sodium tearyl sulphate.

Properties of detergents

- The concentration at which micelles formation starts is called as critical micelle concentration (CMC).
- Aggregation number is the average number of monomers in a micelle.
- Relative micelle size is indicated by micelle molecular weight.
- The temperature at which the detergent solution is around or above its critical micelle concentration separates into two phases is called the cloud point.

Cleaning action of detergents

A detergent is made up of two parts: a long hydrocarbon part and a short ionic part containing COONa^+ group. The long hydrocarbon chain is hydrophobic, so the hydrocarbon part of the detergent molecule is insoluble in water but soluble in oil and grease. The ionic part of the detergent molecule is hydrophilic so it is soluble in water but insoluble in oil and grease. When the detergent is added to dirty clothes, which contains grease and oily substances, the greasy and oily dirt particles attach themselves to the hydrocarbon part and ionic part remains attached to the water. When the dirty clothes are agitated in a detergent solution, the dirt particles attached to the hydrocarbon part molecule get washed away in water and the clothes get cleaned.

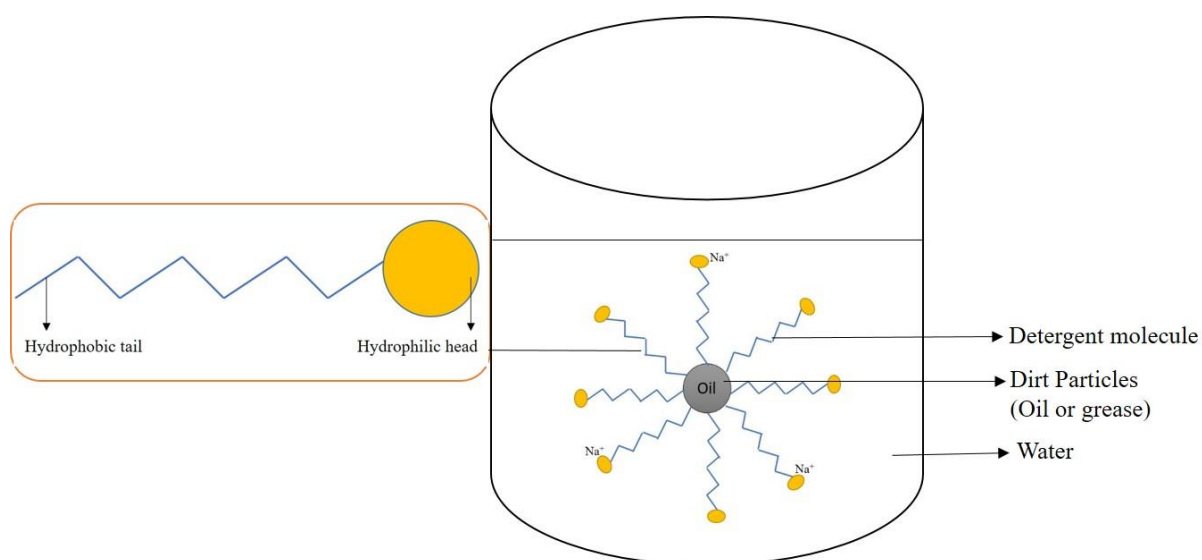


Figure 2.3: Cleansing action of detergent

Cleansing action of detergents in hard water

Synthetic detergents can lather well even in hard water because they do not form insoluble calcium or magnesium salts on reacting with the calcium and whereas when we talk about soaps, they are not suitable for hard water as they form insoluble calcium or magnesium salts on reacting with the calcium and magnesium ions present in the hard water.

Soapless detergents

Soapless detergents, also known as synthetic detergents. They are the substances used for cleaning purposes that do not produce soap scum when combined with hard water. These science-driven alternatives to traditional soaps are primarily used in industrial, medical, and personal care contexts, where soaps may react with minerals in the water and affect their

cleaning capabilities. Synthetic detergents are created artificially using a variety of petrochemicals and/or oleochemicals. Their main components typically include one or more surfactants (which enable water to effectively wet surfaces, emulsify oils, and suspend soil), as well as various additives to modify the properties of the detergent. While synthetic detergents can clean effectively, they're also formulated to inhibit the precipitation of calcium and magnesium ions present in hard water. This makes them suitable for usage in hard water scenarios where soap would form an unwanted 'scum'.

Classification of detergents (Surface acting agents)

According to the nature of the hydrophilic group surfactants are mainly classified as:

- Anionic
- Cationic
- Non-ionic
- Ampholytic

Anionic Surfactant

- Those surfactant in which surface active ion is negatively charged in solution, are known as anionic surfactant.
- Anionic groups may be directly connected to hydrophobic part of these may be connected through ester, amide and amidine links.
- Eg: Sodium dodecyl sulphate
- Surfactant having anionic groups connected directly to the hydrophobic unit.

Ex: Fatty acid soaps, alkyl sulphonates, alkyl sulphates, alkyl aryl sulphonates and alkyl phosphates.

- Surfactant having anionic groups connected through ester links.

Ex: Monoglyceride sulphates, dialkyl sulphosuccinate, polyethylene glycol ester and sulphate isoethionates.

- Surfactant having anionic groups connected through ether links.

Ex: Alkyl ether sulphate, phenol ether sulphates and alkyl ether carboxylates.

- Surfactant having anionic groups connected through amide links.

Ex: Alkalonamide sulphates, taurined and sarcosinates.

- Surfactant having anionic groups connected through amidine links.

Ex: Imidazole sulphate

Cationic Surfactant

- Those surfactant in which surface active ion is positively charged in solution, are known as cationic surfactant. Cationic detergents have tetra alkyl ammonium or pyridinium salts.

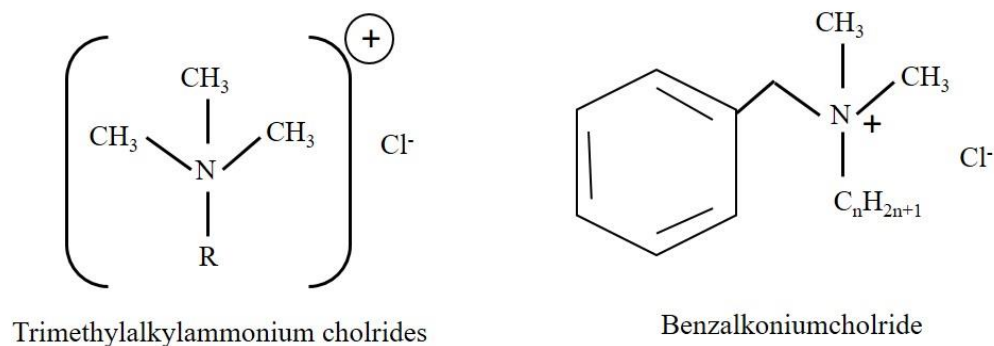


Figure 2.4: Structure of Trimethyl alkyl ammonium and Benzalkonium chloride

Non-Ionic Surfactant

- Hydrophilic part of the molecule is made up of multiple uncharged polar groups.

Eg. Hydroxyl group or ether linkage in ethylene oxide chains.

Table 2.4: Different type of non-ionic surfactant and its examples

Type of non-ionic surfactant	Examples
Fatty alcohol	Cetyl alcohol, Stearyl alcohol, Cetostearyl alcohol, Oleyl alcohol
Ethers	Brij, Decyl glucoside, Lauryl glucoside, Octyl glucoside, Triton X-100, Nonoxynol-9
Esters	Glyceryl laurate, Polysorbates, Spans
Block copolymers	Poloxamers

Amphoteric (Zwitter-Ionic) Surfactant

It's able to form a surface active ion with both positive and negative charges.

Three types:

- Alkyl B aminopropionates, betaines.
- Acylaminoacids: Acyl B amino propionates, acyl peptides.
- Alkylimidazolines.

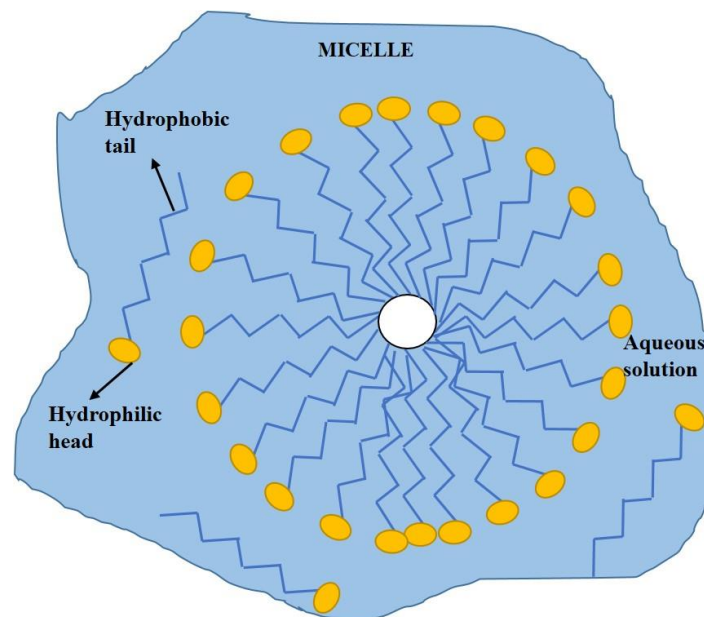


Figure 2.5: Pictorial representation of amphilphilic surfactant molecular structure

Uses of detergents as surfactant

Detergents is also known as surfactants or surface active agents. These are used to clean surfaces by lowering surface tension and emulsifying dirt.

i) Lowering surface tension

Surfactants disrupt the forces of attraction between the water molecules and reducing their surface tension.

ii) Emulsification

Surfactants have both hydrophilic (Water attracting) and hydrophobic (water repelling) ends. The hydrophobic end binds to dirt and grease and hydrophilic end interacts with water. This

creates an emulsion. Once emulsified, the dirt and grease are suspended in water and prevent their re-deposition. This allows for their easy removal through rinsing.

Bio-degradability of soaps and detergents

- i) Soaps are biodegradable (ie) they can be broken down by microorganisms in the environment. But detergents are less or non-biodegradable.
- ii) Soaps are sodium or potassium salts of long chain fatty acids from natural vegetable oils and animal fat. The straight chain hydrocarbon in soap molecules are easily broken down by microorganisms and biodegradable. Hence soap is an environmental friendly product.
- iii) Detergents are synthetic compounds contain long chain hydrocarbon chains with branches. These are not easily degraded by microorganisms and non-biodegradable. This can lead to their accumulation in water causing water pollution.

UNIT – III

Sugar Industry, Food Preservation and processing

Sugar Industry

Sugar

Sugarcane is the cash crop and sugarcane juice is used for products like white sugar, brown sugar and jaggery. Bagasse and molasses are the two main by-products of sugarcane industry. Bagasse is mainly used as fuel and for the production of compressed board paper, plastic etc. Molasses is used in distilleries for the manufacturing of ethyl alcohol, butyl alcohol, etc. Cane tops and leaves are also good source of cattle feed.

Manufacture of sugar from sugarcane

Collecting the harvested cane: Mature canes are gathered by a combination of manual and mechanical methods. Canes are cut at ground level, its leaves are removed and the top is trimmed off by cutting off the last mature joint. Cane is then placed into large piles and picked up, tied and transported to a sugar factory.

Prevention of moisture loss in the harvested cane: Covering the harvested cane with trash and sprinkling with water both under sun and shade reduced the moisture loss and prevented a quality deterioration.

Cleaning and Crushing: Stalks are thoroughly washed and cut when reaching the sugar mill. After the cleaning process, a machine led by a series of rotating knives, shreds the cane into pieces. This is known as "grinding." During grinding, hot water is sprayed on to the sugarcane to dissolve any remaining hard sugar. The smaller pieces of cane are then spread out on a conveyer belt.

