

**III YEAR – V SEMESTER**  
**COURSE CODE: 7BCHE2A**

**ELECTIVE COURSE II (A) INDUSTRIAL CHEMISTRY**

**Unit I**

**1.1. Paints:** Paint – definition – classification of paints based on their applications – constituents – Requisites of a good paint

**1.2. Pigments:** Definition – composition, characteristics and uses of white lead, Zinc oxide, Lithopone and TiO<sub>2</sub> – Blue pigments – Ultra marine blue – characteristics – uses. Red pigments – red lead – characteristics and uses. Green pigments – chrome green, Guigwet's green and chromium oxide – characteristics and their uses.

**1.3. Varnishes:** Definition – constituents of varnish – characteristics of a good varnish – uses – Japans varnish, Enamel – definition – Types – Ingredients and uses.

**Unit II**

**2.1. Ceramics:** Definition, classification of ceramics, general properties of ceramics – permeable (porous) and impermeable (non porous wares) – Basic raw material – Manufacture – applications of colour to pottery.

**2.2. Glass:** Definition – physical and chemical properties of glass – raw materials – Manufacture – types of glasses.

**2.3. Cement:** Raw materials – Portland cement – composition – types of Portland cement – Manufacture – Uses of Cement – Cement Raw Materials in India – Growth of Cement Industry in India. Chemistry of setting of cements.

**Unit III**

**3.1. Soap:** Definition – General consideration in soap making – manufacture of soap – toilet and transparent soaps.

**3.2. Detergents:** Definition – classification of face active agents – anionic detergents – cationic detergents – shampoo – raw materials

**3.3. Refractories:-** Introduction, Classification – Properties – Manufacture – Fire clay bricks – manufacture – Uses

**Unit IV**

**4.1. Fertilizers:** Definition – manufacture of Ammonium sulphate, CAN. Manufacture of urea and estimation of urea. Manufacture of phosphoric acid. Manufacture of superphosphates and uses of phosphate as fertilizer. Mixed fertilizers (NPK) – Fertilizer industries in India.

**4.2. Sugar Industry:** Manufacture of sugar from molasses and beetroot – sugar industries in India. Fermentation: Manufacture of spirits and wines. Distillation: Manufacture of vinegar and ethyl alcohol.

**4.3. Match industries:** Manufacture – chemistry of lighting and pyrotechny

**Unit V**

**5.1. Adhesives:** definition – classification of adhesives – animal glue – preparation – uses – protein adhesives – starch adhesives – preparation – uses.

**5.2. Enamels:** Introduction – Raw Materials – Manufacture and Applications

**5.3. Explosives:** Definition – Classification – Characteristics of explosives – Nitro cellulose, T.N.T, Picric acid, Gun Powder, Cordite and Dynamite.

**Books for Reference:**

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## PAINTS. PIGMENTS & VARNISHES

### PAINTS :

#### Definition :

Paint is a mechanical dispersion of one or more pigments in medium (liquid, non-volatile, drying oil and thinner) when a metallic surface is painted. The thinner evaporates while the drying oil forms a dry pigmented film after oxidised itself.

#### Classification of paints :

Paints are classified into several types are given below :

##### i) Emulsion paints :

Emulsion paint is a dispersion of rubber-like resin in water. It contains film-forming vehicle, pigment and extender. The main constituent of emulsion paint is stabilizer, drier and antifoaming agent. Emulsion paint provide.

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- (i) easy to apply on surface of metal or wood
- (ii) quick drying
- (iii) more durable and
- (iv) more impermeable and to dust and dirt.

### 2) Luminescent paints :

It contains luminescent pigment which fluoresces under the influence of UV light. Such pigments absorb UV and emit radiation in the visible region of the spectrum.

Example : ZnS, sulphides or Zn, Cd, titania with a small amounts of colour modifiers like Cu, Ag, Mn and B - called activators.

### 3) Heat-resistant paints :

Heat-resistance paints are paints <sup>that</sup> withstand temperature, even upto red heat. composition : lamp-black - 8 kg, graphite - 3 kg, black oxide of Mn - 1 kg - Japan gold zinc - 1 lit. turpentine - 1.5 lit, boiled linseed oil - 1 lit.

Heat-resistant paint is suitable for space technology. It is developed by NASA.

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composition : (i) (c pigment) + water solution of an alkali metal silicates (vehicle), aluminium orthophosphate (wetting agent) and water (thinner)

uses : It is used as finishes of ovens, furnace, distills, air craft combustion chambers, diesel - engine exhaust pipes, smoke-stacks.

#### 4) Distempers :

Distempers are water paints.

ingredients : i) chalk powder (base) ii) glue (binder)  
iii) colouring pigments and iv) water (thinner)

uses : Distempers are used as finishing coat on:  
i) white - washed surface on interior walls  
ii) plastered surfaces of interior walls  
iii) External surfaces of brick - works,  
concrete etc. after adding a weather resisting  
compound , at the time of mixing.

#### 5) Water repellent paints :

water repellent paints are made by hydrolysis and condensation of organo ethoxy silanes and organo chloro silanes. It is more durable. It can last for more

than 5 years

### b) coal-tar paints:

It consists of melt of coal tar and spirit. It is applied on the surface at hot condition.

uses: It is used for protecting iron and steel surfaces and materials used under the ground.

### c) anti-fouling paints:

anti-fouling agents: mercuric oxide, oxide, pentachloro phenol, phenyl mercury naphthalate etc.

uses:

i) Anti-fouling paints are used in marine constructions.

ii) It retards the fouling or ship's pipes etc. marine worm, fungi etc.

### constituents of paint:

#### i) pigment:

Pigment are various inorganic and organic insoluble substance which of

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different colours depending upon the composition.  
It is used for surface coating.

Example :

1. zinc oxide, white lead, lithophane, titanium dioxide are white pigments.
2. red lead, ferric oxide, chrome red are red pigments.
3. chromium oxide is green pigments.
4. carbon black is black pigments.

Pigments provide :

- i) strength to paint
- ii) protection to the film by reflecting harmful ultraviolet light
- iii) resistance against abrasion / wear
- iv) impermeability to moisture
- v) aesthetic appeal to the paint film.

A good pigment should be :

- i) opaque
- ii) chemically inert
- iii) non-toxic so that there is no bad effect on the health of painter as well as inhabitant
- iv) cheap
- v) mixable with film forming constituent oils.

(b)

## 2) Extenders or fillers :

Extenders or fillers reduce the cost and increase the durability of the paint. Hence, it improves consistency, leveling and setting of paint. They serve to fill voids in the film and act as carriers for pigment colour.

e.g : barite ( $\text{BaSO}_4$ ), talc, asbestos, gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) etc.

## 3) Drying oil or film forming materials :

Drying oil is also called vehicle. It is a film forming constituent. They are glycerides of higher fatty acids (saturated or unsaturated). Drying oil may be vegetable oil. Drying oil absorbs oxygen and forms peroxides, hydroperoxides etc. and forms tough coherent, insoluble and highly cross-linked structure on the surface.

They provide toughness, durability, adhesion and water proofness to the film when paint is applied. In the form of a film the drying oil absorbs oxygen from

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o<sub>2</sub> and forms peroxides and hydroperoxides at double bonds. These peroxides isomerise polymerise and condense to form a tough elastic, insoluble, infusible polymer film.

#### 4) Driers :

The driers acts as an oxygen carrier catalyst and accelerate the drying of the film through oxidation and polymerization processes.

Example : formerly, PbO are used as drier modern dries are Co, Mn, Pb, Zn, resinates, linoleate and naphthalenates.

#### 5) Thinner :

Thinner is highly volatile liquid. It reduced viscosity of the paint and increases its elasticity. It increases the penetration power of drying oil. The common thinner is turpentine oil. Other thinners are benzene, mineral spirit, xylot, kerosene etc.

### b) plasticisers :

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Plasticisers are used to increase elasticity and to minimise cracking.

Example: dibutyl phosphate, triethyl phosphate, dibutyl tartrate etc.

### → Anti-skimming agent:

Anti-skimming agents prevent skinning and gelling of paint film.

example : polyhydroxy phenols.

### Requirements or characteristic of good paint:

A good paint has the following qualities.

- (i) It should be opaque and chemically inert.
- (ii) It should have high covering power
- (iii) It should form a tough, uniform and adherent film.
- (iv) The coating of paint should not crack after drying.
- (v) The ~~coat~~ should be non-toxic, stable and long life.

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(vii) It should neither be oxidized nor reduced in environment.

(viii) The colour due to paint should be shining and stable.

(ix) Various requirements of paints are controlled by pigment volume concentration (PVC) which is defined as.

$$\text{PVC} = (\text{volume of pigment in paint} / \text{total volume of the constituent}) \times 100$$

The PVC range of various paints are.

i) flat paints - 50 - 75%.

ii) Exterior House paint - 28-36%.

iii) metal primers - 25 - 40%.

iv) wood primers - 35 - 40%.

## PIGMENTS :

### Definition :

Pigments are various inorganic and organic insoluble substances which are different colours depending upon the composition. It is used for surface coating.

Example :

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1. zinc oxide, white lead, lithophane, titanium dioxide are white pigments.
2. Red lead, ferric oxide <sup>and</sup> chrome red <sup>are</sup> red pigments.
3. chromium oxide is green pigments.
4. carbon black is black pigments.

White pigments :

White lead :

white lead is basic lead carbonate.  
It is white pigment. The formula of white lead is  $\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ .

Percentage composition :

$$\text{PbCO}_3 = 60.2 - 68.9\% \text{ and } \text{Pb(OH)}_2 = 31.1\%$$

Characteristics :

- i) covering powder : 38 sq. m/10 kg
- ii) refractive index : 1.94 - 2.09
- iii) oil absorption: 8 - 15 gm oil / 100 g
- iv) tinting strength : 120 - 220 pigment
- v) specific gravity : 6 - 7 - 6.8
- vi) white lead is soluble in alkali.

### uses :

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- i) white lead is used for the manufacture of paints.
- ii) it has high covering power due to its high refractive index.

### zinc oxide :

zinc oxide is white pigment. The chemical formula of zinc oxide is  $\text{ZnO}$ .

### characteristics :

- i) It is pure white
- ii) covering power :  $42 \text{ sq. m / 10 kg}$
- iii) refractive index :  $2 - 2.05$
- iv) oil absorption :  $13 \text{ gm oil / 100 g pigment}$
- v) tinting strength :  $210$
- vi) specific gravity : much less than white lead
- vii) its colour is unaffected by gases in the atmosphere.
- viii) it is soluble in acids.
- ix) it is insoluble in oil and solvents.
- x) it is opaque to UV-light
- xi) its film is hard and bright
- xii) it reacts with the linseed oil harden the film

### uses

- i) It is used as white pigment
- ii) The covering power is greater than white lead
- iii) It is opaque to UV-light hence it protects the vehicles and prevents the chalking.

### Lithopone :

Lithopone is white pigment. It is a mixture of barium sulphate and zinc sulphide.

### percentage of composition:

The chemical composition of Lithopone is

$\text{BaSO}_4$  - 71.5-72.5 %

$\text{ZnS}$  - 27.5-28

$\text{ZnO}$  - below 1%

### characteristics :

i) covering power - 95 sq.m/10kg

ii) oil absorption - 12-18 gms oil / 100g pigment

iii) tinting strength - 280

iv) It turns temporarily grey on exposure to sun light.

### uses :

i) It is a valuable white pigment

ii) It is used for cold water paints, traffic paints, floor covering and oil cloth industry.

## titanium dioxide :

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titanium dioxide is the whitest of white pigments. It replaces the other white pigment such as white lead, lithopone etc. due to its superior properties. Its chemical formula is  $TiO_2$ .

### characteristics :

#### 1) Anatase variety :

- i) covering power :  $230 \text{ sq.m}/10\text{kg}$
- ii) refractive index :  $2.55$
- iii) oil absorption :  $20-27 \text{ gm oil}/100 \text{ g pigment}$
- iv) tinting strength.