Juicing: The shredded pieces of sugarcane travel on the conveyer belt through a series heavy-duty rollers, which extract juice from the pulp. The pulp that remains or "bagasse" is dried and used as fuel. The raw juice moves on through the mill to be clarified.

Clarifying: Carbon dioxide and the milk of a lime are added to the liquid sugar mixture and it is heated to the boiling point, as the process of clarifying begins. As the carbon dioxide travels through the liquid it forms calcium carbonate, which attracts non-sugar debris (fats, gums, and wax) from the juice, and pulls them away from the sugar juice. The juice is then pushed through a series of filters to remove any remaining impurities.

Evaporation: The clear juice which results from the clarifying process is put under a vacuum, where the juice boils at a low temperature and begins to evaporate. It is heated until it forms into thick, brown syrup.

Crystallization: By evaporating what little water is left in the sugar syrup, crystallization takes place. Inside a sterilized vacuum pan, pulverized sugar is fed into the pan as the liquid evaporates, causing the formation of crystals. The remaining mixture is a thick mass of large crystals, which is sent to a centrifuge to spin and dry the crystals. The dried product is raw sugar, still inedible.

Refinery: Raw sugar is transported to a cane sugar, Refinery for the removal of molasses, minerals and other non-sugars, which still contaminate the sugar. This is known as the purification process. Raw sugar is mixed with a solution of sugar and water to loosen the molasses from the outside of the raw sugar crystals, producing a thick matter known as “magma.” Large machines then spin the magma, which separate the molasses from the crystals. Crystals are promptly washed and filtered to remove impurities.

Separation and Packaging: Once the final evaporation and drying process is done, screens separate the different sized sugar crystals. Large and small crystals are packaged and shipped, labelled as white, refined sugar.

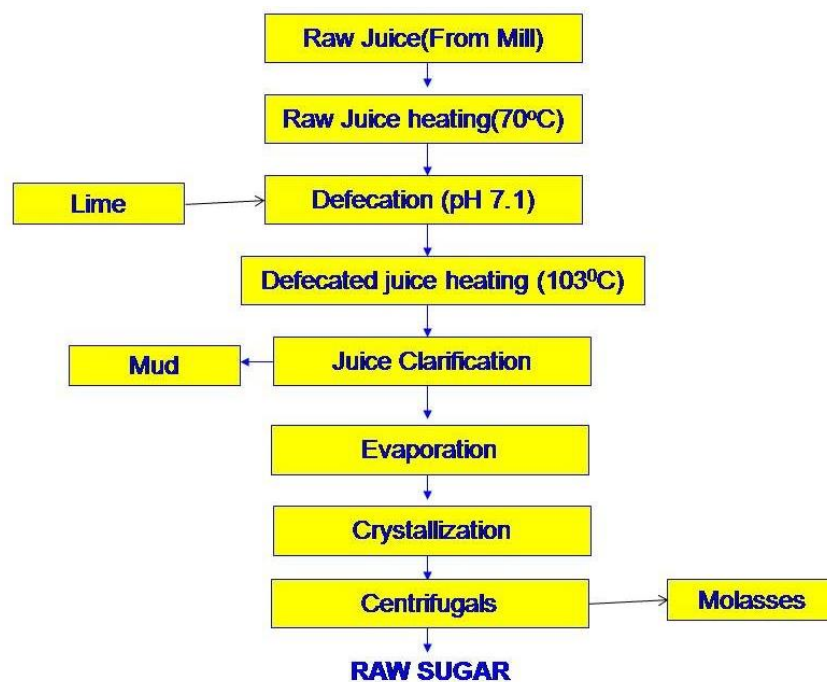


Figure 3.1: Flowchart represents the manufacture process of sugar from sugarcane

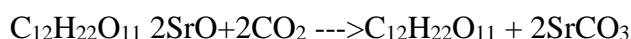
Recovery of sugar from molasses

The molasses (mother liquor) after the separation of sugar crystals contains some amount of sugar. The recovery from molasses involves following steps.

Step 1: The mother liquor is first boiled and cooled slowly to get some sugar crystals and separate out.

Step 2: The liquid obtained after the separation of sugar crystals is diluted with water and treated with strontium hydroxide in a treating tank. A precipitate of strontium sucrosate is formed and filtered.

Step 3: The precipitate is dissolved in water and then heated to boiling. Then CO₂ gas is passed into the solution, sugar and precipitate of strontium carbonate are formed. The strontium carbonate is removed by filtration.



Step 4: The filtrate (sugar solution) is then decolourised by animal charcoal and evaporated to get a syrupy liquid of sugar.

Step 5: The syrupy liquid is crystallised by slow cooling. A crystals of raw sugar is obtained and finally bagged.

Testing of sugar

Sugar may contains non-sugar (glucose and fructose) as impurity. The testing of sugar in the laboratory is as follows:

i) Fehling's test (a)

To 5ml of aqueous solution of sugar, add 2ml of Fehling's solution (Fehling I + Fehling II in 1:1 ratio) and boil. A yellow precipitate or red indicates the presence of non-sugar as impurities. If No precipitate is formed the sugar is pure.

ii) Fehling's test (b)

To 5ml of aqueous solution of sugar, add 0.5ml of conc.HCl and boil for few minutes. The solution is made alkaline with 10% NaOH solution. A yellow or red ppt is formed by boiling with 2ml of Fehling's solution. (Fehling I + Fehling II in 1:1 ratio) This indicates the presence of sugar.

Estimation of sugar

The quickest and commonest method of estimation of sucrose (sugar) and invert sugar (sugar solution) is made by polarimeter. The polarimeter is used to measure the optical rotations of the sample (sugar and sugar solution in water). The rotations are compared by determining the specific rotation of the sample. The specific rotations are measured in degrees (°).

$$[\alpha]_D^t = \alpha / l.d$$

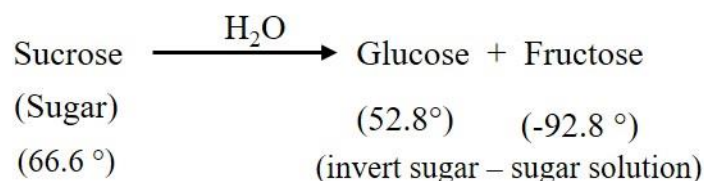
Where, $[\alpha]_D^t$ = specific rotation of the sample

α = Optical rotation in degrees

D = Wave length of the sodium light (589nm)

t = Temperature (20°C)

The specific rotations of sucrose, glucose and fructose are found to be 66.6°, 52.8° and -92.8°



Hence specific rotation of invert sugar is,

$$[\alpha]_D^{20} = [52.8^\circ - 92.8^\circ / 2] = -20^\circ$$

Thus, if the sample is pure sugar, the specific rotation will be -20°. If the value is less than -20°, the sugar contain some impurities like glucose or fructose (non-sugar)

Food preservation and processing

Food spoilage

Food spoilage is defined as "any changes in the visual, smell and texture of food that degrades its nutritional value and makes unsuitable for consumption".

Causes of food spoilage

- Growth and activities of microorganisms, principally bacteria, yeasts and moulds
- Activities of food enzymes, for instance, enzymatic browning
- Infestation by insects, parasites and rodents

- d. Chemical changes in a food, for instance, chemical oxidation of fats causing
- e. Rancidity and non-enzymatic browning reaction.
- f. Physical changes, or the damages caused by freezing or drying etc.
- g. Presence of foreign bodies, and
- h. Physical abuse i.e. contamination with chemical agents.

Food Preservation

Food preservation refers to the process of handling and preserving food using certain techniques that stop or slow down spoilage. Food preservation techniques help prevent loss of quality, nutritional value and edibility. These practices have been essential for centuries as they allow people to store food for future consumption. However, these techniques are not only required for increasing the shelf life. They are also crucial to reduce food waste. There are various types of food preservation methods. However, all these methods aim to preserve food.

Methods of food preservation

Food preservation methods can be classified as follows:

Physical methods

1. Preservation by low temperature

- Refrigeration
- Freezing

2. Preservation by high temperature

- Pasteurization
- Canning

3. Preservation by drying

- Sun drying
- Drying by mechanical driers

4. Preservation by irradiation

1. Preservation by low temperatures

- *Refrigeration:* The temperature maintained in the refrigerator is 0 to 5 °C. Enzymatic and microbial changes in foods are slowed down considerably. Perishable foods like eggs, dairy products, meat, sea foods, fruits and vegetables are stored in refrigerators. Food can be stored safely for few days or a week.
- *Freezing:* The temperature of freezer is -18 to 40 °C. Microbial growth is prevented completely and the action of food enzymes greatly reduced. Frozen foods have better quality and need uninterrupted supply of electricity while storing. Foods like poultry, meat, fish, peas, vegetables, juice concentrates can be preserved for several months from this method.

2. Preservation by high temperatures

- *Pasteurization:* Pasteurization is a mild heat treatment that kills a part but not all the microorganisms present and usually involves the application of temperature below 100 °C.
- *Canning:* Canning is the process in which the foods are heated in hermetically sealed (airtight) jars or cans to a temperature that destroys microorganisms and inactivates enzymes that can cause food spoilage. The general steps to be adopted for canning foods are cleaning, blanching, filling, exhausting, sealing, sterilizing, cooling and labelling.

3. Preservation by drying

Microorganisms need moisture to grow. When exposed to sunlight or subjected to dehydration, the moisture in the food is removed and the concentration of water is brought below a certain level. This prevents the growth of microorganisms and thereby spoilage of food.

- *Sun drying:* It is limited to regions with hot climates and dry atmosphere and to certain fruits such as raisins, prunes, figs, apricots, pears and peaches. It is a slow process.
- *Drying by mechanical drier:* Artificial drying involves the passage of hot air with controlled relative humidity over the food to be dried or the passage of the food through such air. Fruits, vegetables, nuts, fish and meat can be successfully preserved by this method. In the dehydration process, artificial drying methods like

spray drying, vacuum drying, drum drying and freeze drying are used for drying foods.

4. Preservation by irradiation

- ✓ Food irradiation also known as cold sterilization is another preservation technique.
- ✓ The foods are bombarded by high energy rays called gamma rays or by fast moving electrons to kill bacteria, fungi and insects and in some cases to delay fruit ripening or prevent sprouting in onions and potatoes.
- ✓ The goal of irradiation is to kill the microorganisms and inactive the enzymes without altering the food.

Food additives

Food additives are chemical substances added to foods to achieve specific effects. They have been used since ancient times for preservation and to enhance palatability. Modern food processing relies on additives to create many products, such as low-calorie, snack, and ready-to-eat foods.

Food additives are categorized as nutritional, processing, preservatives, or sensory agents. Processing agents maintain food consistency, using emulsifiers for uniform liquid dispersion, stabilizers/thickeners to increase viscosity, and chelating agents to protect against enzymatic reactions. Food colouring enhances the appearance of foods, with sources ranging from natural vegetable dyes to synthetic substances. Additives undergo toxicological analysis to determine acceptable daily intake and ensure they are safe for consumption.

Types food additives

Some important types are as follows:

- a. Preservatives
- b. Flavours
- c. Colours
- d. Anti-oxidants
- e. Sweetening agents

a. *Preservatives*: used to prevent or inhibit spoilage of food due to microorganisms. Sodium benzoate, potassium sorbate, sulfur dioxide, lactic acid, and etc. are used in food processing such as jams and preserves. The food additives used in meat additives are most common, such as bacon additives, fish additives, ham additives, sausage additives.

b. *Flavours*:

Flavouring agents are chemicals that impart flavours or fragrances and are added to food to modify its aroma or taste. They are the most common type of additive used in foods, with hundreds of varieties used in a wide variety of foods, from confectionery and soft drinks to cereal, cake and yoghurt. Flavouring agents can be extracted from naturally occurring sources (e.g. plant or animal sources) or chemically synthesized. Flavours extracted directly from naturally occurring sources are often referred to as natural flavours. Such flavours can also be chemically synthesized and are sometimes referred to as nature made or nature identical to indicate that although the flavour molecule itself is naturally occurring it hasn't been extracted from its source, but synthesized to be identical. Artificial flavouring agents are chemicals that do not exist in nature but are synthesized to imitate natural flavours or elicit other taste sensations. Culinary ingredients, including spices, nuts and dried fruits or vegetables, can also modify aroma or taste, but are generally not considered flavouring agents.

c. *Colours*: commonly used synthetic pigments include carmine, amaranth, lemon yellow, indigo, etc., which can change the appearance of food and increase appetite, Check meat food colouring if you want.

d. *Anti-oxidants*: similar to preservatives, and they can extend the shelf life of foods by inhibiting the degradation of food by oxygen. Vitamin C is a common antioxidant.

e. *Sweetening agents*: commonly used synthetic sweeteners include sodium saccharin, sodium cyclamate, etc., whose purpose is to increase sweetness. Our e953 sweetener and sweetener e420 are processed with high quality.

Hazards of using additives

Carcinogenic Risks: Preservatives like sodium nitrite and nitrates (found in processed meats) can form cancer-causing nitrosamines. Potassium bromate, used in some flours, is also linked to cancer in animal studies.

Neurological Issues: Artificial sweeteners like aspartame and flavor enhancers like Monosodium Glutamate (MSG) have been linked to headaches, dizziness, and "Chinese restaurant syndrome". Some studies suggest additives may contribute to hyperactivity (ADHD) in children.

Allergic Reactions: Coloring agents (e.g., Tartrazine) and preservatives (e.g., Sulfites) can trigger hives, asthma, and even fatal anaphylactic shock in sensitive individuals.

Digestive & Metabolic Disorders: Fat replacers like Olestra can cause severe diarrhea and abdominal cramps by inhibiting vitamin absorption. Other additives may interfere with hormones, contributing to obesity and Type 2 diabetes.

Cardiovascular Risks: Synthetic emulsifiers and trans fat used for texture are linked to an increased risk of cardiovascular disease.

Food standards

Food standards are something that are set up by experts or an authority for measuring quantity, weight, extent, value and quality of a substance.

International food standards

The safety assessments completed by JECFA are used by the joint intergovernmental food standard-setting body of FAO and WHO, the Codex Alimentarius Commission, to establish levels for maximum use of additives in food and drinks. Codex standards are the reference for national standards for consumer protection, and for the international trade in food, so that consumers everywhere can be confident that the food they eat meets the agreed standards for safety and quality, no matter where it was produced.

Once a food additive has been found to be safe for use by JECFA and maximum use levels have been established in the Codex General Standard for Food Additives, national food regulations need to be implemented permitting the actual use of a food additive.

Food standards in India

They are formulated along the lines of codex alimentarius

a. Compulsory standards:

- ✓ The Prevention of Food Adulteration act (PFA) 1955,
- ✓ Essential commodities act 1954,

- ✓ Fruit Products Order (FPO) regulated by ministry of food processing industries,
 - ✓ Meat Products Order (MPO) 1973 regulated by the directorate of marketing and inspection.
 - ✓ Milk and milk products order 1992: cover the sale, purchase and distribution of milk and milk products.
 - ✓ Solvent extracted oils, flour control order, vegetable products order 1976. The license is granted by the ministry of civil supplies consumer affairs and public distribution. It controls the market price of vanaspati (dalda)
- b. Voluntary standards:
- ✓ AGMARK, agriculture produce grading and marketing act 1937.
 - ✓ The director of marketing and inspection grades commodities as 1234 meaning special, good, fair and ordinary. The AGMARK label is an assurance of quality.
 - ✓ Bureau of Indian Standards (BIS). Indian Standards Institute (ISI) is responsible for laying BIS.
 - ✓ These standards are evolved after chemical, biological and physical assessment of the product to be marked.



Figure 3.2: Symbols of AGMARK, BIS, ISI

UNIT – IV

Abrasives, Leather Chemistry and Paper Industry

Abrasives

An abrasive is a sharp and hard substance used for cutting, grinding or polishing materials.

Examples: Quartz, Corundum, Diamonds etc.

Characteristics of Abrasives

Hardness, toughness, and friability

The hardness, toughness, and friability of abrasives are crucial properties that determine their effectiveness in various applications. Hardness refers to the material's ability to resist deformation and wear, allowing it to efficiently remove material from the workpiece. Toughness relates to the ability to withstand stress and impacts without fracturing. Friability is the measure of an abrasive's ability to break down into smaller particles during use, ensuring a continuous supply of fresh cutting edges. These properties directly impact the abrasive's durability, cutting performance, and lifespan.

Grit size and particle shape

Grit size and particle shape are essential factors to consider when selecting abrasives for specific tasks. Grit size refers to the size of abrasive particles, usually measured in microns or mesh sizes. Coarser grits are effective for heavy material removal, while finer grits are ideal for achieving smooth finishes. Particle shape also plays a significant role in the abrasive's cutting action. Irregular shapes, such as angular or sharp-edged particles, provide aggressive cutting, whereas rounded or spherical particles tend to produce finer finishes. Understanding the desired surface quality and material removal requirements helps in choosing the appropriate grit size and particle shape for optimal results.

Abrasive strength and cutting efficiency

The strength of an abrasive material influences its cutting efficiency and the rate at which it removes material from the workpiece. Abrasives with high abrasive strength exhibit excellent cutting performance, allowing for faster material removal. This property is particularly crucial in applications where productivity and efficiency are paramount. Additionally, the cutting

efficiency depends on the bonding between the abrasive particles and the abrasive tool. The bond should be strong enough to retain the particles during the grinding or cutting process while providing the necessary support for effective cutting action. Achieving the right balance between abrasive strength and bonding ensures optimal cutting efficiency and extends the lifespan.

Understanding the properties of abrasives, including hardness, toughness, friability, grit size, particle shape, and abrasive strength, empowers industries to select the most suitable abrasives for their specific applications. Whether it is grinding, cutting, polishing, or surface preparation, considering these properties enables the efficient removal of material, achieving desired surface finishes, and optimizing overall productivity.

Types

Natural Abrasives

Natural abrasives are raw materials extracted from the earth's crust, typically found in minerals and stones. These abrasives are widely used across commercial, technical, and domestic applications due to their availability and cost-effectiveness. Natural abrasives such as, diamond, corundum, emery, garnet, and quartz occur within the earth's crust, are mined, and require little to no processing.

Diamond - Natural diamonds possess excellent hardness and are the hardest known material, lasting the longest compared to other abrasive materials. They are used as core drilling bits, wire-drawing dies, rock and metal cutters, and kit grindstones. It consist of single element carbon.

Uses: indrill points and teeth for saws; as abrasives wheels in cutting machines.

Corundum: Corundum abrasives are composed mostly of aluminum oxide and are known for their durability. They are effective for grinding and cutting applications in metalworking, grinding, finishing, and deburring. It consist of 52.93 % of aluminium and 47.07 % oxygen.

Uses: in grinding wheels; for making abrasive paper and cloth.

Emery: A naturally occurring mixture of corundum (aluminum oxide) and other minerals like magnetite and hematite. Emery is used in grinding, deburring, and lapping of optical lenses. It has 65-68 % of Al_2O_3 and 16-24 % of Fe_2O_3 .

Uses: making emery paper; as abrasive cloth of various grades

Garnet: Garnet refers to a group of silicate minerals with varying compositions. It is used in abrasive papers, grinding wheels, and waterjet cutting. It contains 9-10 % of alumina, 13-19 % of ferrous oxide and 20-25 % of magnesia.

Uses: abrasive cloth; kinds of abrasive papers.

Quartz: Quartz, also known as silica in its purest form, is the most commonly used abrasive in many industries. It can be used as blocks, sand, pumice, sandstone, chert, and quartzite. It contains 46.7 % of silicon and 53.3 % of oxygen.

Uses: making sand papers; grinding pigments in ball mills.

Synthetic abrasives

This group includes materials manufactured to possess very high and consistent hardness, often surpassing natural counterparts in performance predictability. Synthetic abrasives like silicon carbide and aluminum oxide are manufactured to enhance the performance and the capabilities of the materials for more specific applications. This process allows customization of the size, shape, and purity. Examples of synthetic abrasives include:

Carborundum (Silicon Carbide): Carborundum is a composition of carbide and a mix of high-purity sand, sawdust, and coke, commonly referred to as Silicon carbide. Typical applications include abrasive papers and cloth, metal grinding wheels, and gear sharpening blocks. The toughest artificial abrasive after diamond, composed of silicon carbide and manufactured by fusing high-purity sand, coke, and sawdust under high electrical current (e.g., 2482 °C or 4500 °F in an electric arc furnace).

Uses: Grinding wheels; abrasive papers and cloth, and gear sharpening blocks.

Aluminium carbide: Aluminum carbide is a hard, crystalline compound that finds specialized use as an abrasive material. It is a brittle material with considerable hardness and high thermal stability, making it suitable for high-temperature applications where dry conditions are maintained. It consists of 75 % of aluminium and 25 % of carbon.

Uses: It is used in cutting tools, abrasive powders, and as a reinforcing material in metal matrix composites

Boron Carbide (Norbide): Manufactured by heating boric oxide and coke together at 2600 °C (4712 °F). Its hardness level is similar to silicon carbide. It has 85 % of boron and 15 % of carbon.

Uses: Primarily used as a powdered abrasive for lapping and polishing hard materials, and in wear-resistant components.

Boron nitride: Boron nitride exists in several forms, with the cubic form (c-BN) being a superhard abrasive, second in hardness only to diamond. The hexagonal form (h-BN) is soft and primarily used as a lubricant. It offers superior thermal stability and chemical resistance compared to diamond, especially with ferrous metals (iron, steel, etc.). Diamond tends to react chemically with iron at high temperatures, but c-BN does not. It consists of 85 % of 44 % of boron and 57 % of nitrogen.

Uses: c-BN widely used in grinding wheels, cutting tools, and powders for machining hardened steels, cast iron, and superalloys, especially for high-precision finishing.

Synthetic graphite

Synthetic graphite is a man-made substance manufactured by the high temperature processing of amorphous carbon materials. The types of amorphous carbon used as precursors to graphite are many, and can be derived from petroleum, coal, or natural and synthetic organic materials. In some cases graphite can even be manufactured by the direct precipitation of graphitic carbon from pyrolysis of a carbonaceous gas such as acetylene (pyrolytic graphite). One important commonality between all graphite precursors is that they must contain carbon. Graphite is carbon, a specific form of carbon, so it can only be derived from other carbon containing substances.

a) Primary synthetic graphite: It is prepared from high purity (100% pure) amorphous carbon.

b) Secondary synthetic graphite: It is prepared from low purity scrub graphite.

Uses: Synthetic graphites are used as

- i) Primary abrasive for cutting and polishing soft materials.
- ii) An anode in lithium-ion batteries.
- iii) An electrodes and brushes in electrochemical cells due to its good conductivity.

Leather Industry

Structure of skin or hide

A hide or skin has three main layers: the outer epidermis, the thick, protein-rich dermis (corium), and the underlying fatty hypodermis (subcutaneous tissue). The dermis, composed

mainly of collagen, provides strength and forms the true leather, while the epidermis offers protection and contains hair/scales, and the hypodermis connects skin to muscle.