#### 2) Rutile variety :

- i) covering power :  $363 \text{ sq.m}/10\text{kg}$
- ii) refractive index :  $2.07$
- iii) oil absorption :  $20-27 \text{ gm oil}/100 \text{ g pigment}$
- iv) tinting strength :  $1500 - 1650$ .

uses : it finds applications in paints, paper, textiles etc., industries.

## Blue pigments - ultramarine blue :

ultramarine is a dark blue pigment. It is a complex sulphate of aluminium.

and sodium associated with about 12% sulphur.  
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composition:

The chemical formula of ultramarine blue is  $\text{Na}_8\cdot\text{Al}_2\text{Si}_5\text{O}_10$ . The composition of ultramarine is not stoichiometric - because the degree of exchange that takes place depends upon the various factors, such as concentration of solution time of heating etc.

#### Characteristics:

- i) ultramarine blue is used as bluing in laundering to neutralize the yellowish tone in cotton and linen fabrics.
- ii) it is used for whitening paper and other products.

#### Red - pigment - Red lead.

The chemical formula of red lead is  $\text{Pb}_3\text{O}_4$ .

#### Characteristics :

- i) Red lead has a brilliant red colour.
- ii) it is stable to light.
- iii) it has corrosion inhibition properties.

#### uses :

- i) Red lead is used as a primary coat for structural steel.

It is used for imparting red colour to the paint for making bangles.

### Green pigments

#### chrome green or chromium oxide green:

chrome green contains chromium tetroxide ( $\text{Cr}_2\text{O}_3$ )

#### characteristics:

- i) chrome green is unaffected by acids and alkalies.
- ii) it is stable in light and heat fast.
- iii) it has higher oil absorption.
- iv) it is more expensive.

#### uses:

- i) it is used as green pigments.
- ii) it is used in certain glazes, alkali proof, printing inks, cement, colours, <sup>rubber</sup> compounds, bridge paints etc.

#### Griegel's green:

griegel's green is hydrated chromium oxide. The chemical formula is  $[\text{Cr}_2\text{O}(\text{OH})_4]$ .

#### characteristics:

- i) griegel's green is much more brilliant green than the chromium oxide green.

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iii) it is used in ceramic glazes, alkali proof, printing inks, varnishes, colours, rubber compounds, bridge paint etc.

## VARNISHES

### DEFINITION :

A varnish is a homogeneous colloidal dispersion - solution of natural or synthetic resin in oil or thinner or both when it is applied on surface. It gives a transparent crack free film. The film dries by evaporation, oxidation and polymerization of some portion of its constituents.

### constituents of varnishes :

#### 1) RESINS :

Resins may be natural or synthetic. natural resins are shellac, copal, kauri, manila, etc. synthetic resins are phenolic aldehydes, alkyd resins, mannitol esters, melamine, urea formaldehyde, chlorinated rubber, vinyl resins etc.

resin in varnish provides an element of hardening, resistance to weathering, durability, resistance to chemical action and

water - proofness.

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### 2) Drying oils :

Principle oils used are linseed oil which undergo dehydrated castor oil, castor oil, fish oil, cottonseed oil, coconut oil, etc. They dry by oxidation or polymerization.

### 3) Solvents or thinners :

Thinner is highly volatile liquid, it reduces viscosity of the varnishes and increases its elasticity. It increases the penetration power of drying oil.

Example : turpentine oil, kerosene, naphthalene, xylene, toluene, diethanol etc.

### 4) Driers :

Driers are increased the rate of drying or hardening of varnish film. Example : cobalt, Co, Mn, Pb, Zn, resinate, linoleate and naphthalenates.

### 5) Anti - skinning agents :

Anti - skinning agents prevent skinning and getting of varnish film.

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Example : guaiacol, terebinth amylphenol.

Characteristic of good varnishes :

A good varnish should possess the following characteristics.

- i) It should be soft and tender
- ii) It should adapt itself to the contraction or expansion of coated material like wood, due to the temperature variation.
- iii) It dries quickly.
- iv) It produces a protective film.
- v) It produces glossy and shining film on drying.
- vi) It should yield aesthetical appealing film.
- vii) It should yield elastic film.
- viii) The colour of the film is ~~not fades~~ not fade or change on exposure to atmospheric weather.
- ix) It should not shrink or crack after drying.

Uses :

- i) Varnishes are used for protection of articles against corrosion.

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- (i) It is used as a brightening coat to painted surfaces.
  - (ii) It is used for improving the appearance and intensifying of the ornamental grains of wood surfaces.

### Japan varnish :

Japanes are special type varnishes. They are added to the paint which gives a good colour and lustre.

### types of Japanes :

Japanes are two types. They are painter's Japan and decorative Japan (opaque varnish).

### 1) painter's Japan :

The painter's Japan are made up of a resin dissolved in a drying oil containing drier and thinner. They give more lustre of the paint.

### 2) Decorative Japan :

Linseed oil is heated with litharge at  $280^{\circ}\text{C}$  for about 5-6 h. The solid mass lead oil is obtained. The lead oil is

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mixed with asphaltum and thinner like kerosene to obtain decorative Japan uses :

Japan varnishes are used for such products as bicycles, bed stands and electrical devices.

### ENAMELS :

#### Definition :

Enamel is an intimate dispersion of pigments in varnish. They dry into a very lustrous and glossy finish. Enamels have got very good flow. The object of preparing enamels is to get good gloss.

#### Types of enamels :

Enamels are classified into two types. They are oleoresinous enamel and resin enamel.

#### 1) Oleoresinous enamel :

The following ingredients are used for making of oleoresinous enamel

- i) Titanium-calcium pigments (30%  $TiO_2$  and 70% of  $CaSO_4$ )
- ii) Fine particle size  $CaCO_3$

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- iii) Hardt bodiod linseed oil.
- iv) Ester gum solution
- v) cobalt naphthalenate (6% (o))
- vi) Lead naphthalenate (24% pb)
- vii) mineral spirits.

Pigment volume concentration of glaze known enamel is 35.5% The non-volatile vehicle portion contains 52% oil and 48% of resin.

## 2) Resin enamel:

The following ingredients are used for making of white resin enamel.

- i) Titanium dioxide
- ii) fine particle size zinc oxide
- iii) long - oil alkyd.
- iv) Mineral spirit
- v) cobalt naphthalenate (6% (o))
- vi) Lead naphthalenate (24% pb)
- vii) calcium naphthalenate (4% (o))

Pigment volume concentration of white resin enamel is 27%.

USES :

- i) Enamels are used in refrigerators, dairy and food processing equipments.
- ii) It is used in hospital furniture, motor cars, sanitary wares etc

CERAMICS, GLASS AND CEMENTCeramics

Definition:- Ceramics are inorganic, non-metallic materials. It is possessed at high temperature. They include silicates, metallic oxides and their combination.

Classification of ceramics:-

Ceramics are classified into three types, according to their common characteristic features. These are clay products, refractories and glasses.

(1) clay Products:- Clay is hydrated aluminium silicates. The chemical formula is  $\text{Al}_2\text{Si}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ . Clay products are divided into three types.

(i) The Structural clay Products:- It contains iron oxides. They are used for bricks, tiles and similar products.

(ii) The White wares:- It is pale substances such as Porcelain and china.

(iii) Chemical stone wares:- It has been specially treated to be hard, resilient and non-porous.

(2) Refractories:- Refractories are inorganic materials that can withstand high temperature without softening or undergoing any deformation in shape. Examples:- Silica,

alumina, fire-clay refractories, zirconia  
bricks etc.

Mores:- 1. Refractories are used for the  
construction of lining of the furnaces, kilns  
crucibles etc.

(2). They are employed for the manufacture  
of cements, glass, ceramics, paper, metals etc.

(3) Glass:-

Glass is amorphous, hard, brittle,  
transparent, super-cooled liquid of infinite  
viscosity. It is obtained by fusing a mixture  
of a number of metallic silicates. It possesses  
no sharp melting point, definite formula or  
crystalline structure. It may be represented  
as  $xR_2O \cdot yMO \cdot 6SiO_2$ . Where x and y are  
number of moles, R is an alkali metal and  
M is a divalent metal. The composition of  
ordinary glass is  $Na_2O \cdot CaO \cdot 6SiO_2$ .

Properties of ceramics:-

(1) Permeable or porous wares:- Permeable

ceramics materials absorb water. It shows a  
rough fracture and sticks to the tongue  
when tested in this fashion. Example:-  
Heavy clay ware, refractory ware, terracotta  
and earthen.

(2) Impermeable or non-porous wares:-

Impermeable ceramics materials  
absorb very little or none water. Example:-  
Stone ware, vitreous china and porcelain.

## Manufacture of ceramics :-

Basic raw materials of ceramics:- The raw materials for making ceramics can be divided into three basic groups.

- (i) Plastic materials - clay
- (ii) Non plastic or leading and Mixtures - silica (quartz, sand) crushed chamotte
- (iii) fluxes or Mineralizes - Feldspar ( $K_2NaO$ ).  
 $Al_2O_3 \cdot 6SiO_2$ ,  $CaCO_3$ ,  $MgCO_3$ .

(1) Preparation of Slip:- Clay, feldspar, sand, etc., are mixed with water and stirred in a revolving blunger. A cream like paste is formed. It is known as Slip. The slip is filtered through vibrating screen and removes the coarse materials.

(2) Filtering & Aging:- The slip is passed through filter paper. Water is removed and moist cake is obtained. The moist cake contains 10-30%. The moist cake is stored in damp of water. The moist cake is stored in damp cellars for a few weeks. This is called aging of the slip. This process increases the elasticity of the clay.

(3) Shaping of the articles:- The shaping of the articles is done by Potter's wheel. When cast required,  $Na_2CO_3$  or  $K_2CO_3$  or water glass is added to the clay.

(4) Drying the articles:- The articles are dried in air or warm air circulated chambers.

(5) Firing:- During the process of firing the

Following changes occur:

- (i) At  $150-600^{\circ}\text{C}$ , water is completely removed
- (ii) At  $800-900^{\circ}\text{C}$ , lime stone is decomposed
- (iii) At  $350-900^{\circ}\text{C}$ , ferruginous materials and organic matters are oxidized.

(iv) At  $1200-1300^{\circ}\text{C}$ , metallic oxides combine with silica to form metallic silicates. After the firing, the article is porous like biscuit. It is called biscuit.

(b) Glazing of biscuit:- Dipping, pouring, spraying, dusting, volatilization, etc., are the methods of applying the glazes on the articles. The biscuit is again fired in a furnace at a temperature  $700-900^{\circ}\text{C}$ . During firing, the article appears as smooth and shining.  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , lead oxide, zinc oxide etc., are the examples of the glazes. The glazes at least one alkaline earth metal.

(c) colouring of the articles:- The colouring agent is mixed in glaze components. Example: Cobalt oxide - blue, copper oxide, chromium - green or red, iron oxide - yellow, orange or red, gold chloride - pink  $\text{MnO}_2$  - violet,  $\text{TiO}_2$  - faint yellow, etc.

Applications of colors to Pottery:-

Colour to the pottery are applied by the following methods.

- (1) Painting (a) hand-painting and (b) lining banding
- (2) spraying (3) stenciling.

- (4) Stamping (5) printing lithography (6) silk screen  
painting (7) Ground laying (8) Sgraffito  
decoration (9) Gilding (10) Relief decoration.

(1) painting:- (a) Hand painting: This is old method of colouring of pottery. The colour is mixed with oil and turpentine. This is applied to the ware by the use of brush.

(b) Line banding:- Banding Machines contain three or more adjustable brushes. Each brush is connected with separate colour container. In this manner three or more bands of different colours can be made at the same time.

(c) Spraying:- Large coloured areas are produced by using spraying. The combining method of spraying and stencils are used for producing the white designs on coloured background.

(d) Stenciling:- Positive or negative Paper Pattern is produced on the surface of the articles. It is dipped into a coloured glaze or sprayed over with colour. The paper is removed subsequently.