Layers of Skin/Hide

1. Epidermis (Outer Layer)

- The thin, protective outer boundary.
- Contains hair (in mammals) or scales (in reptiles/fish).
- Provides protection against microbes and water loss.

2. Dermis (Corium or True Skin)

- The thickest and most important layer for leather making, rich in collagen.
- Provides strength, flexibility, and resilience.
- Contains elastin, reticulin, blood vessels, and nerves.

3. Hypodermis (Subcutaneous Tissue)

- A layer of fatty tissue (adipose tissue) beneath the dermis.
- Connects the skin to underlying muscle and bone.

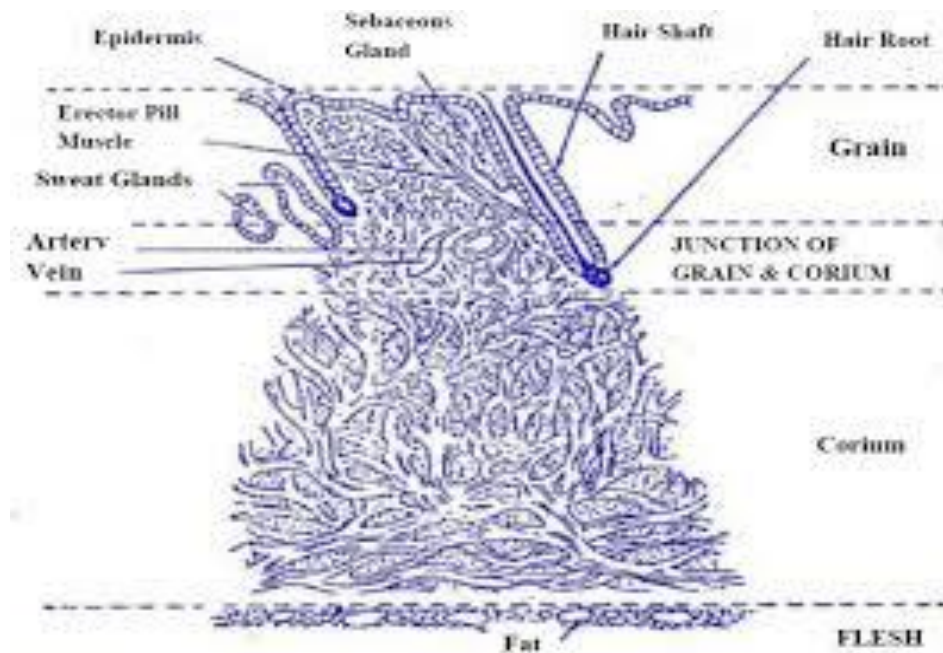


Figure 4.1: Cross section of skin or hide

Composition of skin or hide

Raw hides and skins are primarily composed of water (60-70%), proteins (20-30%, mainly collagen), fats (1-10%), and trace minerals, with collagen forming the essential fibrous network that becomes leather after tanning, while other components like epidermis, hair, and fat are removed during processing. The dermis, rich in collagen and elastin, provides the strength and flexibility, making it the valuable part for the leather industry.

Chemical Composition

- Water: (60-70%) Essential moisture, partly free and partly bound to fibers, needs removal.
- Proteins: (20-30%) The main structural component, primarily:
 - Collagen: Forms strong, fibrous bundles, providing leather's strength.
 - Keratin: Found in hair and epidermis.
 - Elastin: Contributes to skin elasticity.
 - Non-fibrous proteins: Albumins, globulins, etc., forming a gel-like substance.
- Lipids: (1-10%) Vary by animal, removed during processing.
- Minerals and pigments: Trace amounts (0.3-1.5%).

Manufacture of leather

Leather tanning is the first step in the leather making process, after the hides come from the beamhouse and are cleaned from dirt, blood, salt and hair. To use a hide or skin for a leather product it needs to be processed. This process is called the tanning process. Tanning changes the chemistry inside the leather fibers to make it more difficult for the enzymes from bacteria and fungi to break them down – this makes the leather durable.

Pre-tanning process:

The pre-tanning process of leather, prepares raw hides for tanning through steps like soaking (cleaning/rehydrating), liming (removing hair/flesh), deliming (removing lime), bating (enzymatic treatment for softness), and pickling (acid bath for pH adjustment), making the collagen receptive to tanning agents. These stages remove impurities, swell the

pelt, and adjust its chemistry for better penetration and uniform results in the main tanning (chrome/veg) and post-tanning (dyeing, fatliquoring) stages.

Steps

1. **Curing/Preservation:** Raw hides are salted or brine-cured to prevent bacterial decay before processing.
2. **Soaking:** Soaking is done to remove any excess salt or dirt. All non-leather making components should be removed from the hide to prepare for the production a clean and flat pelts.
3. **Liming:** The goal of liming is to split the fibre bundles and to remove any unwanted hair from the hide through the introduction of alkali. Hair saving or semi-hair saving systems yield particularly good results. Here, lime is typically added before alkaline swelling occurs from subsequent additions of sodium sulphide and sodium hydrosulphide. This enables the lime to penetrate and diffuse evenly through the pelts, for optimal fibre splitting and separation. From this stage the skin is often referred to as a pelt.
4. **Unhairing/Fleshing:** Hair is mechanically removed, and flesh/fat is scraped off the hide.
5. **Deliming:** The pelt requires an efficient and complete removal of lime and the neutralization of residual alkalinity, after fleshing and/or splitting. This is done most effectively using proprietary organic acids and acid-salts which form highly soluble lime complexes. Additional care must be taken to adequately buffer the de-liming bath and avoid the precipitation of soluble proteins through a rapid drop in float pH. Lime is neutralized and removed from the hide, often using ammonium salts, lowering the pH.
6. **Bating:** The network of elastin fibers, which are insoluble in the highly alkaline conditions of liming, should now be evenly relaxed and flattened through the extended action of suitable enzyme preparations. An enzymatic treatment that further cleanses the pelt, removes unwanted proteins, and helps de-swell the skin, making it softer and more pliable.

7. Pickling: Hides are immersed in an acid (like sulfuric acid) and salt solution to lower the pH to a level (around 2.5-3.0) suitable for tanning agents, often using a retanning agent like polymers as a pre-tanning step.

Purpose of Pre-Tanning

- Cleanliness: Removes dirt, salt, blood, and flesh.
- Hair Removal: Eliminates hair effectively.
- Swelling & Softening: Opens up the fiber structure for better chemical penetration.
- pH Adjustment: Prepares the skin's pH for optimal tanning.
- Uniformity: Ensures consistent absorption of tanning agents and even leather quality.

Tanning process

Vegetable tanning

Vegetable tanning is the oldest tanning method. It uses extracts from wood, and nuts of trees and shrubs. Responsible suppliers ensure these come from a sustainable source. It usually takes longer to tan leather using this method, but the result is a leather with a distinctive aesthetic and handle, which ages beautifully.

Its naming, as well as the tanning materials used, make it seem as if vegetable tanned leather is more 'eco-friendly'. However, we need to take the entire balance across the whole process into account, to make a more meaningful comparison with other methods. For example, vegetable tanning uses a few times the amount of tannins than for chrome-tanned leathers. The effluent produced also requires more treatment before it can be discharged. However, it has the benefit of using natural, sustainable and renewable raw materials.

- Extraction: Tannins are extracted from materials like oak, mimosa, chestnut, and quebracho.
- Soaking: Hides are soaked in pits or rotating drums with weak tannin solutions, gradually increasing concentration over time (days to months) to allow tannins to penetrate and bind to collagen.

Characteristics of Vegetable-Tanned Leather:

- ✓ Appearance: Warm, rich colours, develops a unique patina (vintage look) with age.

- ✓ Texture: Sturdy, firm, and thick, yet becomes supple with use.
- ✓ Uses: Ideal for crafting, belts, wallets, saddlery, and tooling.
- ✓ Process: Longer, more labour-intensive, but uses natural materials.

Chrome tanning

Chrome tanning uses chromium salts to turn hides into stable leather, with the one bath method being a modern, efficient process that combines pickling and tanning into a single operation for reduced water/time, producing soft, durable leather; the older two-bath method, once favoured for uniform tannage, involved separate pickling and tanning steps but is now largely obsolete due to environmental concerns and the effectiveness of newer one-bath systems.

One-Bath Chrome Tanning:

- Process: Combines the pickling (acid/salt) and tanning (chromium sulphate) steps into a single drum, increasing efficiency and reducing waste.
- Benefits: Significantly cuts water usage, time, and power; produces soft, smooth leather with good tear resistance.
- Characteristics: Creates "wet blue" leather, known for its blue-green colour, softness, and high heat resistance (stable in boiling water).

Two-Bath Chrome Tanning;

- Process: A traditional, multi-step method where hides are first pickled in one bath, then transferred to a separate tanning bath.
- Historical Use: Valued for achieving uniform tannage and leaving a sulphur deposit, leading to specific leather properties.
- Status: Largely superseded by the one-bath method due to inefficiency and environmental concerns, though sometimes used for specialized results.

Finishing process

The leather finishing process is the final stage after tanning, involving treatments to enhance aesthetics, durability, and feel, using methods like surface coating (polyurethane/acrylics), impregnation (oils/waxes for water resistance), and pigment

finishing (adding colour/stain resistance). Key steps include dyeing, sealing, buffing, applying antique finishes or waxes for effects, and edge finishing (burnishing/painting) to protect and beautify the final product.

Paper industry

Pulp:

Pulp in the paper industry is the fundamental fibrous material, derived mainly from wood, bamboo, or recycled paper, processed mechanically or chemically to separate cellulose from lignin, forming a water-based slurry that's the raw material for making paper, paperboard, and other products.

Types of pulp:

Sulfate or Kraft Pulp

a) Raw Material:

- ✓ Primarily produced from wood chips obtained from softwood trees, such as pine, spruce, or fir.
- ✓ Softwood fibers contribute to the strength and durability of the resulting pulp.

b). Kraft Pulping Process:

Cooking Phase:

- ✓ Wood chips are treated with a mixture of sodium hydroxide (caustic soda) and sodium sulfide in a large vessel called a digester.
- ✓ High temperature and pressure break down lignin, separating it from the cellulose fibers.
- ✓ Delignification:
- ✓ The cooking process removes lignin from the wood chips, leaving behind cellulose fibers.
- ✓ Lignin is dissolved and becomes a byproduct known as black liquor.

c). Byproducts:

Black Liquor:

- ✓ A byproduct of the kraft pulping process containing dissolved lignin, chemicals, and other impurities.
- ✓ Can be used for energy generation through recovery boilers.

Lignin:

- ✓ Separated from cellulose fibers during the pulping process.
- ✓ Used for various applications, including energy generation, chemicals, and as a bio-based material.

Rag Pulp:

a) Raw Material:

- ✓ Produced from textile waste, old clothes, and rags.
- ✓ Typically made from cotton or linen fibers obtained from discarded textiles.

b). Pulping Process:

Rag Cutting:

- ✓ Old clothes and textiles are collected and sorted.
- ✓ Rags are cut into smaller pieces to facilitate the pulping process.

Hydration:

- ✓ Cut rags are hydrated with water to soften the fibers.
- ✓ This step prepares the material for pulping.

Pulping:

- ✓ Rags undergo mechanical or chemical pulping processes to break down fibers.
- ✓ Chemical pulping may involve the use of caustic soda or other pulping chemicals.

c) Byproducts:

Waste Streams:

- ✓ Byproducts from rag pulping may include waste materials and impurities.
- ✓ These need to be properly managed and treated.

Manufacture of pulp:

Mechanical processes

Steps

1. Preparation: Debarking and chipping logs (for refiner methods).
2. Pulping: Applying mechanical force (grinding/refining) with or without heat/steam to separate fibers.
3. Screening: Removing oversized fiber clumps and impurities.
4. Further Refining (Optional): Beating fibers to increase surface area for better bonding.

Characteristics

- High Yield: Retains most of the wood (90-99%), including lignin.
- Low Strength: Lignin prevents strong hydrogen bonding between fibers, making paper less durable.
- Bulky & Opaque: Good for printing due to bulk and opacity.
- Yellowing: Lignin causes discoloration over time (colour reversion).
- Energy Intensive: Requires significant electrical energy, though TMP recovers heat.

Chemical processes

The chemical process of pulp in the paper industry, primarily the dominant Kraft process, uses powerful alkaline chemicals (sodium hydroxide & sulphide) in large digesters to dissolve lignin, the natural glue binding wood fibers, leaving pure cellulose for strong paper, followed by washing, and often bleaching (using chlorine dioxide/oxygen) to remove colour, contrasting with acid-based sulphite pulping for purer cellulose but weaker fibers.

Steps in i) Kraft (Sulfate) Pulp:

Beating:

- Involves mechanical treatment of kraft pulp to improve fiber flexibility and bonding ability.
- Enhances the paper's strength, formation, and printability.

- Controlled beating ensures desired paper properties without excessively breaking down fibers.

Refining:

- Kraft pulp can undergo refining processes using equipment like refiners.
- Refining enhances fiber flexibility, bonding, and sheet density.
- Balancing refining intensity is crucial to achieve the desired paper quality.

Filling:

- Involves adding mineral fillers to kraft pulp to improve opacity, brightness, and surface smoothness.
- Common fillers include calcium carbonate or kaolin.
- Filling enhances printability and paper surface properties.

Sizing:

- Chemical sizing is applied to kraft pulp to control its water absorption characteristics.
- Rosin or synthetic sizing agents are added to improve resistance to water penetration.
- Important for applications like printing where ink absorption needs to be controlled.

Colouring:

- Bleaching processes are employed to remove residual lignin and color from kraft pulp.
- Bleaching agents like chlorine, chlorine dioxide, or hydrogen peroxide are used.
- Achieves a brighter and whiter appearance in the final paper product.

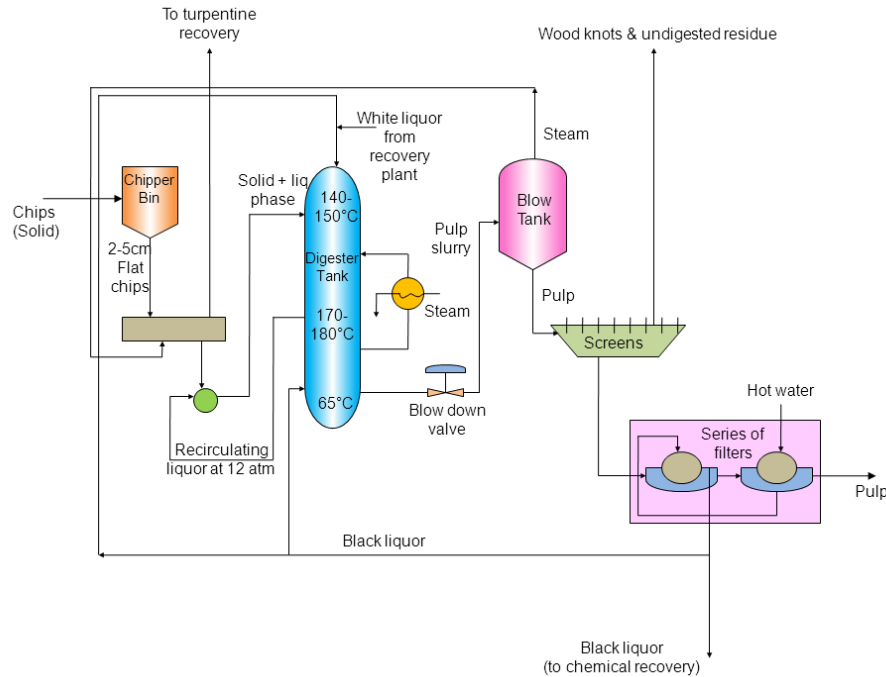


Figure 4. 2: setup for sulphate of kraft pulp

Steps in ii) Rag Pulp:

Beating:

- Rag pulp undergoes beating to improve fiber flexibility and bonding properties.
- Influences the softness and texture of the final paper.
- Requires controlled beating to achieve the desired characteristics.

Refining:

- Refining is applied to rag pulp to enhance fiber quality and sheet density.
- Improves paper strength and uniformity.
- Optimal refining conditions prevent excessive fiber damage.

Filling:

- Rag pulp may undergo filling processes to enhance certain paper properties.
- Fillers are added to improve opacity, brightness, and surface smoothness.
- Selection of fillers depends on the intended use of the paper.

Sizing:

- Sizing agents may be applied to rag pulp to control water absorption characteristics.
- Ensures the paper meets specific requirements for printing or writing applications.
- Influences the paper's interaction with inks and water.

Colouring:

- Bleaching processes can be employed to achieve desired brightness levels in rag pulp.
- Selection of bleaching agents considers environmental impact and end-use requirements.
- Improves the visual appearance of the final paper product.

Manufacture of paper from pulp



Figure 4. 3: Pulp and paper manufacturing process

In the papermaking process, several critical steps determine the final sheet's quality, texture, and functionality. These stages are often categorized under "Stock Preparation" and "Finishing."

1. Beating & Refining

These are mechanical treatments applied to the pulp fibers to improve their bonding potential.

--Refining: Usually refers to fiber separation and cutting to ensure a uniform mixture.

--Beating: A more intensive process that includes bruising or "fibrillation," which increases the surface area of the fibers, making the final paper stronger and more flexible.

--Key Equipment: Disc refiners, conical refiners, and Hollander beaters.

2. Filling (Loading)

Filling involves adding mineral pigments (fillers) to the fiber furnish to occupy the spaces between fibers.

--Purpose: Improves the paper's opacity, brightness, and smoothness.

--Common Materials: China clay (kaolin), calcium carbonate, and titanium dioxide.

3. Sizing

Sizing is the process of adding chemicals to the paper to control its resistance to liquid penetration.

--Internal Sizing: Additives like rosin or AKD are mixed into the pulp before the paper is formed.

--Surface Sizing: Applied after the sheet is formed (often at a "size press") to improve surface strength and ink receptivity.

4. Colouring

Adding dyes or pigments to the furnish to achieve the desired shade or whiteness.

--Dye Types: Acid dyes, basic dyes, or direct dyes are used depending on the fiber type and required color fastness.

--Methods: Can be done "in-the-beater" (pulp dyeing) or as a surface coating.

5. Calendering

This is a finishing process where the dried paper sheet is passed between a series of heavy rolls (the calender stack).

--Action: Uses high pressure and sometimes heat to compress the sheet.

--Result: Enhances gloss, smoothness, and ensures a uniform thickness (caliper) across the web

Card boards

1. **Pulping:** Used cardboard and other fiber sources are processed using the kraft pulping method (sulfate process) to break down lignin and separate cellulose fibers, resulting in strong pulp. This process is efficient at creating high-quality, durable fibers.
2. **Kraft Paper Production:** The resulting pulp is formed into durable kraft paper, which is used as the linerboard (flat outer layers) and medium (fluted inner layer) in corrugated board production.
3. **Corrugation and Adhesion:** In the corrugation process, the medium is fluted (shaped into a wave pattern) by heated rollers. Adhesion is achieved by applying a starch-based adhesive to the tips of the flutes and bonding them between two sheets of linerboard, creating strong and protective corrugated fibreboard

Unit – V

Lubricants, Cement Industry and Intellectual Property Rights

Lubricants

In all type of machines, the surfaces of moving (sliding or rolling) parts rub each other. Due to this rubbing of one part against another, a resistance arises to their movement. This resistance is said to be friction which causes a lot of wear and tear of moving parts and a large amount of energy is dissipated in the form of heat. This dissipated heat decreases the efficiency of machines. A substance which is introduced between these two moving surfaces to reduce the friction and wear and tear is said to be a lubricant. The process by virtue of which the frictional resistance and wear and tear is reduced is called lubrication.

Classification of lubricants

1. Liquid Lubricants or Lubricating Oils

Lubricating oils decrease the friction and wear between two sliding and moving metallic surfaces. These oils also act as cooling medium, sealing agent and corrosion preventer. Lubricating oils must possess adequate viscosity, low freezing point, high boiling point, and high oxidation resistance and non-corrosive properties. These are further classified as follows:

- Vegetable and Animal Oils

The oils of the vegetable and animal origin were used as lubricants. They possess good oiliness. They are such as rapeseed oil, castor oil, sperm oil, rosin oil, olive oil, coconut oil and palm oil etc.

- *Mineral or Petroleum Oils*

These are obtained by distillation of petroleum. The number of carbon atoms in their chains varies from 12 to 50. The shorter number carbon atoms chain oils exhibit low viscosity than longer chain oils. These oils possess low oiliness. Sometimes minerals oils compounded with fatty oils have been used as lubricating oils. These are said to be blended oils.

2. Semi-solid Lubricants or Greases

The semi-solid lubricants are greases and Vaseline. These are obtained by the dispersion of soap along with some specific additives in lubricating oils. The amount of mineral oil present

in these semi solid lubricants determines the consistency. The added soaps act as gelling agents which interconnect the oils. Overall the greases behave like gels. To get more heat-resistant greases, some thickening agents like colloidal silica, clay or carbon black etc. are added. These greases have some merits as well as demerits also.

Merits

- (i) Due to the presence of soap in oils, these stick well on the surfaces.
- (ii) Grease can support heavier load at low speed.
- (iii) Greases can be used in machinery parts i.e. bearing and gears that work at high temperatures.
- (iv) Greases exhibit higher frictional resistance than oils.
- (v) Greases can be used in situations where sealing is required against entry of dust, dirt or grit etc.
- (vi) These require less attention than oils.

Demerits

- (i) Due to gelling in nature, these are unable to dissipate heat from the bearings as oils.
- (ii) Greases have tendency to get separate into oils and soaps.
- (iii) On longer use, the oil may get evaporated from greases.
- (iv) Greases have high coefficient of friction.

The greases are further classified on the basis of the soaps used in their preparations like sodium soap, lithium soap, calcium soap or aluminum soap greases.

3. Solid Lubricants

The two solid lubricants are usually in practice. These are graphite and molybdenum disulphide. These are used either in powdered form (dry state) or mixed with water or oil. These solid lubricants fill up the low spots in the surfaces of moving/sliding parts and form a solid film which exhibits low frictional resistance. The coefficient of friction between solid lubricants is between 0.005 and 0.01. The following are the merits of solid lubricants.

Merits

These can be used where operating temperature is high.

(ii) These can be used where load is high and even semi-solid lubricant cannot sustain.

(iii) These can be used where the contamination (by the entry of dust or grit or clay particles) of greases or lubricating oils is unacceptable, for example, in commutator bushes of electric generators and motors.

(iv) These can be used where the operating conditions are such that a lubricating film cannot be sustained with lubricating oils or greases.

(v) These can be used in a situation where combustible lubricants must be avoided.

Graphite, molybdenum disulphide (MoS_2), boron nitride (BN)_x are predominantly used as a solid lubricants. They are used under high temperature and high load (pressure).