(e) Stamping:- The rubber stamps are charged with colours from a pad covered with a layer of sticky pigment. The pattern is transferred to the ware by pressing the rubber stamp against surface of the ware.

(f) Printing:- A sticky mixture of the colouring material and linseed oil is spread over copper plates with the help of spatula. The plate is covered with a sheet of thin paper. It is placed

On a steam heating printing table. As a result the design is transferred to the paper. The paper pattern is rubbed on the pottery by rollers. The article is dipped in water and the paper is detached.

(b) Lithograph printing:- Lithograph printing is another method. It is an art of drawing and printing from stone. It is used to incorporate the designs on large coloured areas and several different colours.

(c) Silk screen printing:- Silk screen consists in rubbing or squeezing colour through a pattern. This method is useful for printing patterns on both round and flat surfaces.

(B) Ground laying:- In this process the area first covered with linseed oil and tempera. The powder ceramic colour is dusted on the sticky surface and excess dust is blown off.

(a) Sgraffito decoration:- The fired article is covered with a thin layer of slip of a different colour. The covering layer is dried and scrapped off. The articles is then fired and glazed.

(b) Gilding:- The precious metallic powder such as gold, platinum, silver etc., are applied on ware as an overglaze decoration.

(c) Relief carving:- The ornament is scratched from the surface. The scratched relieves are applied on the ceramic ware.

Glass:- Definition:- Glass is amorphous, hard, brittle, transparent, super-cooled liquid of infinite viscosity. It is obtained by fusing a mixture of a number of metallic silicates. It possesses no sharp melting point, definite formula or crystalline structure. It may be represented as  $xR_2O \cdot yMo \cdot bSiO_2$  where  $x$  and  $y$  are number of moles,  $R$  is an alkali metal and  $M$  is a divalent metal. The composition of ordinary glass is  $Na_2O \cdot CaO \cdot 6SiO_2$ .

Physical Properties of glass:-

- (i) They are transparent amorphous solids.
- (ii) Glass is completely Vitrified Product.
- (iii) They are hard and rigid.
- (iv) They have no definite melting point.
- (v) They have high viscosity, greater than  $10^{13}$  Poise
- (vi) They are insulator of heat & electricity
- (vii) can incorporate colouring material preserving transparency.

Chemical Properties:-

1. Glass is not affected by air & Oxidizing agent.
2. Ordinary glass is resistant to acids except hydrofluoric acid.



3. Ordinary glass is affected by alkalies.
4. Ordinary glass is alkaline in reaction. The water slowly reacts on glass, to form NaOH. This reaction is enhanced in the presence of acids.

5. If acids kept in glass bottles for long time, acidic acid is deposited on the glass of bottles. The glass is known as neutral glass like Pyrex. Glass which contains small amount of alkali silicate.

6. Glass is fused with excess of fusion mixture. It decomposes into alkali chlorides and carbonates of other metals. The resulting mass is cooled and treated with dilute HCl to form silicic acid and chlorides of metals.

Manufacture of glass:-

Raw materials:- (1) Sodium is Soda,  $\text{Na}_2\text{CO}_3$  - soft glass.

(2) Potassium is potash,  $\text{K}_2\text{CO}_3$  - Hard glass.

(3) Calcium is limestone, chalk and lime.

(4) Lead is litharge and red lead - float glass.

(5) Silica is quartz, white sand and ignited flint.

(6) Zinc is zinc oxide - Heat & shock-proof glass.

(7) Borate is borax & boric acid - Heat & shock-proof glass.

(8) canlets or pieces of broken glass to increase the fusibility.

(9) colours:-

(a) Yellow - ferroic salt.

(b) Green - ferrous & chromium salts

(c) Blue - cobalt salts

(d) Purple - manganese salts

(e) Red - Nickel or  $\text{Cu}_2\text{O}$

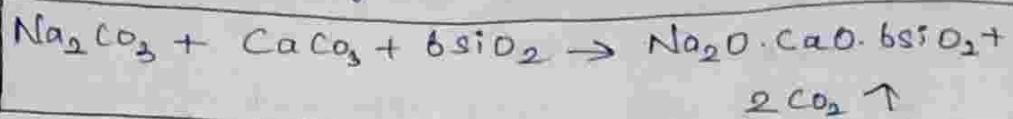
(f) Lemon yellow - CdS

(g) fluorescent greenish yellow - uranio oxic

(h) opaque milky white - cryolite or calcium phosphate.

Manufacturing steps:- (1) Fusion of raw materials:-

Fine Powder of  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$  and sand are mixed together in proper proportions, is called batch. This is mixed with pieces of scrap glass, which is known as cullets. These mixture are fused either in the pots of the pot furnace or in the tank of the tank furnace. The furnace is heated by producer gas, on the regenerative principle of heat. The following reaction takes place:



In beginning, considerable frothing is produced on account of the formation of  $\text{CO}_2$ . On continued heating, the whole of the  $\text{CO}_2$  escapes out. A clear, viscous, fused mass is obtained. To get coloured glass, colouring material is added. The mass is heated till it becomes homogenous.

(2) Shaping:- The fused mass is allowed to cool and then blown into moulds. The desired shape of the article is formed. If the sheet glass is required, it is between the rollers.

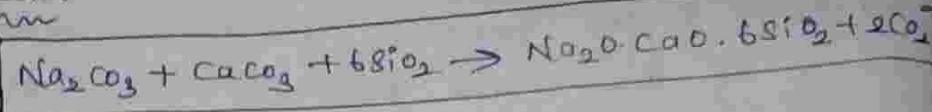
(3) Annealing:- The shaped glass articles are cooled slowly. This process is known as annealing.

During this process, the molecules of glass arrange themselves without strain. If the articles are cooled quickly, they become brittle on account of high strain.

(4) Finishing:- After annealing, the articles require some finishing touch such as cutting, grinding, polishing, etc. The finished products are sent to the market.

Types of glass:- (1) Soda glass or soft glass or ordinary glass: This is also called as window glass. It is a mixture of Potassium and Sodium Silicates. The chemical formula is  $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$

Preparation:-



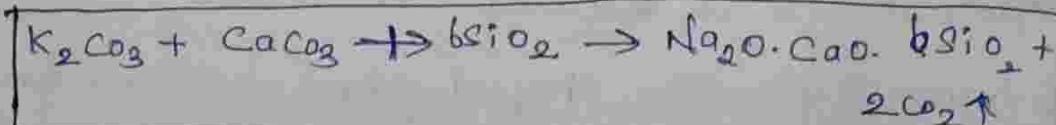
Properties:- (1) It softens at lower temperature and can be shaped into different shapes. Hence, it is called soft glass.

(2) It is very slowly attacked by chemical reagent and water.

Uses:- It is used in making glass tubes, window panes, bottles, dishes, etc.,

(2) Potash glass or hard glass:- This is also called as Bohemian glass. It is a mixture of Potassium and Calcium Silicates. The chemical formula is  $\text{K}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$ .

Preparation:-

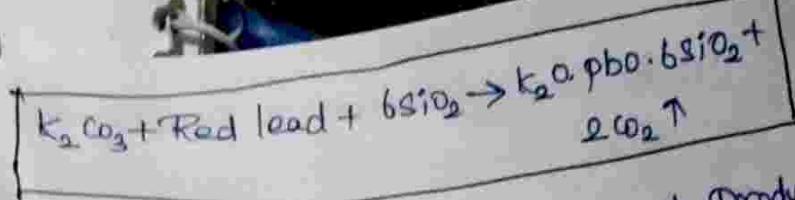


Properties:- It is resistant to the action of water and acids.

Uses:- It is used in making combustion tubes and chemical apparatus which can withstand high temperature.

(3) Potash-lead glass or flint glass:- It is a mixture of Potassium and lead Silicates. The chemical formula is  $\text{K}_2\text{O} \cdot \text{PbO} \cdot 6\text{SiO}_2$ .

Preparation:-



Properties:- (i) It is lustrous and transparent product.  
(ii) It has high refractive index. Hence, it is soft and scratches easily.

Uses:- It is used in making prisms, lenses, optical instruments, electric bulbs, etc.

(4) Jena glass:- (i) Jena glass is a mixture of barium and zinc borosilicates.

(ii) It contains  $\text{BaO} \cdot \text{ZnO} \cdot \text{Al}_2\text{O}_3$  and  $\text{B}_2\text{O}_3$ .

(iii) It has low coefficient of expansion.

(iv) It is resistant to heat, shock, acid & alkali.

(5) Pyrex glass:- (i) Pyrex glass is a mixture of boro and aluminosilicates of Zn and Ba.

(ii) The composition is 80-1. of  $\text{SiO}_2$ , 4-1. of  $\text{Na}_2\text{O}$ , 0.5-1. of  $\text{CaO}$ , 0.5-1. of  $\text{K}_2\text{O}$ , 12-1. of  $\text{B}_2\text{O}_3$  & 3-1. of  $\text{Al}_2\text{O}_3$ .

(iii) It can withstand sudden changes of temperature.

(iv) It is used in making laboratory glass wares such as flasks, beakers, etc.

(6) Crooke's glass:- (i) Crooke's glass contains oxides of Pb, Ba, Zn, Cd or Mg.

(ii) Cerium oxide is also added. This oxide cuts ultraviolet rays.

(iii) Thus, this glass used in making special type of lenses.

(7) Quartz glass or silica glass:- (i) Quartz glass is prepared by melting of silica in the electric furnace.

(ii) It has low co-efficient of expansion.

(iii) It does not break.

- (v) It can withstand a temperature of over  $1000^{\circ}\text{C}$ .
- (vi) It is resistant to chemical reagents.
- (vii) It is used in making tubes, Crucibles, basin etc.
- (viii) Vitreosil is an opalescent form of quartz glass.
- (ix) Crown glass:- A partial replacement of silica by  $\text{P}_2\text{O}_5$  gives crown glass.
- (x) Ground glass:- It is prepared by grinding ordinary glass by emery and suspending oil or sand blasting.
- (xi) Safety glass:- (i) Safety glass is prepared by a layer of transparent plastic between two layers of glass by means of suitable adhesives. Transparent plastic is a sheet of vinyl acetate resin. The three layers are joined together tightly by the action of heat and pressure.
- (ii) It does not break under heavy impact.
- (iii) This glass does not shatter because they are held by plastic.

The following table gives the different types of glass, their properties & uses:-

Sl. No	Type	Special additives	Property	uses
1.	Soda glass	Aluminium oxide	Fuses easily at relatively low temperature	Window panes, bottles, tumblers.
2.	Boro silicate glass	Boron	Withstand high temperature fluctuation	Laboratory equipments

1. Lead glass	Lead oxide, Potassium carbonate	Highly transparent; high refractive index; absorbs radiations	Lenses, prisms, window panels of nuclear installations.
2. Coloured glass	Metal oxide	choice of metallic oxide is decided by the colour to be imparted	window panels, decorative materials.
3. Safety glass	Synthetic Plastic is sandwiched between two thin glass sheets	Withstands high stress. Sharp edges are not formed when it breaks (it is splinter-proof).	windshields of automobiles bullet-proof glass.
4. Fibre glass	Molten glass is drawn into thin fibres & sheets prepared	Light, strong, and fire proof	fire proof curtain dresses, manufacture of parts of automobiles.

## CEMENT

Definition:- A material possessing adhesive & cohesive properties, and capable of bonding other materials like stones, sand, bricks, building etc.; is called as cement. The cements have the property of setting and hardening under water. Some chemical reaction with it are, therefore called hydraulic cement.

Manufacture:- Raw materials:-

1. Calcareous materials like lime, chalk etc.,
2. Argillaceous materials like alumina, silica, clay etc.

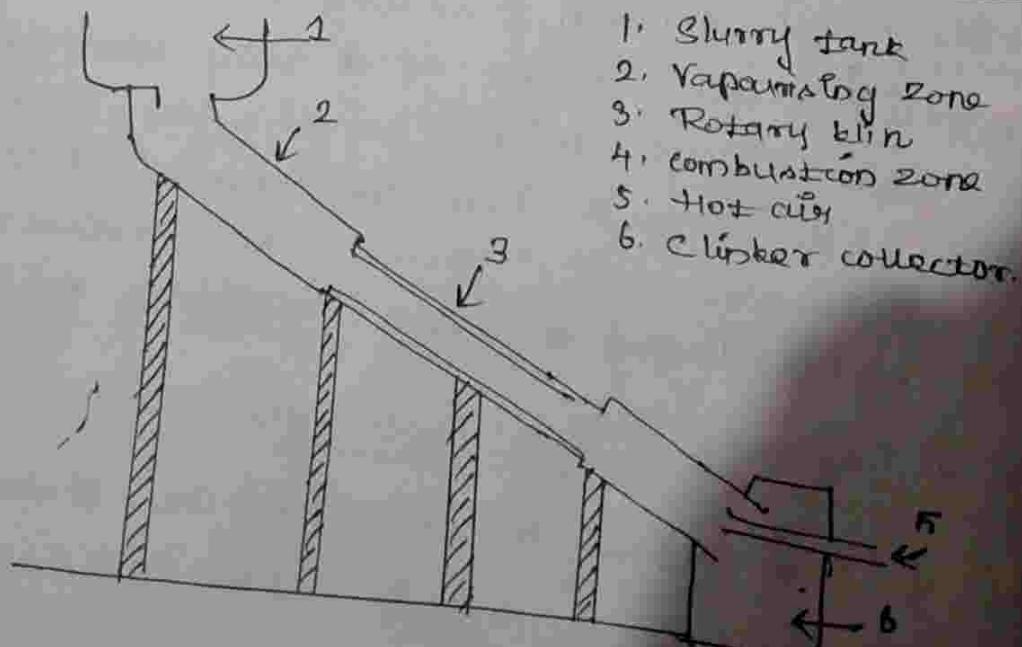
(3) Powdered coal. (4) Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )

Manufacturing steps:- (1) Mixing of raw materials

(a) Dry Process:- Lime stone as well as clay are separately crushed into 2-5 cm size and converted into fine powder by ball mills. These powdered materials are mixed together and stored in storage bins (silos).

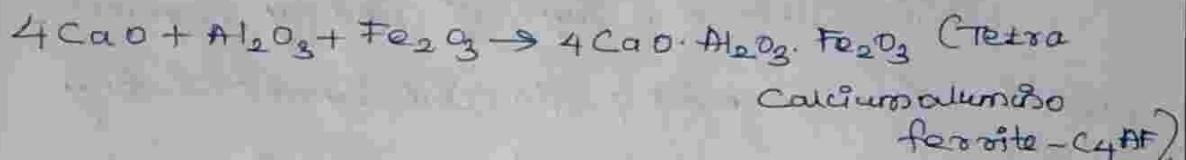
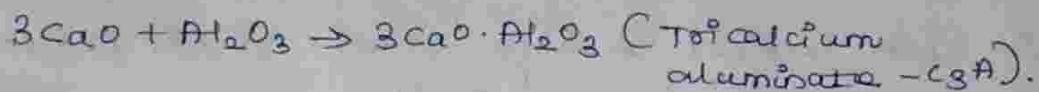
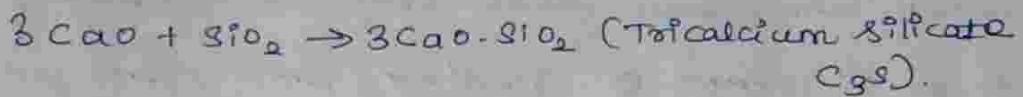
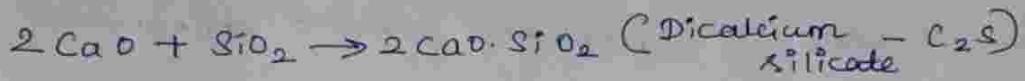
(b) Wet Process:- Lime stone are crushed and stored in big storage tank. Clay mixed with water and washed several times. Both materials are allowed to flow in a channel & grinding where they are converted to paste called Slurry. Slurry has 40% of water.

(2) Burning:- Raw mixture is burnt by rotary kiln. Rotary kiln is a steel tube; it has 3m diameter and 120m length. Its inside lined with refractory bricks and rotation speed of kiln is 1 rpm (rotation per minute). Hot flame is produced by injecting coal and air, about 1450°C. Raw mixture is injected into upper part of the kiln. Due to the slope of kiln, the mixture fed in moves towards the hottest end about 15 m per hour.



upper part:- water is evaporated at  $400^{\circ}\text{C}$  and  
 central part: Slurry is decomposed to form  $\text{CaO}$  and  
 $\text{CO}_2$  at  $100^{\circ}\text{C}$ .  
 lower part:  $\text{CaO}$  reacted with Silica, alumina and  
 iron oxide at  $100^{\circ}\text{C}$ .

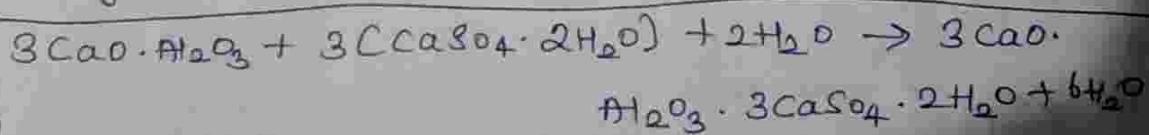
The reaction as follows;



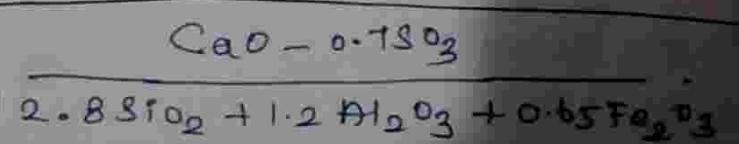
Aluminate and silicate of calcium fused together to form small hard (1 cm diameter), greyish stone called clinkers. These hot clinkers fall into another small rotary kiln and are cooled.

(3) Grinding:-

cooled clinkers are ground to a fine powder in a ball mills. During this time 3-4% gypsum is added. So cement does not set quickly if it comes in contact with water. Gypsum act as retarding agent for early setting of cement.



(4) Packing:- The ground cement is stored in 19 kg and packed automatically about 50 kg. The composition of the Portland cement is calculated form.



### 5) Setting and curing

Cement sets into a hard mass when mixed with water. Therefore it makes an excellent binding material in construction work. The mixture of sand and cement along with water undergoes many complex changes. The first stage of setting takes place within 24 hours after adding water to the cement.

The second stage of setting requires about two weeks. The subsequent setting of cement is achieved by adding water. The method of hardening cement by treating it with water is known as curing. During curing cement absorbs water. Calcium silicate and aluminates of cement are converted into a colloidal gel. This process is exothermic; hence it requires continuous water treatment.

### b) cement concrete

The mixture of cement, gravel and sand in the ratio of 1:2:4 or 1:3:6 is known as concrete. An iron skeleton inside concrete gives mechanical strength to the structure.

## composition of portland cement

- i) Lime,  $\text{CaO} = 50 - 60\%$ .
- ii) Silica,  $\text{SiO}_2 = 20 - 25\%$ .
- iii) Alumina,  $\text{Al}_2\text{O}_3 = 5 - 10\%$ .
- iv) Magnesia,  $\text{MgO} = 2 - 3\%$ .
- v) Ferric oxide,  $\text{Fe}_2\text{O}_3 = 1 - 2\%$ .
- vi) Sulphur trioxide,  $\text{SO}_3 = 1 - 2\%$ .
- vii) Sodium oxide,  $\text{Na}_2\text{O} = 1\%$ .
- viii) Potassium oxide,  $\text{K}_2\text{O} = 1\%$ .

## Types of portland cement

portland cement are divided into five types. It contains varying amount of clinker compounds, dicalcium silicate ( $\text{C}_2\text{S}$ ), tricalcium silicate ( $\text{C}_3\text{S}$ ), tricalcium aluminate ( $\text{C}_3\text{A}$ ), tetracalcium aluminoferrite ( $\text{C}_4\text{AF}$ ) and  $\text{MgO}$ .

### 1) Regular portland cements.

They are usual products for general concrete construction and attain to full strength in about 28-30 days. They contain 40-60%  $\text{C}_3\text{S}$ , 10-30%  $\text{C}_2\text{S}$  and 7-13%  $\text{C}_3\text{A}$ . Example: White cement, oil well cement, etc.

### 2) Modified portland cements.

These are sulphate resistant cement. The heat evolved from these cement should not exceed 70 and 80 cal/gm after 7 and 28 days respectively.

These cements are characterized by higher ratio of  $C_2S$  and  $C_3S$ .

3) High early strength portland cements:

These cements contain higher percentage of  $C_3S$  and  $C_3A$ . The higher proportion of  $C_3S$  causes quicker hardening than regular portland cement. Thus this cement attains strength is only three days.

4) Low heat portland cements: Thus, this cement attains strength is only three days.

4) Low heat portland cements.

These cements contain lower percentage of  $C_3A$ . The heat evolved should not exceed 60 and 70 cal/gm after 7 and 28 days respectively. These cements are designed for massive structure work.

5) Sulphate resisting portland cement

These are good for sea water contact.

It resists the sulphates better than the other types. These cements contain lower percentage of  $C_3A$  and higher percentage of  $C_4AF$ .

is used for structural purposes.

### uses of cements

- i) cements are used in the construction of roads, buildings, dams, bridges, etc. for construction purpose, it is used in the form of a paste with sand and water.
- ii) concrete is a mixture of cement, sand, gravel and water. The concrete sets to a hard mass. Hence, it is used in foundations, floors, roads, walls of buildings, dams, bridge and building of roofs.
- iii) concrete is filled in and around skeleton of iron rods and allowed to set. The resulting structure is very hard and rigid. This is known as reinforced concrete. Reinforced concrete is used in the construction of bridges and roofs.

### Raw Materials in India

- 1) Lime & Stone

Lime & Stone Deposits are common in every State in India, except, perhaps, Kerala.

Madhya pradesh : High grade lime stone -  
Jabalpur, cement and flux grade lime stone -  
Rewa and cement grade limestone - Akola, Agra,  
Mahali, Kawardah, Beladih and Chattisgarh.

Tamilnadu : cement grade limestone - Ramanathapuram  
Trichy, Tiruchirapalli, Salem, Coimbatore  
and madurai districts.

In Andhra pradesh : cement grade limestone -  
Nalgonda district.

In Gujarat : Cement grade limestone - Kherod  
and Ganapiply

In Haryana : cement grade limestone

In Himachal Pradesh : Cement grade limestone -  
Bilaspur district.

In uttar Pradesh : High grade lime stone. Dehradun  
and Mussoorie area

In Bihar : Cement grade lime stone. Bundu,  
Basaria and Kurukuta - Religara area of  
Hazaribagh district.

(2) clay : - In India best quality of china clay  
occurs at kundara in kerala and Singhbhum  
in Bihar. China clay is also occurs at Karnataka,  
Tamil Nadu, West Bengal, Rajasthan, Himachal  
Pradesh, Andhra Pradesh and Haryana.

Good quality of fire clay is found in Bihar, Orissa, Madya Pradesh, Gujarat, Maharashtra, Andhra Pradesh, Karnataka and Rajasthan.

Growth of cement industry in India:-

(1) Responsible for 7-8% of global cement production, India is the second largest cement market in the world, and also an exporter to 30 countries.

(2) The cement industry in India is divided into five geographical segments. These are North, South, East, West and Central regions.

(3) North and south regions are the leading suppliers of cement.

(4) The east, west and central regions face deficit of cement. Hence, these regions purchase the cement from the North and South.

(5) According to the Cement Manufacturers Association (CMA), there are 139 large cement plants and 365 mini and white cement plants in the country.

(6) According to the Cement Manufacturers Association (CMA), cement sales for May 2012 were registered at 16.26 million tonnes (MT), which signifies a 14.1% growth over the same period in 2011.