Graphite:

It is most widely used as a solid lubricant. Graphite has layer structure; layers are held together with the help of weak Vander Waals' forces which facilitate the easy sliding of one layer on the other layer. It is very soapy to touch, non-inflammable. It is used at higher temperature (around 450°C) condition. They are either used as powder form or mixed with oil or water.

Molybdenum disulphide (MoS_2):

It is sandwich like structure in which hexagonal layer of molybdenum (Mo) lies between two hexagonal layers of sulphur (S) atom. Like graphite each layers are held together with weak Vander Waals' forces. It is stable up to 400°C . It is differ from graphite because it is used in high vacuum unlike graphite (graphite is mixed with water or oil). It adheres even more strongly to the metal or other surface.

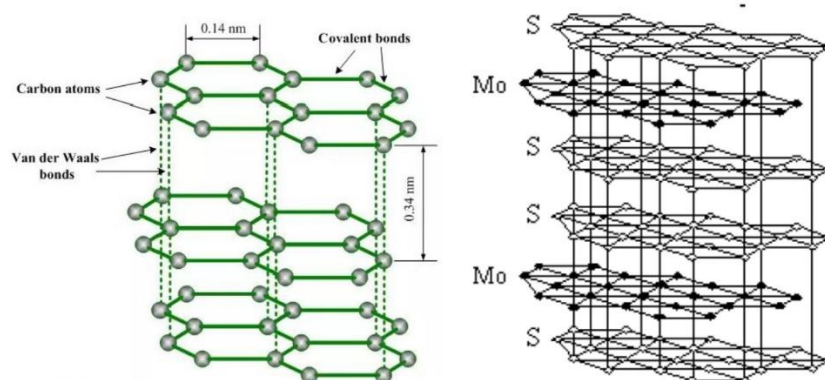


Figure 5.1: Structure of Graphite and Molybdenum disulphide

4. Synthetic Lubricants

Synthetic lubricants have been developed to meet the most drastic and severe conditions such as existing in aircraft engine where the same lubricant has to be used in the temperature range of -50°C to 260°C . These lubricants possess low freezing point, high viscosity index and non-inflammability. Synthetic lubricants show following characteristics also:

- (i) High thermal stability
- (ii) High chemical stability
- (iii) High flash points

Some of the important synthetic lubricants are described below.

Silicones

These are very good synthetic lubricants because these are not oxidized upto 200°C . These possess high viscosity index also. Silicones undergo oxidation rapidly above 200°C and start cracking onwards 230°C . Therefore, these are not advised to be employed onwards 200°C operating conditions.

Polyglycols

Polyethylene glycol, polypropylene glycol, polyglycidal ethers and higher polyalkylene oxides etc. can be used as water soluble and water insoluble lubricants in rubber bearing and joints. They fulfil all the above mentioned characteristics.

Chlorinated and Fluorinated Hydrocarbons

These hydrocarbons show very good chemical resistance, thermal resistance as well as oxidation resistance.

Polymer Hydrocarbons

These are like polyethylene, polypropylene and polybutylene etc. (weight average molecular weight upto 50,000). Polymer hydrocarbons are residue free, chemically inert and thermally stable lubricants which do not possess non-carbon impurities therein.

Organic Amines and Imines

These exhibit low pour points and high viscosity index. Organic amines and imines are good lubricants which can be used in the temperature range of 50°C to 250°C.

Properties of lubricants

Viscosity Index

The variation of viscosity of a liquid with temperature is called viscosity index. A relatively small change in viscosity with temperature is indicated by high viscosity index whereas, a low viscosity index shows, a relatively large change in viscosity with temperature.

Flash point

The flash point of a volatile material is the lowest temperature at which vapors of the material will ignite for a moment when an ignition source brought near to it. The lubricating oil should have flash point reasonably above its working temperature.

Cloud Point

The temperature at which lubricating oil becomes cloudy in appearance is called cloud point.

Pour Point

The lowest temperature at which the lubricant oil become semi-solid and ceases to flow is called pour point. It indicates the suitability of lubricants used in cold condition. Good lubricant should possess low pour point.

Aniline Point

Aniline point of the lubricant oil is defined as the minimum equilibrium solution temperature for equal volumes of aniline and lubricant oil samples. It gives an indication of the possible deterioration of the lubricant oil in contact with rubber sealing; packing, etc. Aromatic hydrocarbons have a tendency to dissolve natural rubber and certain types of synthetic rubbers. Consequently, low aromatic content in the lubricant oil is desirable. A higher aniline point means a higher percentage of paraffinic hydrocarbons and hence, a lower percentage of aromatic hydrocarbons. Aniline point is determined by mixing mechanically equal volumes of the lubricant oil samples and aniline in a test tube. The mixture is heated, till homogenous solution is obtained. Then, the tube is allowed to cool at a controlled rate. The temperature at which the two phases (the lubricant oil and aniline) separate out is recorded at the aniline point.

Drop point

Drop point is the temperature at which a solid lubricant melts or liquefies. It is an important criterion for lubricating greases which means, drop point of a grease should have higher than the operating temperature of the machine. Usually high temperature grease (close to 300°C) is desirable.

Grease

Lubricating grease is defined as a solid to semi fluid product of dispersion of a thickening agent in liquid lubricant. There are three components that form lubricating grease. These components are oil, thickener and additives. The base oil and additive package are the major components in grease formulations. The thickener is often referred to as a sponge that holds the lubricant (base oil plus additives).

Base Oil

Most greases produced today use mineral oil as their fluid components. These mineral oil based greases typically provide satisfactory performance in most industrial applications. In temperature extremes (low or high), a grease that utilizes a synthetic base oil will provide better stability.

Thickener

The thickener is a material that, in combination with the selected lubricant, will produce the solid to semifluid structure. The primary type of thickener used in current grease is metallic soap. These soaps include lithium, aluminum, clay, polyurea, sodium and calcium. Lately, complex thickener-type greases are gaining popularity. They are being selected because of their high dropping points and excellent load-carrying abilities.

Additives

Additives can play several roles in lubricating grease. These primarily include enhancing the existing desirable properties, suppressing the existing undesirable properties, and imparting new properties. The most common additives are oxidation and rust inhibitors, extreme pressure, anti-wear, and friction-reducing agents.

Function of grease

The function of grease is to remain in contact with and lubricate moving surfaces without leaking out under the force of gravity, centrifugal action or being squeezed out under pressure.

Its major practical requirement is that it retains its properties under shear forces at all temperatures it experiences during use.

Types of grease

Grease lubricants are primarily categorized by their thickener type, which determines their temperature range, water resistance, and mechanical stability.

Lithium Grease: The most popular multi-purpose grease. It is durable, stable at high temperatures, and provides long-lasting protection against corrosion.

Lithium Complex Grease: An advanced version of lithium grease with even higher heat resistance (up to 200°C) and better load-carrying capacity.

Calcium Grease: One of the oldest types, highly valued for its water resistance and corrosion protection. It is ideal for marine and agricultural use but has poor heat resistance.

Polyurea Grease: A non-soap grease known for its extreme oxidation stability and long service life. It is commonly used in electric motors and steel plants.

Aluminum Complex Grease: Offers excellent resistance to high temperatures and water. It is widely used in the food industry and for automotive chassis components.

Bentone (Clay) Grease: A non-melting lubricant that remains effective at extreme temperatures. It is often used in heavy-duty mining, steel, and ceramic industries.

Barium Complex Grease: A high-performance, premium option for heavy loads and high-speed machinery in aerospace and marine sectors.

Sodium Grease: Known for good rust protection and shear stability, though it lacks water resistance. It is mostly used for rolling contact bearings.

Functional Properties of Grease

1. Grease functions as a sealant to minimize leakage and to keep out contaminants. Because of its consistency, grease acts as a sealant to prevent lubricant leakage and also to prevent entrance of corrosive contaminants and foreign materials. It also acts to keep deteriorated seals effective.
2. Grease is easier to contain than oil. Oil lubrication can require an expensive system of circulating equipment and complex retention devices. In comparison, grease, by virtue of its rigidity, is easily confined with simplified, less costly retention devices.

3. Grease holds solid lubricants in suspension. Finely ground solid lubricants, such as molybdenum disulfide (moly) and graphite, are mixed with grease in high-temperature service or in extreme high-pressure applications. Grease holds solids in suspension while solids will settle out of oils.

4. Fluid level does not have to be controlled and monitored.

Characteristics of ideal grease

The characteristics commonly found on product data sheets include the following:

Pumpability:

Pumpability is the ability of a grease to be pumped or pushed through a system. More practically, Pumpability is the ease with which a pressurized grease can flow through lines, nozzles and fittings of grease-dispensing systems.

Water resistance:

This is the ability of grease to withstand the effects of water with no change in its ability to lubricate. Soap/water lather may suspend the oil in the grease, forming an emulsion that can wash away or, to a lesser extent, reduce lubricity by diluting and changing grease consistency and texture.

Consistency:

Grease consistency depends on the type and amount of thickener used and the viscosity of its base oil. Grease's consistency is its resistance to deformation by an applied force. The measure of consistency is called penetration. Penetration depends on whether the consistency has been altered by handling or working. ASTM D 217 and D 1403 methods measure penetration of unworked and worked greases. To measure penetration, a cone of given weight is allowed to sink into a grease for five seconds at a standard temperature of 25°C (77°F).

Dropping point:

Dropping point is an indicator of the heat resistance of grease. As grease temperature increases, penetration increases until the grease liquefies and the desired consistency is lost. The dropping point is the temperature at which a grease becomes fluid enough to drip. The dropping point indicates the upper temperature limit at which a grease retains its structure, not the maximum temperature at which a grease may be used.

Oxidation stability:

This is the ability of grease to resist a chemical union with oxygen. The reaction of grease with oxygen produces insoluble gum, sludges and lacquer-like deposits that cause sluggish operation, increased wear and reduction of clearances. Prolonged exposure to high temperatures accelerates oxidation in greases.

High-temperature effects:

High temperatures harm greases more than they harm oils. Grease, by its nature, cannot dissipate heat by convection like circulating oil. Consequently, without the ability to transfer away heat, excessive temperatures result in accelerated oxidation or even carbonization where grease hardens or forms a crust. Effective grease lubrication depends on the grease's consistency. High temperatures induce softening and bleeding, causing grease to flow away from needed areas. The mineral oil in grease can flash, burn or evaporate at temperatures greater than 177°C (350°F).

Low-temperature effects:

If the temperature of grease is lowered enough, it will become so viscous that it can be classified as hard grease. Pumpability suffers and machinery operation may become impossible due to torque limitations and power requirements. As a guideline, the base oil's pour point is considered the low-temperature limit of grease.

Cutting Fluids

Cutting fluids are specialized liquids or gases used in metalworking to manage the intense heat and friction generated during machining. While the terms are often used interchangeably, coolants and lubricants perform distinct primary functions to extend tool life and improve surface quality.

Main Types of Cutting Fluids

- **Straight Oils (Neat Oils):** Pure mineral, vegetable, or animal oils used without water. They offer the best lubrication but have poor cooling properties.
- **Soluble Oils (Emulsions):** A mixture of mineral oil and water (typically 5–10% oil). They provide a balance of cooling and lubrication.

- **Synthetic Fluids:** Purely chemical-based fluids containing no mineral oil. They offer superior cooling and are resistant to bacterial growth.
- **Semi-Synthetic Fluids:** A blend of synthetic fluids and soluble oils (usually 5–30% oil). They combine the cooling efficiency of synthetics with the better corrosion protection of oils.

Advantages of Cutting Fluids

- ✓ It performs lubrication between the job and the cutting tool.
- ✓ Save the job from burning.
- ✓ Save the job and tool from blending.
- ✓ Save the job from rust.
- ✓ Increase the life of tool.
- ✓ Keeps the tips and edge of the tool away from the chips.
- ✓ The rate of cutting increases.
- ✓ Good finishing on the job during cutting.