(7) Although India is one of the largest cement markets in the world, its per capita consumption is only around 170 kg, much lower than the global average consumption of about 480 kg.

(8) According to the latest report from the working group on the industry for the 12th

Five-year Plan (2012-17), India would require overall cement capacity of around 480 million tonnes.

(9) This would mean the industry will have to add another 150 million tonnes of capacity during the period.

(10) Leading players in the sector (by market share) are Shree Cem, Ultratech Ambuja, Bisani, Ace, India Cem, Dalmia Cem, Madras Cem, Lafarge, and others India.

## UNIT - II

### Soap, Detergents and Refractories.

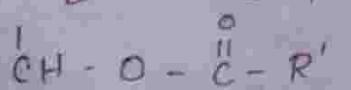
SOAP

definition:

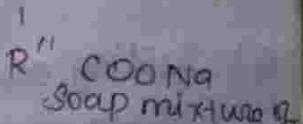
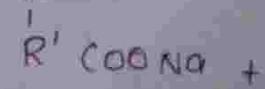
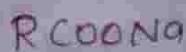
The Sodium or potassium salt of higher fatty acids. Such as Oleic, Stearic, Lauric, Palmitic acid are called Soap. Sodium salt of higher unsaturated fatty acid like Palmitic acid. Stearic acid are called hard soap. Potassium salt of higher saturated fatty acid like Oleic acid are soft soap.

General consideration of making of soap.

The basic principle of making of all kind of soap is the combination of higher fatty acid with sodium or potassium Hydroxide or carbonate.

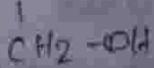
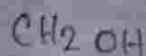


Fat



Soap mixture

Sodium carbo  
xylates



Glycerol

## Manufacture of Soap.

There are generally three methods used

For ~~the~~ Soap Manufacture.

- i) Hot Process or Kettle process.
- ii) Cold process
- iii) Hydrolysis Process or Modern Process

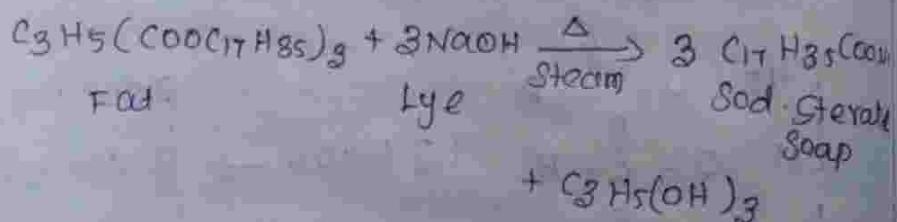
### Hot Process or Kettle process

The kettle process is now used in small factories or for special production on a limited scale. This process is carried in a steel tank or kettle.

### Manufacturing Step.

#### 1) Boiling

The Fat and NaOH solution are charged into the kettle and boiled with steam. This boiling is continued till saponification is complete about 80%.



#### 2) Salting out

Glycerol.

NaCl is added and boiled upto the separation of soap. The soap floats on the surface as curly mass. The lower layer containing glycerol and salt is drawn off. The leaving

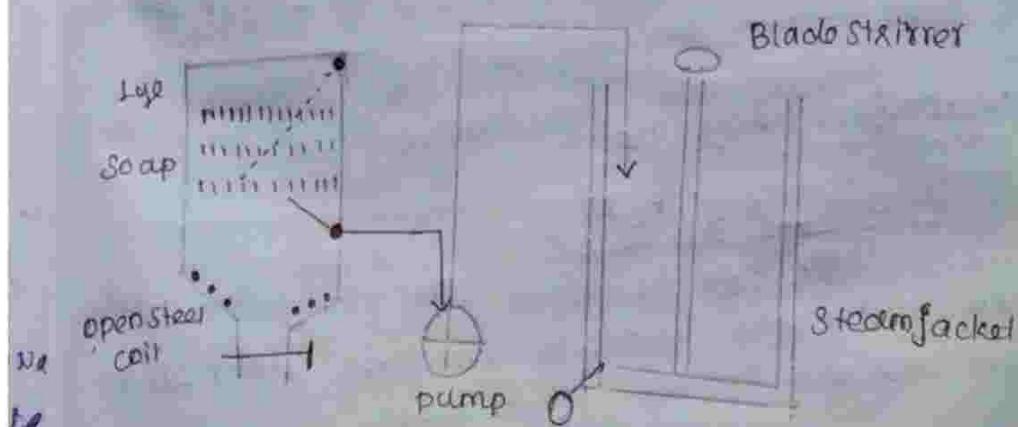
Soap contains Soap Fat.

### a) Addition of Fresh Lye.

The Soap contains Fat are removed by esterification process. It is boiled with a fresh supply of NaOH solution. More soap is formed. The soap layer left in kettle. It is boiled with H<sub>2</sub>O and wash away excess of lye.

### b) Finishing:-

The neat Soap is pumped into the crutcher. Here the Soap is mixed with colour, perfumes, Germicides etc. till it becomes a homogeneous mass. The crutched Soap is poured into frames and on solidification cut into cakes.



### b) Cold Process.

The oil or the molten Fat is taken in an iron pan fitted with a stirrer. It is treated with caustic soda solution (lye).

The Charge is stirred until the soap begins to set.

Soap is solidified frames and cut into cakes.

All the glycerin got from soap contains starch or some other filling material which is thoroughly mixed with the soap prior to the addition of caustic soda.

The proportion of the various ingredients are : alkali (1 part) water (1 part) and starch (1 part).

This process does not yield pure stuff. The hot process is superior to this.

### Hydrolysis process or Modern process.

This is the Modern continuous process for soap manufacture. It is economical than the Kettie process and gives better quality of soap.

### Manufacturing Step:-

#### 1) Hydrolysis of Fat.

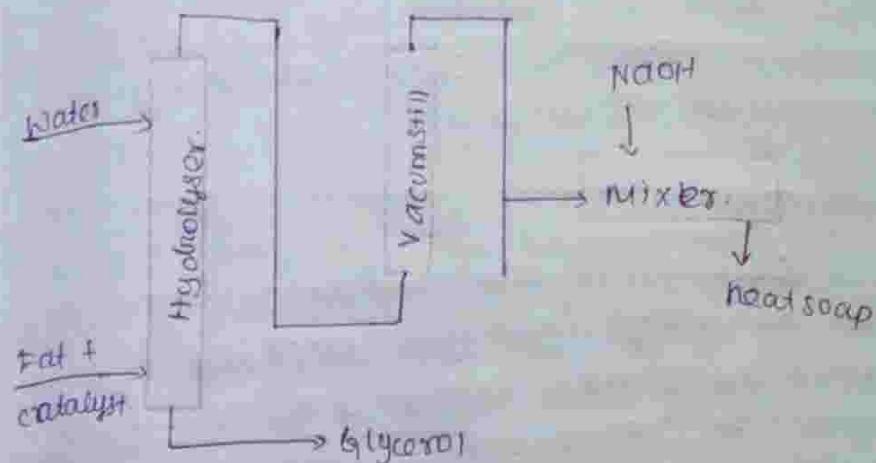
The fat is mixed with zinc oxide catalyst and water are heated to 230-250°C under 40-50 atm pressure in the hydrolyser.

#### 2) Distillation of Fatty acids.

The fatty acid is mixed with water. This is discharged at the top into a steam flash tank. The water is vapourised. The fatty acid is distilled under vacuum still.

g) Neutralization of the fatty acids.

The vapours of fatty acid are passed through condenser. The condensed fatty acid are neutralized in the mixture containing alkali. The product is soap.



Toilet Soap:-

Toilet Soap are manufactured from the best quality Fat or Oil and good care is taken to add the right amount of lye. There is no free alkali in the finished products. Toilet soap is injurious to the skin.

Toilet soap contain:-

Fine White Tallow. 50 to 70%.

Coconut oil 15 to 30%.

Lard upto 20%.

Palm Kernel oil upto 20%.

Castor oil upto 20%.

Resin upto 5%.

Trace amount.

For saponification, NaOH is used. This makes hard and stable soap. KOH produces a

Soft Soap.

Transparent soap:-

Transparent soap are prepared by dissolving soft soap in methylated spirit and then removing the insoluble part by filtration. The solid transparent soap is obtained on evaporating off alcohol.

Detergents:-

Detergents are sodium salt of Sulphonic acid or alkyl hydrogen sulphates. It is reduced the surface tension of the water. This is known as surface active agent. Since, they are used for washing and cleaning purposes. Detergents contain one end of hydrophilic and other end of hydrophobic molecules.

Classification of Surface active agent

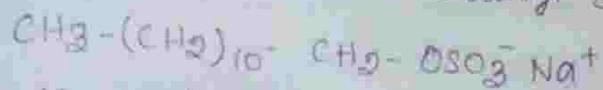
Detergents can be classified into three classes:

- i) Anionic detergent
- ii) Cationic detergent
- iii) Non-ionic detergent.

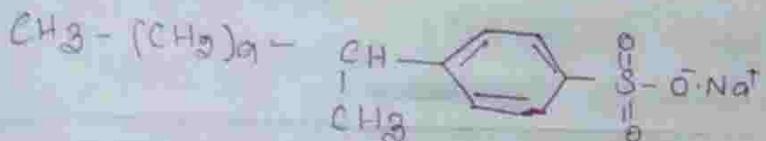
Anionic detergents.

Anionic detergent are sulphates of Long chain primary alcohol ( $C_{10}$  to  $C_{18}$ ) alcohol or Sulphonate salt of hydrocarbons.

Example: Sodium Lauryl Sulphate.



sodium dodecyl benzene sulphonate.

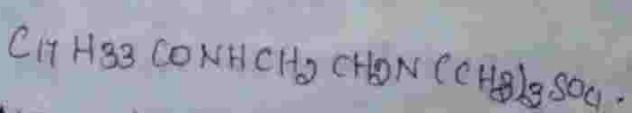
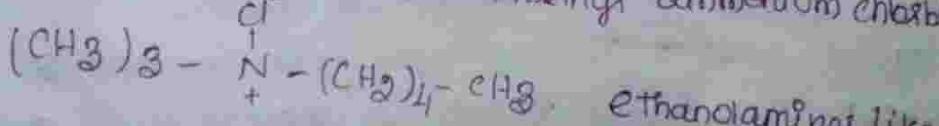


The hydrophilic end is  $\text{SO}_3^- \text{Na}^+$  or  $\text{OSO}_3^- \text{Na}^+$  and hydrophobic end is long chain alkyl, aryl part. They are effective cleaning agent for fabrics like cotton, wool, silk etc.

## 2) Cationic detergent

cationic detergent are amino acetates and alkyl trimethyl ammonium chlorides. These are called as invert soap / detergent because their water soluble end carries a positive (cation) charge rather than negative charge. These are good cleaning agent. They possess germicidal properties.

Example: n-hexadecyl trimethyl ammonium chloride.



Non-ionic detergent.

In non-ionic detergent, the polar water structures provides the required water solubility. These are used in dishwashing liquid.

## Difference between soap and detergent

Soap	Detergent
Soap cannot be used in hard water because it forms insoluble precipitate.	Detergent can be used in hard water.
It cannot be used in acidic water.	There is no such problem.
It is biodegradable.	It is non-biodegradable.
The ionic part of a soap is $\text{COO}^-\text{Na}^+$ .	The ionic part of a detergent is $\text{SO}_3^-\text{Na}^+$ or $\text{OSO}_3^-\text{Na}^+$ .
Soap takes more time to dissolve in water.	Detergent dissolves faster in water.
Example: Sodium Stearate.	Sodium Lauryl Sulphate.

## Shampoo:-

Shampoo is a liquid detergent. The liquid solution is massaged into wet hair. It creates lather and breaks up deposits of oil and dirt. The lather is rinsed from the hair after a few minutes, leaving the hair cleaning. Hence it is used as cleaning agent to hair.

## Raw materials:-

Water - Basic element

Ammonium Lauryl sulfate and ammonium laurate sulfate - Surfactants.

Cocamidopropyl or cocamidopropyl - Foaming agent

Sodium citrate or Citric acid - Maintain the pH level.

Dimethicone - conditioner. It creates smoothness and shine of the hair.

Polyquaternium - It makes manageable hair.

Panthenol, Fatty alcohol and nut oil - common additives for moisturize.

Midazolidinyl urea, Iodopeppynyl, Isothiazolinone and sodium benzoate - It retard the growth of bacteria.

### Refractories:-

Introduction:-

Definition:-

Refractories are inorganic materials that can withstand high temperatures without softening or undergoing any deformation in shape.

Function:- The function of a refractory is to confine heat (construction of inner lining of a furnace), to maintain high temperature and to resist the abrasive and corrosive action of molten metals.

Characteristics or requisites of a good refractory.

It should not be fused at the operating

temperature.

Its physical, chemical and mechanical properties should not undergo any changes at high temperature.

It should ~~be~~ not be crack and spherical at the operating temperature.

It should be able to withstand overheat at the operating temperature.

It should be chemically inert towards the corrosive action of molten metals, slags and gases.

It should expand and contract uniformly with temperature rise respectively.

### Classification of refractories:

Refractories are classified into three types.

i) acidic ii) basic and iii) Neutral Refractories

#### i) Acidic refractories:

These are made up of acidic materials like alumina and silica. They are not attacked by acidic materials, but are easily attacked by basic materials.

Ex) Si, Al, Fire clay refractories.

#### ii) Basic refractories.

They are made up of basic material like calcium oxide and magnesium oxide. They are not attacked by basic materials, but

are easily attacked by acidic substances.

Ex:- Magnesite (magnesia) and dolomitic  
refractories

### 3) Neutral refractories:

They are made up of neutral materials like graphite, zirconia, and silicon carbide.

They are inert towards both acidic and basic substances.

Example: Graphite, Zirconia.

## Properties of Refractories:-

### 1) Refractoriness:-

Definition:- Refractoriness is the ability of a refractory material to withstand high temperature without softening or deformation under working conditions.

### Measurement of refractoriness:-

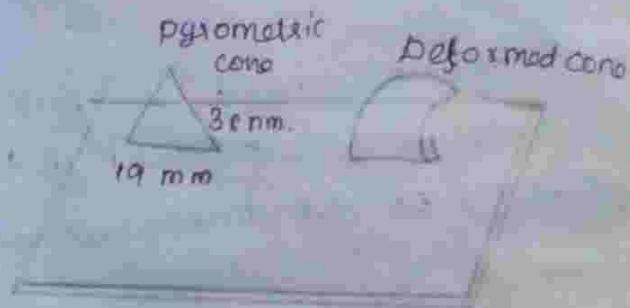
Refractoriness is usually measured by the softening or fusion temperature of the material. A refractory material should have softening temperature high than the operating furnace temperature. The softening temperature of refractory is determined by the Standard pyrometric cone equivalent (PCE) test or Seger cones test.

Pyrometric cone equivalent (PCE) test:-

Pyrometric cone equivalent is the number which represent the softening temperature of a refractory specimen of standard dimension and composition.

Measurement:-

In this test, pyrometric cones or Segor cones of standard dimension (38 mm high with triangular base of 19 mm side) are prepared from various refractory materials. These are known as standard cones. The test cone is prepared from a refractory as the same dimension of standard cone.



When a test cone is heated on a base along with standard cone under standard condition ( $10^{\circ}\text{C}/\text{minute}$ ) at one stage, the apex of the cone bends and touches the base. The temperature of the cone. The PCE value of the test refractory is taken as the number of standard cone which softness along with the test cone. A good refractory should have high refractoriness.

## 2) Thermal Spalling or Spalling resistance.

**definition:** Thermal spalling is the property of breaking, cracking or peeling of a refractory material under high temperature. A good refractory should be resistant to thermal spalling.

The reason for the thermal spelling:

uneven thermal expansion or contraction due to temperature differences (rapid heating or cooling) is the main cause for thermal spalling.

The spalling tendency is directly proportional to the coefficient of expansion.

Thermal Spalling can be decreased by

- i) low coefficient of expansion
- ii) good thermal conductivity refractory.
- iii) avoiding sudden temperature changes.

## 3) Strength or Refractoriness under Load (RUL)

Refractories used in metallurgical operation and industries have to withstand varying load.

Refractories like alumina do not bear loads, but refractories like silica bricks bear maximum load under operating temperature, so refractories should have high mechanical strength under operating temperature.

**Definition:-**

Strength or refractoriness under load of a refractory is its ability to withstand high temperatures under the influence of maximum load without breaking.

The Load bearing capacity of a refractory can be measured by RUL test.

RUL TEST :- RUL is performed on a test specimen of standard size (cylinder diameter 60 mm and height 40 mm). The specimen is heated in a furnace at a rate of 10°C/min under a load of 1.75 kg/cm<sup>2</sup>. RUL is expressed in terms of the temperature at which 10% deformation occurs to the specimen. A good refractory should have a high RUL value.

#### 4) Porosity:

Definition:- Porosity of a material is defined as ratio of its pores volume to that of its bulk volumes. Thus, porosity is given as

$$P = \frac{W - D}{W - A} \times 100 \quad W = \text{Weight of Std Specimen in air}$$

A Saturating of

Specimen may be carried out by boiling in vacuum for two hours.

D = Wg of dry Specimen in air

A = Wg of Std Specimen Submerged in water

#### Disadvantages:-

Due to porosity, slags, gases etc are likely to enter more easily to greater depth and also react with a refractory.

i) Reduces the strength.

ii) Reduces resistance to corrosion.

So a good refractory in general should have lower porosity.

### Advantage:

The lower porosity increase thermal conductivity due to the absence of voids and increased resistance to thermal spalling.

The high porosity refractories possess lower thermal conductivity due to the presence of more air voids, which act as insulators and hence it can be used for lining in furnace, oven etc.

### 6) Dimensional Stability:

Definition: It is the resistance of a refractory to any volume changes when exposed to high temperature over a prolonged time.

These dimensional changes may be i) reversible  
ii) irreversible

#### i) Reversible dimensional changes.

The refractory material will result in uniform expansion and contraction refractory materials should have reversible dimensional changes.

#### ii) Irreversible dimensional changes.

Irreversible changes may lead to contraction or expansion of refractory on heating magnesite bricks (specific gravity is 3.05) is gradually converted into more dense shrinkage crystalline form of periclase (specific gravity 3.6)

But in certain refractories, prolonged heating may lead to expansion e.g., on heating there is an increase in the volume of silica brick due to transformation of quartz from (specific gravity is 2.65) into cristobalite (specific gravity is 2.34)

### Manufacture of Refractories:

i) Crushing: - The big lumps raw materials are crushed to small size about 25 mm.

ii) Grinding: - The crushed material are removed from raw materials. This is done by splitting, magnetic separation and chemical method using grinding machine to 200 mesh size.

iii) Screening: - The unwanted materials are removed from raw materials. This is done by screening, magnetic separation and chemical methods.

iv) Storage: - After Screening and mineral dressing the pure materials are stored in strong bins.

v) Mixing: - It is done in order to distribute the plastic materials equally throughout the mass. This makes moulding easier.

vi) Moulding: - Moulding may be done either manually or mechanically by the application of pressure. Hand modelling ~~process~~

produce the ~~low~~<sup>high</sup> density and ~~less~~<sup>new</sup> strength refractories. Airing the mechanical moulding of the do-airing refractories. Mechanical moulding the do-airing process is essential. De-airing is done i) by applying vacuum ii) by allowing air to inside the void space, iii) by double pressing.

7) Drying:- Drying is carried out slowly in tunnel dryers. The bricks are placed in a long tunnel. Hot steam passes through the tunnel. Drying is used to remove the moisture from refractories.

8) Fixing:- The refractories are fired to stabilize and strengthen their structure. Fixing is done in tunnel kilns or rotary kilns. The fixing temperature of different bricks are; high Fired super duty brick - 1480°C Kaolin brick - 1700°C basic brick - 1870°C.

Manufacture of Fire-clay refractories:

Fire-clay refractories contain 50-80% Alumina and 20-50% Silica. The chemical formula is  $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ .

Raw materials:-

Fire-clay and ~~charcoal~~ calcined Fire-clay.

## Manufacturing steps:

- 1) Crushing: The big lumps raw materials are crushed to small size about 25 mm.
- 2) Grinding: The crushed materials are ground in grinding machine to 200 mesh size.
- 3) Screening: The unwanted materials are removed from materials. This is done by setting magnetic separation and chemical methods.
- 4) Storage:  
After Screening and mineral dressing, the pure materials are stored in storage bins.
- 5) Mixing: It is done in order to distribute the plastic materials equally throughout the mass. This makes moulding easier.
- 6) Moulding: Moulding may be done either manually or mechanically by the application of pressure. Hand moulding produced low density and low strength refractories. Mechanical moulding produced high density and high strength refractories. After the mechanical moulding, the de-airing process is essential. De-airing is done i) by applying vacuum ii) by allowing air to insinuate the void space  
iii) by double pressing.

7) Drying:- Drying is carried out slowly in tunnel ovens. The bricks are placed in a long tunnel. The hot steam passes through the tunnel. Drying is used to remove the moisture from refractories.

8) Fixing:- The refractories are fixed to stabilize and strengthen their structures. Fixing is done in tunnel kilns or rotary kilns. The fixing temperature of fire clay bricks is 1300°C. After the fixing the bricks are cooled slowly.

### Uses:-

- 1) They are used in steel industries.
- 2) They are used for lining of blast furnaces, open hearths, furnaces and lime kilns.
- 3) They are used for construction of stoves, ovens, crucible furnaces, flues, charging doors etc.

## Unit IV

Fertilizers:

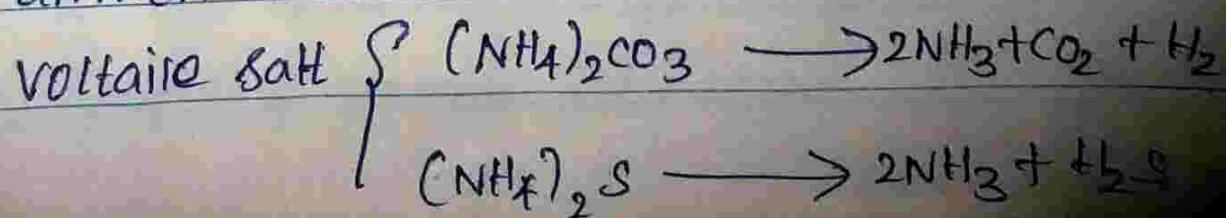
Definition:

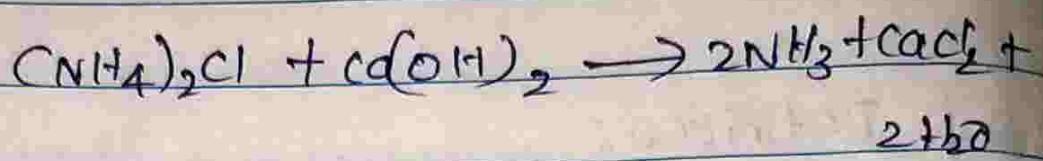
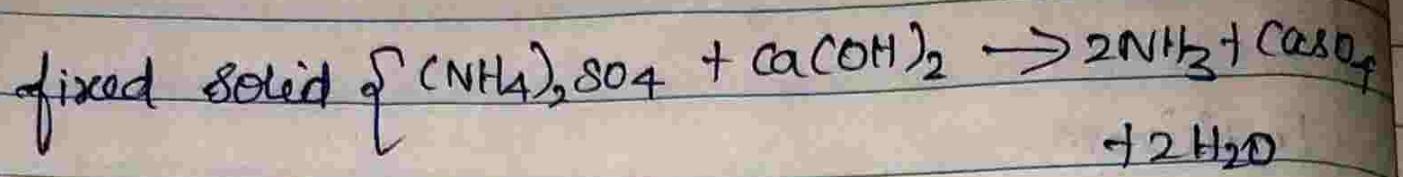
Fertilizers are substances which are added to the soil in order to make up the deficiency of essential elements like nitrogen, phosphorous and potassium required for the growth of plant.