Table 5.1: Important key importance of lubricant and coolant

Lubricant	Coolant
Thin layer of this fluid between two machine parts helps in keeping them cool.	It helps to cool down the job and cutting tool while cutting operations carried out.
It gives long life to m/c parts	It gives long life to cutting tools
It saves m/c from rust	It saves job from rust
It helps in the smooth running of m/c and its parts	Cutting is done easily with its use.
It protects the m/c and tools from becoming jam.	It protects the job and tools from becoming jam.
It helps in keeping the m/c fit and in good working condition	It helps in giving fine finishing on the jobs.

Selection criteria for good lubricants

Primary Selection Criteria

1. Viscosity & Viscosity Index (VI): Viscosity is the most critical property, representing the lubricant's resistance to flow.

- High VI: Indicates that the oil's viscosity remains relatively stable across a wide temperature range.
- Correct Grade: Too thin, and it won't prevent metal-to-metal contact; too thick, and it increases friction and operating temperatures.

2. Original Equipment Manufacturer (OEM) Recommendations: Always start with the OEM's specified viscosity grade, performance properties, and cleanliness levels.

3. Operating Environment:

- Temperature: Extremes (hot or cold) often necessitate synthetic base oils like PAO or Esters, which offer better stability than mineral oils.
- Contaminants: Environments with high dust, moisture, or salt water require lubricants with superior filtration capabilities and anti-corrosive properties.

4. Additive Performance: Depending on the application, you may need specific additives:

- Anti-Wear (AW): For moderate loads and high speeds.
- Extreme Pressure (EP): For heavy loads or shock loading.
- Rust/Oxidation (R&O): For applications without metallic interaction.

5. Material Compatibility: Ensure the lubricant is compatible with seals, paints, and metallurgy to prevent cracking, swelling, or degradation.

6. Cleanliness Levels: Adhere to standards like ISO 4406 to minimize particulate contamination, which is a leading cause of machine failure.

Cement Industry

Cement is a dirty greenish heavy powder and finds its importance as a building material. It can be described as material possessing adhesive and cohesive properties and capable of bonding materials like stones, bricks, building blocks etc. Cement has the property of setting and hardening in the presence of water. So, it is called as hydraulic cement. The essential

constituents of cement used for constructional purposes are compounds of calcium (calcareous) and Al +Si (argillaceous).

Types of cement

Table 5.2: Different types of cement, their composition and uses

TYPES OF CEMENT	COMPOSITION	PURPOSE
Rapid Hardening Cement	Increased Lime content	Attains high strength in early days it is used in concrete where form works are removed at an early stage.
Quick setting cement	Small percentage of aluminium sulphate as an accelerator and reducing percentage of Gypsum with fine grinding	Used in works is to be completed in very short period and concreting in static and running water
Low Heat Cement	Manufactured by reducing tricalcium aluminate	It is used in massive concrete construction like gravity dams
Sulphates resisting Cement	It is prepared by maintaining the percentage of tricalcium aluminate below 6% which increases power against sulphates	It is used in construction exposed to severe sulphate action by water and soil in places like canals linings, culverts, retaining walls, siphons etc.,
Blast Furnace Slag Cement	It is obtained by grinding the clinkers with about 60% slag and resembles more or less in properties of Portland cement	It can use for works economic considerations is predominant.
High Alumina Cement	It is obtained by melting mixture of bauxite and lime and grinding with the clinker it is rapid hardening cement with initial and final setting time of about 3.5 and 5 hours respectively	It is used in works where concrete is subjected to high temperatures, frost, and acidic action
White Cement	It is prepared from raw materials free from Ironoxide.	It is more costly and is used for architectural purposes such as precast curtain wall and facing panels, terrazzo surface etc.,

Coloured cement	It is produced by mixing mineral pigments with ordinary cement.	They are widely used for decorative works in floors
Pozzolanic Cement	It is prepared by grinding pozzolanic clinker with Portland cement	It is used in marine structures, sewage works, sewage works and for laying concrete under water such as bridges, piers, dams etc.,
Air Entraining Cement	It is produced by adding indigenous air entraining agents such as resins, glues and sodium salts of sulphates etc., during the grinding of clinker.	This type of cement is especially suited to improve the workability with smaller water cement ratio and to improve frost resistance of concrete.
Hydrographic cement	It is prepared by mixing water repelling chemicals	This cement has high workability and strength
Quick setting cement	Small percentage of aluminium sulphate as an accelerator and reducing percentage of Gypsum with fine grinding	Used in works is to be completed in very short period and concreting in static and running water

Raw materials

The main raw materials are listed below

Limestone, Clay, Sand, Gypsum, Fly, ash, Slag (a by-product of iron and steel production) and Marl (a type of sedimentary rock which contains both limestone and clay).

Manufacture process

Manufacture of Portland cement:

Raw materials: 1. Calcarious matter, CaO (lime stone, chalk, marl etc)

2. Argillaceous matter, Al₂O₃ and SiO₂(clay, slate etc)

3. Powdered coal or fuel oil

4. Gypsum

Functions of the ingredients of cement:

1. Lime: Its proportion must be properly regulated. Excess or lesser amount of lime reduces strength of cement and makes it quick setting.

2. Silica: Gives strength to cement

3. Alumina: Makes the cement quick setting
4. Gypsum: It enhances the initial setting time of cement.
5. Iron Oxide: Provides color, strength, hardness to the cement.
6. Alkalies: If present in excess, causes cement efflorescent.

Manufacture of portland cement involves the following steps:

1) Mixing of raw materials:

(a). Dry process: The raw materials and clay are crushed into small pieces, then these are ground to fine powder. Each separate powdered ingredients are stored in a separate hopper. Then, the powdered materials are mixed to get dry raw mix, which is stored in storage bins and kept ready to be fed in a rotary kiln.

b). Wet process: The calcareous raw materials are crushed, powdered and stored in a big storage tank. The argillaceous material is thoroughly mixed with water in wash mills and made into slurry. The powdered lime and clay slurry are mixed in requisite proportions and then fed to a rotary kiln.

2). Burning:

It is done in rotary kiln, which is a steel tube lined inside with refractory bricks. The kiln is laid in slightly inclined position towards the lower end. The upper part of kiln temperature is 400 °C but the temperature gradually increases upto 1750 °C at the bottom. The raw slurry from the wet process and the dry process is passed into the rotary kiln through the lower end. The following reactions takes place in the rotary kiln.

a). Drying zone:

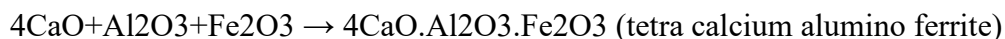
The upper part of the kiln where the temperature is only 400 °C and the slurry gets dried.

b). Calcination zone:

It is the central part of kiln where the temperature is around 1000 °C. Lime stone or dry mix or slurry undergoes decomposition to form quick lime and $\text{CO}_2 + \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$

c). Clinkering zone:

In the lower part of the rotary kiln, the temperature is between 1500- 1700 °C. Here the lime and clay combine to form calcium silicates and aluminates.



The aluminates and silicates of calcium fuse together to form hard greyish stones called clinkers. The cooled clinkers are collected in trolleys.

3). Grinding:

The cooled clinkers are ground to fine powder in ball mills together with 2-3% gypsum. The mixture of clinkers and gypsum powder is called cement. Here, gypsum acts as a retarding agent for easily setting cement.

Constituents of cement

The constitution and their composition of cements are

Table 5.3: Main constitution of cement with its percentage

Name	Formula	Percentage (in %)
Lime	CaO	61.5
Silica	SiO ₂	22.5
Alumina	Al ₂ O ₃	7.5
Magnesia	MgO	2.5
Iron oxide	Fe ₂ O ₃	2.0
Sulphur trioxide	SO ₃	1.0
Sodium oxide	Na ₂ O	1.5
Potassium oxide	K ₂ O	1.5

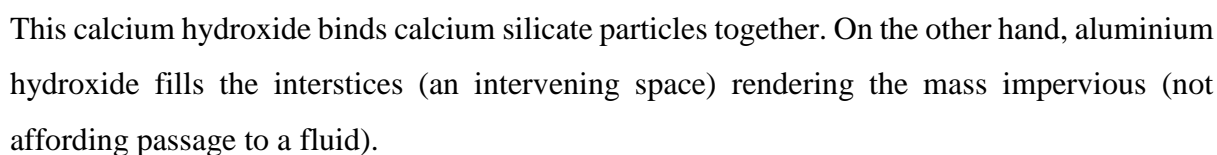
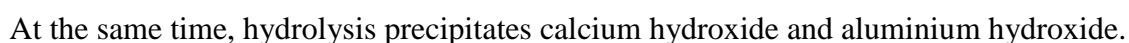
Setting and hardening of cement

When mixed with water, cement sets to a hard mass. It first forms a plastic mass which hardens after some time due to 3-dimensional cross-links between the --Si-O-Si-- and --Si-O-Al-- chains. The first setting occurs within 24 hours whereas the subsequent hardening requires a fortnight, when it is covered by a layer of water. This transition from plastic to solid state is called setting.

Reactions Involved in Setting of Cement:

$$3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 6\text{H}_2\text{O} \longrightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$$

Tricalcium aluminate Hydrated colloidal gel of
tricalcium aluminate



Properties of Ordinary Portland Cement (OPC)

Table 5.4: Physical and chemical requirements of OPC for different grades of cement

S.no	Property		33 grade OPC (IS 269 – 1989)	43 grade OPC (IS 8112 – 1989)	53 grade OPC (IS 12269 – 1987)
1	Fineness(m ² /kg) minutes		225	225	225
2	Soundness by	Le Chatelier (mm) Max.	10	10	10
		Autoclave (%) Max.	0.8	0.8	0.8
3	Setting Time	Initial(minutes) Min.	30	30	30
		Final (minutes) Max.	600	600	600
4	Compressive Strength	1 day (MPa) Min.	N S	N S	N S
		3 days (MPa) Min.	16	23	27
		7 days (MPa) Min.	22	33	37
		28 days (MPa) Min.	33	43	53

Mortar

In the cement industry, mortar is a workable paste created by mixing a binding agent (typically Portland cement) with water and a fine aggregate, most commonly sand. Unlike concrete, which contains large stones for structural mass, mortar acts as the "glue" of construction, primarily used to bond masonry units like bricks, stones, and blocks together.

Key Characteristics & Composition

Ingredients: A standard mix consists of cement, fine sand, and water. Lime is frequently added to improve flexibility, water retention, and workability.

Hydration: Once water is added, a chemical reaction called hydration begins, causing the paste to harden and bind the surfaces it touches.

Properties: Good mortar must be adhesive (stick to units), workable (easy to spread), and durable (resistant to environmental stress).

Common Types of Mortar

Mortars are classified by their strength and intended application:

Type M (High Strength): ~2,500 psi. Used for heavy loads, foundations, and retaining walls.

Type S (Medium-High Strength): ~1,800 psi. The standard for general exterior and below-grade masonry.

Type N (Medium Strength): ~750 psi. The most common "general purpose" mortar for above-grade exterior and interior walls.

Type O (Low Strength): ~350 psi. Primarily used for non-load-bearing interior work or historical restoration.

Concrete

Concrete is a mixture of cement, water, and aggregates like sand and gravel. Once combined, it hardens over time, forming a solid substance that can be formed into almost any shape. Its affordability and strength make it the go-to choice for various construction needs.