Manufacture of ammonium sulphate:

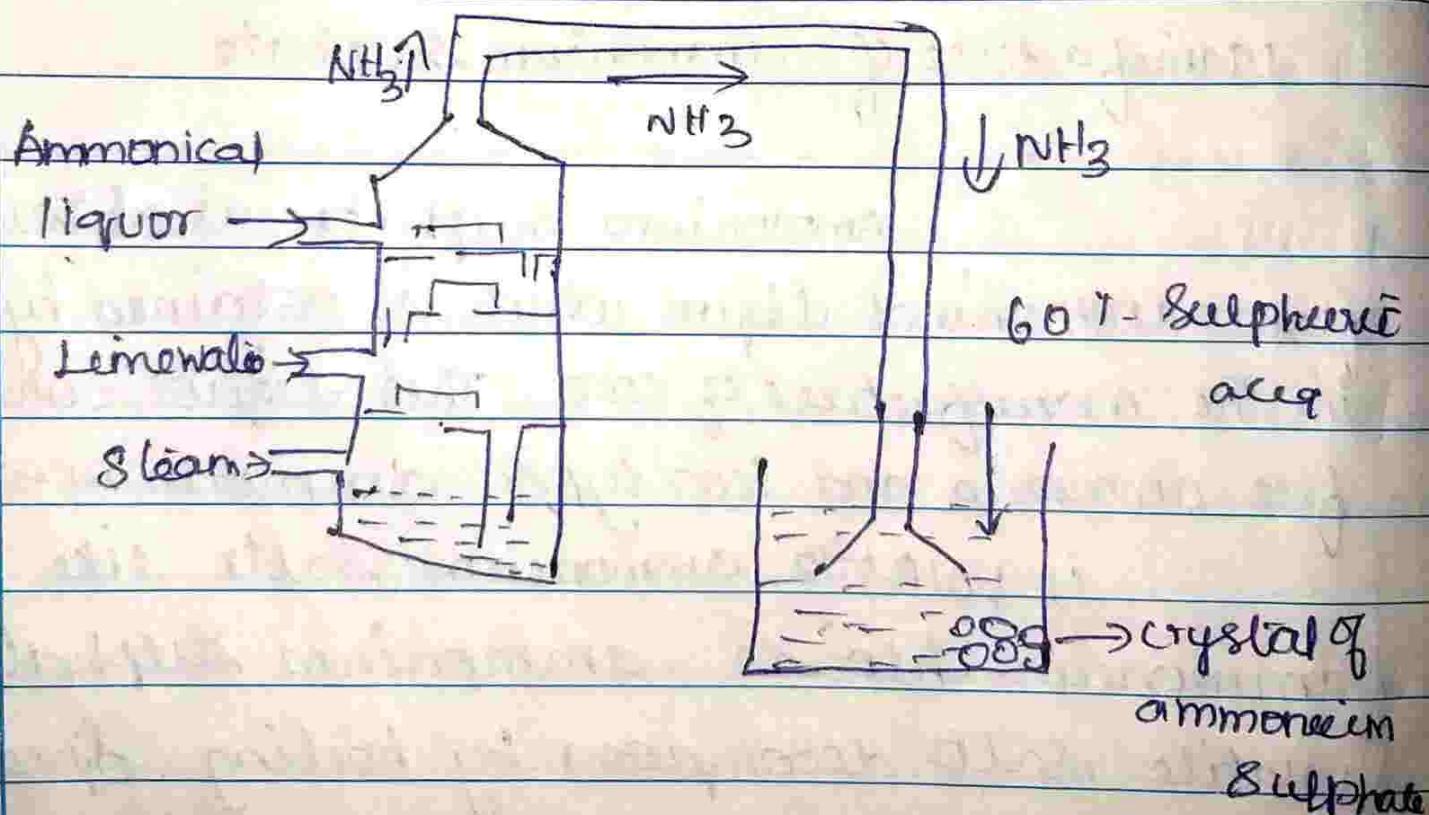
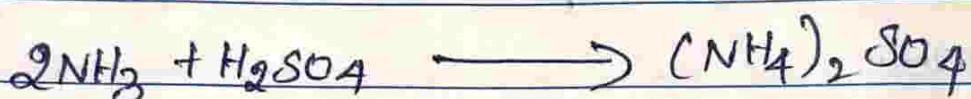
Ammonium Sulphate is obtained from ammonical liquor which is obtained by product in the manufacture of coke. This liquor contains free ammonia and two types ammonium salts

i) volatile ammonium salts like ammonium chloride, ammonium sulphate etc  
volatile salts decomposes by boiling. fixed salt decomposes by lime water. These salts decompose to evolve ammonia.





This ammonia is passed through 60% Sulphuric acid and crystals of ammonium sulphate separate on cooling.



## Sindri process of ammonium sulphate:

The process employed at Sindri fertilizers factory. It consists of various steps

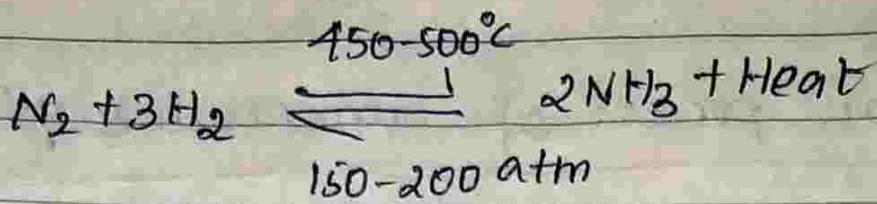
1) Air and steam are passed over red hot coke. A mixture of  $\text{CO}$ ,  $\text{N}_2$ , and  $\text{H}_2$  is formed



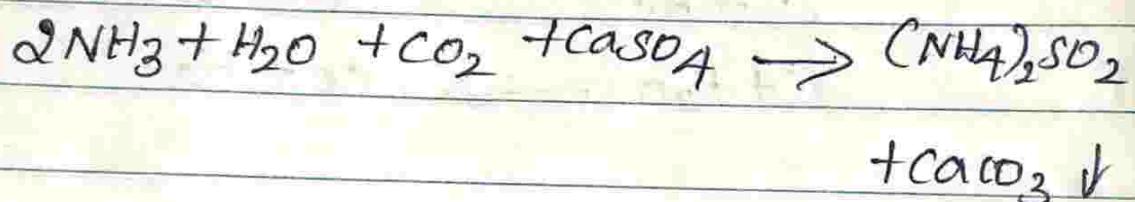
2) The mixture of  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{H}_2$  is passed over a hot catalyst bed consisting of  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ . Here  $\text{CO}$  get oxidized to  $\text{CO}_2$ .

Now the gaseous mixture consists of  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{H}_2$ . This is compressed to about 20 atm pressure in the presence of water. Hence  $\text{CO}_2$  dissolve in water under these conditions.

3) The resulting mixture of  $\text{N}_2$  and  $\text{H}_2$  is adjusted in the ratio 1:3 and converted into ammonia by Haber process.



4) The resulting ammonia is mixed with  $CO_2$  solution. An adequate amount of calcium sulphate is also added



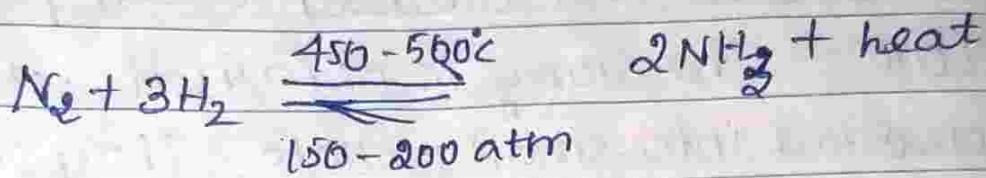
calcium carbonate precipitate out. it is removed by filtration. This is called precipitated chalk. It is important by product. The solution is concentrated and crystallized.

Manufacture of calcium ammonium nitrate:

CAN is manufactured at Nangal Punjab. It is also known as Nitro lime stone. Manufacture of CAN consists of

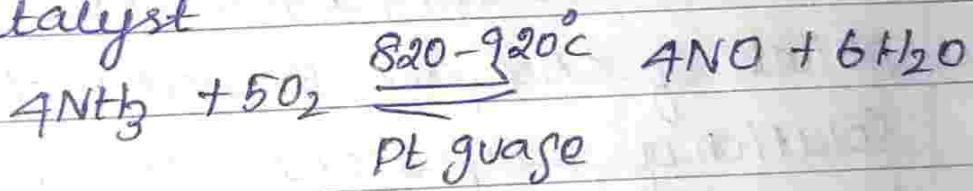
## Variants Steps

1) Ammonia is synthesized by haber process by direct combination of nitrogen and hydrogen under specified condition

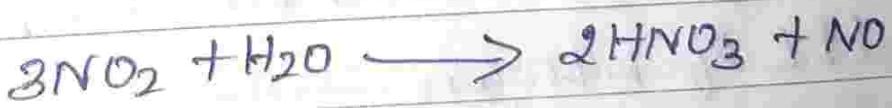


2) Ammonia is converted into nitric acid

by Ostwald's process using platinum or palladium catalyst



(b)



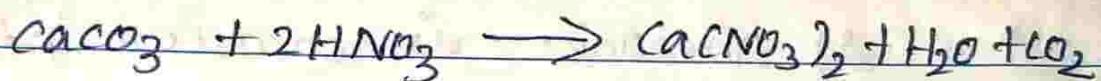
3) Solution of nitric acid is concentrated and heated to about  $75^\circ\text{C}$  it is allowed to neutralize

Ammonia gas is heated to about  $70^\circ\text{C}$  is introduced from the bottom of the neutralizer

This operation results in neutralization of nitric acid by ammonia and ammonium nitrate is formed



4) The ammonium nitrate solution is concentrated and treated with powder lime stone. The slurry is obtained. It is converted into small pellets. They sold under the name calcium ammonium nitrate



5) CAN is very hygroscopic. Hence the pellets of CAN are stirred with concentrated solution of soap stone (sodium silicate). This treatment protects the CAN from moisture. The pellets are dried and packed. It contains 19.1% of nitrogen.



Manufacture of urea:

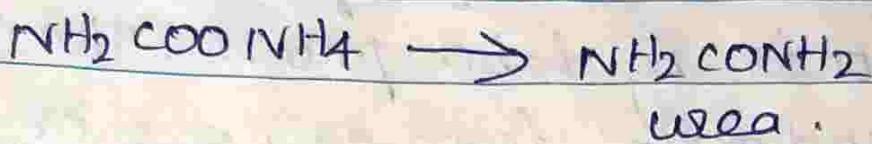
Large scale:

Urea is prepared on a

large scale by reacting liquid ammonia with gaseous carbon dioxide at  $135^{\circ}\text{C}$  and about 220 atm pressure to yield ammonia carbonate. Some of ammonia carbonate decomposes simultaneously to give urea.



ammonium carbonate



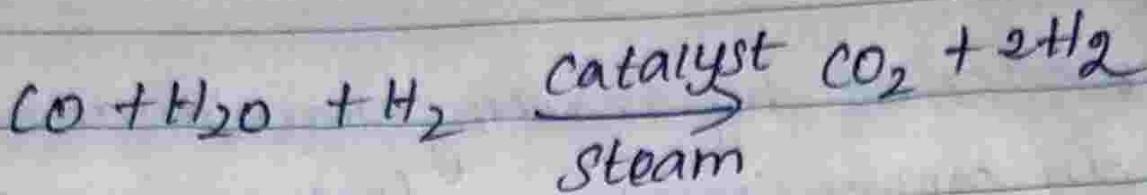
urea.

The undecomposed ammonium carbonate is processed separately under reduced pressure to give urea.