When it comes to your home, the foundation is everything, and it all starts with the right cement. The cement you choose determines the quality of the concrete and, ultimately, the strength of your home. Since you build your home only once, choosing the best cement ensures your concrete mix stands the test of time.

Concrete advantageous in construction

Durability and Strength: It withstands heavy loads and harsh weather conditions, making it suitable for foundations, bridges, and high-rise buildings.

Fire Resistance: Reduces the risk of structural damage in case of fire.

Low Maintenance: Requires minimal upkeep, lowering long-term costs.

Versatility: Can be molded into various shapes, meeting different construction needs.

Types of Concrete

➤ Reinforced Concrete

This type of concrete is reinforced with steel bars or mesh to increase its tensile strength and durability. It is commonly used in the construction of high-rise buildings, bridges, and other structures that require extra strength and stability.

➤ Lightweight Concrete

As the name suggests, this type of concrete is lighter in weight than normal concrete, making it ideal for construction projects where weight is a concern. It is commonly used in the construction of precast concrete elements, such as wall panels, roof slabs, and paving blocks.

➤ High-Strength Concrete

This type of concrete has a compressive strength of over 40 MPa and is used in the construction of structures that require extra strength, such as tall buildings, bridges, and dams.

➤ High-Performance Concrete

This is a specialized type of concrete that has enhanced properties, such as high durability, increased strength, and resistance to extreme temperatures and environmental conditions. It is commonly used in the construction of nuclear power plants, offshore structures, and other high-tech projects.

➤ Precast Concrete

This type of concrete is manufactured off-site and then transported to the construction site. It is commonly used in the construction of precast concrete elements, such as wall panels, columns, beams, and staircases. Precast concrete offers several advantages over traditional cast-in-place concrete, including reduced construction time and increased quality control.

Curing and decay of concrete

Curing

Curing may be defined as the operation of maintaining humidity and temperature of freshly placed concrete during some definite period following placing, casting (or) finishing to assure the satisfactory hydration of cement and proper hardening of concrete. If the curing is neglected in early hydration, the quality of concrete will experience some irreparable loss.

Methods of Curing:

- Water Curing – Preventing the moisture loss from the concrete surface by continuously wetting the exposed surface of concrete.
- Membrane Curing – minimizing moisture loss from the concrete surface by covering it with an impermeable membrane.
- Steam Curing – Keeping the surface moist and raising the temperature of concrete to accelerate the rate of strength gain.

Decay of concrete

Decay of concrete, often called deterioration, is the progressive loss of a structure's performance and integrity over time due to chemical, physical, or biological factors.

Key Mechanisms of Decay

Chemical Attack:

Carbonation: Carbon dioxide from the air reacts with calcium hydroxide in the concrete, lowering its pH from 13 down to 9. This destroys the "passivating layer" that protects steel reinforcements from rust.

Sulfate Attack: Sulfates from soil or groundwater react with cement components to form expansive crystals like ettringite and gypsum. These cause the concrete to swell, crack, and eventually crumble.

Chloride Ingress: Exposure to seawater or de-icing salts leads to pitting corrosion of the internal steel rebar. As the steel rusts, it expands up to 6–7 times its original volume, causing the surrounding concrete to crack and spall (flake off).

Alkali-Silica Reaction (ASR): Sometimes called "concrete cancer," this occurs when alkalis in the cement react with certain silica-rich aggregates to form a swelling gel that cracks the structure from within.

Physical Decay:

Freeze-Thaw Cycles: Water trapped in concrete pores expands when it freezes, creating internal pressure. Repeated cycles lead to surface scaling and structural weakening.

Abrasion & Erosion: High-velocity water, wind-borne particles, or heavy traffic physically wear down the concrete surface over time.

Thermal Stress: Extreme heat (like fires) causes large temperature gradients, leading to spalling as the surface layers expand faster than the core.

RCC – Reinforces Cement Concrete

Reinforced Cement Concrete (RCC) is a composite material made by embedding steel bars, wires, or mesh (reinforcement) into concrete to enhance its strength. While concrete is strong in compression, it is weak in tension. The addition of reinforcement makes the material strong in tension and compression, making it ideal for various construction projects. RCC is commonly used in foundations, beams, columns, and slabs in residential and commercial buildings.

Uses

- ✓ Beams, columns and slabs in residential, commercial and industrial building.
- ✓ Highways, flyover and railway bridges.
- ✓ Power plants
- ✓ Chimneys and towers
- ✓ Tunnels
- ✓ Electric poles
- ✓ Bunkers and silos

Advantages of RCC

Strength: RCC has very good strength in tension and compression.

Durability: RCC structures are durable and can last even upto 100 years

Economy: RCC is cheap in long run as its maintenance cost is very low.

Fire resistance: RCC structures are more fire resistant than any other construction material.

Aesthetics: RCC structures give good aesthetic appearance.

Disadvantages of RCC

RCC structures are heavier than other structural materials.

The initial cost of RCC work is high.

Skilled labour is required for construction of RCC structures.

RCC structures take time to attain its full strength.

Intellectual property

Intellectual property is an intangible creation of the human mind, usually expressed or translated into a tangible form that is assigned certain rights of property. Examples of intellectual property include an author's copyright on a book or article, a distinctive logo design representing a soft drink company and its products, unique design elements of a web site, or a patent on the process to manufacture chewing gum.

Intellectual Property Rights (IPR)

IPR is a general term covering patents, copyright, trademark, industrial designs, geographical indications, layout design of integrated circuits, undisclosed information (trade secrets) and new plant varieties.

Patent

A patent is an exclusive ownership right granted by a country to the owner of an invention, provided the invention satisfies certain conditions stipulated in the law. A Letters Patent (a kind of certificate) is issued to the owner of the invention by the patent office of the country conferring this right. Exclusivity of right implies that no one else can make, use, manufacture or market the invention without the consent of the patent holder. This right is available to the owner of the invention only for a limited period of time. However, the use or exploitation of a patent may be affected by other laws of the country which has awarded the patent. These laws may relate to health, safety, food, security etc.

A patent in the law is a property right and hence, it can be gifted, inherited, assigned, sold or licensed. As the right is conferred by the State, it can be revoked by the State under very special circumstances for the benefit of public even if the patent has been sold or licensed or manufactured or marketed in the meantime. The patent right is territorial in nature meaning thereby, that a patent granted in India can only be enforced in India. In case the owner of the invention wishes to obtain patents in other countries, the owner will have to file separate patent applications in countries of his interest, along with necessary fees.

Factors for patentability

An invention is patentable, then the following criteria be—

- i. It should be novel.
- ii. It should have inventive step or it must be non-obvious
- iii. It should be capable of Industrial application.
- iv. It should not attract the provisions of section 3 and 4 of the Patents Act 1970.

Novelty - The patentable invention must create new knowledge or product or process which is called novelty. It should not be in any form which is already available in the public domain. It must be different from what is already known.

Non-obviousness - Non-obviousness patent means 'the invention must have some creative input which is not expected by the person skilled in the field'.

Five step test is usually used to grant non-obvious patent in India

- i) Decide obviousness
- ii) Compare with prior art or skill
- iii) Assess general knowledge
- iv) Define inventive concept
- v) Identify PSA (person skilled in the art or problem solution approach)

Industrial applications - The patent which is granted is used in industries in the form of product, process and even software-based solutions. Examples: The patents which are used in

- i) pharmaceuticals for new drug molecules.
- ii) electronics with innovative circuit designs.
- iii) agriculture for a modified crop variety with increased pest resistance or higher yield.
- iv) software for an innovative program for data analysis.
- v) Chemical industries to produce new chemical compounds with unique properties.

Patent office in India

- i. The Patent Offices (including the Design Wing) at Chennai, Delhi, Kolkata & Mumbai.
- ii. The Patent Information System (PIS) and Rajiv Gandhi National Institute of Intellectual Property Management (RGNIIPM) at Nagpur.
- iii. The Trade marks Registry at Ahmadabad, Chennai, Delhi, Kolkata & Mumbai.
- iv. The Geographical Indications Registry (GIR) at Chennai.
- v. The Copyright Office at Delhi.
- vi. The Semiconductor Integrated Circuits Layout-Design Registry at Delhi.

Table 5.5: Patent offices in Territorial Jurisdiction

Office	Territorial Jurisdiction
Patent Office Branch, Chennai	The States of Telangana, Andhra Pradesh, Karnataka, Kerala, Tamil Nadu and the Union Territories of Pondicherry and Lakshadweep
Patent Office Branch, Mumbai	The States of Maharashtra, Gujarat, Madhya Pradesh, Goa and Chhattisgarh and the Union Territories of Daman and Diu & Dadra and Nagar Haveli.
Patent Office Branch, New Delhi	The States of Haryana, Himachal Pradesh, Jammu and Kashmir, Punjab, Rajasthan, Uttar Pradesh, Uttarakhand, Delhi and the Union Territory of Chandigarh
Patent Office, Kolkata	The rest of India

Trademark

A trademark is a distinctive sign, which identifies certain goods or services as those produced or provided by a specific person or enterprise. A trademark may be one or a combination of words, letters and numerals. It may also consist of drawings, symbols, three-dimensional

colours and combination of colours. It is used by traders/companies/firms etc, to distinguish their goods and services from those of their competitors. A consumer associates some level of quality/price/prestige with the goods of a particular trademark. In other words the consumer uses the trademark for making a choice while buying a particular product. There are so many examples in our day to day life such as TATA, BATA, Liberty, Brooke Bond, Dabur, Baidyanath, Park Avenue, SAIL and so on. Trademarks do not protect the design or the ideas behind the goods or services from imitation or duplication, but prevent other traders/company/firm from deceiving customers into believing that goods or services actually produced by them were produced by the trademark holder.

Types of Trademark

Certification trade mark

Certification trade mark means a mark capable of distinguishing the goods or services in connection with which it is used in the course of trade which are certified by the proprietor of the mark in respect of origin, material, mode of manufacture of goods or performance of services, quality and accuracy.



Figure 5.1: Certificate mark of ISI and ISO

Logos

It is a legal protection that gives the owner's exclusive rights to use the product. It distinguishes from other competitors and prevents trade mark infringement.



Figure 5.2: Logos of Apple, Nestle, Coca-cola and Nike brands

Brand name

A brand name is a company's name or image used for marketing the products. It is easy to remember and recall.

Examples:

- a) 'Apple' - It is associated with consumer electronics
- b) Nike (athletic wear)
- c) Amazon (online retail)
- d) Samsung (electronics)
- e) Microsoft (software)

Signature

It is a registered trade mark that is the signature of a person or company.

Examples:

- a) Sachin Tendulkar's signature
- b) Kareena Kapoor's signature
- c) Paul Smith's signature (A British Fashion Designer signature)
- d) Philip Morris's signature (Philip morris International seller over 130 brands)

Symbols

It is a trademark symbol, used to indicate that a word, phrase, logo or other mark.

Examples:

- a) ® - Registered trade mark symbol for selling goods and services.
- b) TM-Unregistered trade mark symbol for selling goods and services.
- c) SM - It tells the public that you are seeking to protect the services of the sold goods.

Service mark

A service mark is the same as a trademark, but instead of a particular product, it identifies and differentiates the source of a service. A service mark is nothing but a mark that distinguishes the services of one proprietor/owner from that of another. Service marks do not represent goods, but the services offered by the company. They are used in a service business where actual goods under the mark are not traded. Companies providing services like computer hardware and software assembly, restaurant and hotel services, courier and transport, beauty and health care, advertising, publishing, etc. are now in a position to protect their names and marks from being misused by others. The rules governing for the service marks are fundamentally the same as any other trademarks.



Figure 5.3: Few Service mark logos of Master card, Qantas and Amazon.