### Modern process:

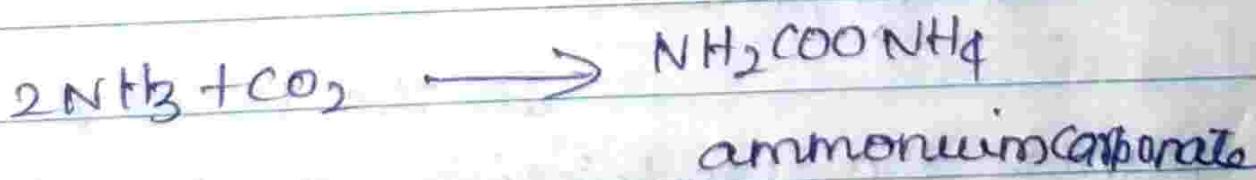
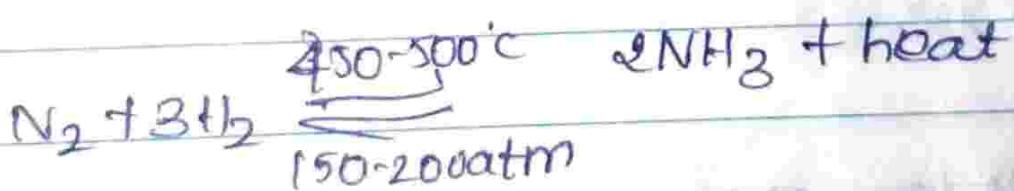
In the modern manufacturing plant, the production of urea has been made highly economical. Crude naphtha is subjected to partial combustion processes. It gives a mixture of hydrogen and carbon monoxide.

The mixture reacts with steam in the presence of catalyst like mixture of Fe, Cr and Co. Here CO is oxidised to  $\text{CO}_2$ .



carbon dioxide is separated by washing with water under pressure or by treatment with  $\text{KHCO}_3$  solution.

The above hydrogen is converted into ammonia by haber process. The regenerated carbon dioxide from aqueous or alkali carbonate solution is compressed and reacted with ammonia to give urea.



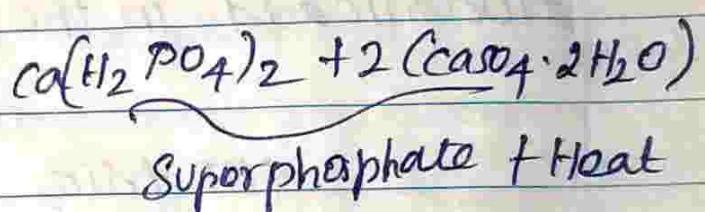
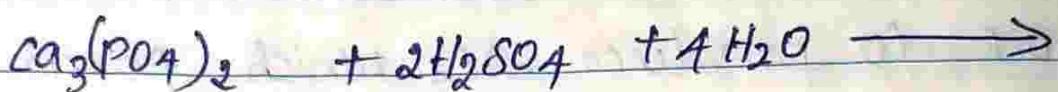
calcium super phosphate or super phosphate

Calcium super phosphate is a mixture of calcium phosphate (94%)

The chemical formula is  $\text{Ca}(\text{CH}_2\text{PO}_4) + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Manufacture of calcium phosphate or super phosphate

It is manufactured by treating calcium phosphate with calculated quantity of sulphuric acid



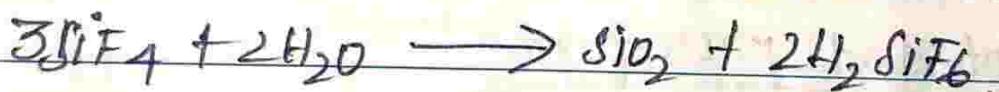
Plant and procedure:

The powdered phosphate rock is placed in a cast iron mixture. A calculated quantity of sulphuric acid is added to it. The whole mass is stirred mechanically about 2 to 5 min. The mixture is left for about 24 hrs. The temperature rises to  $100-110^\circ\text{C}$  because of exothermic reaction. The phosphate

contain  $\text{CaCO}_3$  and  $\text{CaF}_2$  as impurities. They react with sulphuric acid to evolve  $\text{CO}_2$  and HF.



Free HF reacts with silica in the phosphate rock to produce  $\text{SiF}_4$  which form hydrofluosilicic acid in the presence of water.



The gases like  $\text{CO}_2$ , HF and  $\text{H}_2\text{SiF}_6$  are led into suitable absorption tower. As result the hard mass is obtained. It is solidified to a porous dry solid due to the formation of gypsum. The mass is allowed to stand few days in sun and it becomes dry. The dried mass is kept in the open for 4-6

weeks. During this period the excess of sulphuric acid is completely consumed and the mass is completely dried. The dry mass is crushed to fine powder and is sold in the name of super phosphate of lime.

### Mixed fertilizers:

A fertilizer which contains more than one of the major plant nutrients, is called a mixed fertilizer.

Mixed fertilizers contain nitrogeneous, phosphatic potash fertilizers, ammonium sulphate, calcium ammonium nitrate is used as a source of nitrogen. Calcium super phosphate is used as a source of phosphorous potassium chloride or sulphate is used as a source of potassium. These are referred to as NPK fertilizers.

## Fertilizer industry in INDIA:

India is the largest producer of nitrogenous fertilizers in the world only behind China and US. At present there are 30 large size units in the country producing urea, 21 units produce DAP and 5 units produce complex nitrogenous fertilizers.

Besides, there are about 80 small and medium scale units in operation producing single super phosphate. The total installed capacity of fertilizer production which was 119.60 LMT of nitrogen and 53.60 LMT of phosphate as on 31.03.2004 has marginally increased to 120.61 LMT of nitrogen and 56.59 LMT of phosphate as on 31.3.2011. At the national level, the total consumption of all nutrient based fertilizers in 2010-11 is estimated at 590 lakh tones.

Out of the 16 plant nutrients nitrogen, phosphorous and potash (NPK) are

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Out of the 16 plant nutrients nitrogen, phosphorous and potash (NPK) are

Major three nutrients that contribute more on the productivity. The governments aimed at achieving the maximum self sufficiency in the production of nitrogenous fertilizers in India more than 60 fertilizers industry present in private as well as "public Sectors".

### Factories in public sector:

The important factories are,

1) Fertilizer corporation of India: This ~~cor~~ corporation contains nine units. These units are situated at Sindri (Bihar), Nangal (Punjab), Nampur (UP), Trombay (Maharashtra), Korba (MP), Barauni (Bihar), Talchar (Orissa) and Durgapur (West Bengal).

2) Fertilizer and chemical Travancore Ltd.

Always

3) Madras fertilizer, Chennai

2) Factories in private sector:

The important units are.

1. DCM chemical works Delhi and Rota
  2. Indian explosive Ltd kanpur
  - 3) Zerai agrochemicals Ltd Gurga
  - 4) Coimandal fertilizer Ltd
- Visakha patnam.
- 5) ELD paroy's Ltd, chennai
  - 6) phosphate company Ltd calcutta

## Sugar Industry:

Manufacture of sugar from molasses:

### 1) Extraction of juice:

There are three roller mills connected each with metal plates which is used to crush the cane and forms canemat. The can mate is passed into a long tank containing number of compartments. The sucrose is extracted from the partially exhausted cane mat. it is passed on the conveyor by washing with cold or hot water and forms juice. The juice is

diluted by a counter current method. Water is sprayed on to mat in all compartment the ~~richish~~ richest juice is formed. The juice is pumped to the classification unit. This method is called as diffusion process.

## 2) Purification of sugar:

Raw juice contains 15-20% of sucrose and much impurity. The impurities are organic acids, mineral phosphates, proteins and colloidal colouring matter. The raw juice is slightly acidic in nature. Hence the juice is purified by the following operations.

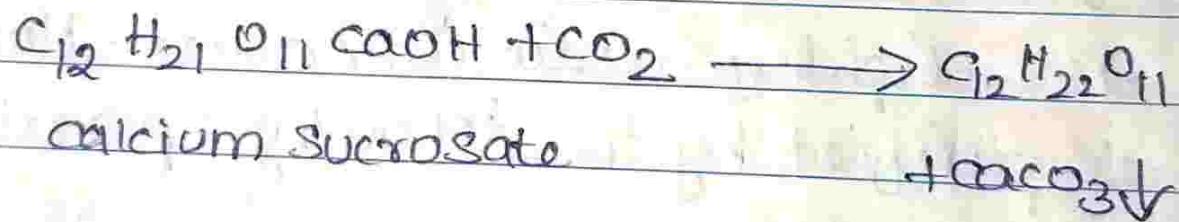
### 1) Defecation:

The raw juice is transferred into tanks. It is heated by steam and treated with 2-3% lime. This process is called defecation. This operation removes the organic acids and phosphates are insoluble calcium salts.

The protein and the colloidal colouring matter are thrown out as a solution of thick gum. The precipitated calcium and the scum are removed by filtration.

### ii) carbonation:

The juice after defecation is treated with carbondioxide. This operation is known as carbonation. This process <sup>is</sup> to remove the excess of lime and decomposes Calcium Sucrosate to give sugar and Calcium carbonate.



### iii) sulphitation:

The juice after carbonation is treated with  $SO_2$ . This operation is known as sulphitation. This process complete the neutralization of lime and decomposition of calcium sucrosate. The colour of juice

is also bleached. The Clarified juice is obtained by filtration.

### 3) Concentration and crystallization of the juice:

The clarified juice is concentrated by boiling under reduced pressure in multiple effect of evaporators. The concentrated juice is passed to the vacuum pan. The water content reduces from 6-7%. The contents of pan are known as masscuite. The masscuite and discharged in a tank. Crystals grow in size and form a thick mass.

### 4) Separation and drying of crystals:

The masscuite is charged into centrifugal machines. The sugar crystals are separated from the mother liquor. The crystal are sprinkled with little water to wash the impurities sticking on the surface. The crystal are dried by hot air. The sugar is 96% pure.

further purification, it may be dissolved in hot water and recrystallized.

The Mother liquor obtained after the removal of crystals is called as molasses. It contains large amount of sugar. It is concentrated to get fresh crop of crystals. Molasses contains also glucose and fructose.

### Manufacture of sugar from Beet Root

The various stages in the manufacture of sugar from beet roots are

- 1) Extraction of sugar solution by diffusion
- 2) Purification
- 3) Concentration and crystallization
- 4) Separation and drying of crystals

### Extraction of sugar solution:

The washed beet roots are cut to be V-shaped slices. This is called

as coselites. The crude sugar solution is extracted from coselites. It is passed into a series of large tanks called diffusers. Hot water is pumped through these tanks. The extraction is conducted on counter current principle. Sugar is removed from beet root by two fold process.

1) Leaching: it means washing out sugar with water.

2) Dialysis: The sugar solution is passed through the cell wall membrane and leaves the larger colloidal material.

### Fermentation:

Big molecules of organic compound are slowly decomposed into simpler ones under catalytic influence of non-living complex substance or yeast called ferment. The phenomenon is called as fermentation since a number of ferments present in yeast they are also called enzymes. Yeast is a single celled living plant.

## Manufacture of spirit from molasses:

Molasses is the mother liquor left after the crystallization of cane sugar from the concentrated juice. It is dark coloured thick syrup mass. Molasses contain about 30% sucrose which cannot be separated by crystallization. It is converted to spirit by the following steps.

### i) Dilution:

Molasses is first diluted with water to bring down the concentration of sugar to about 8 to 10 percent.

### ii) Addition of ammonium salts:

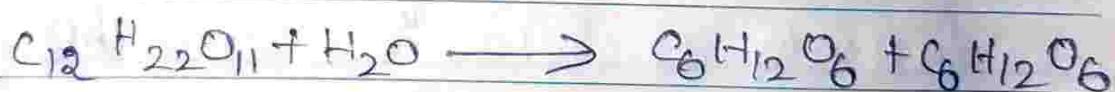
Molasses usually contains enough nitrogenous matter to act as food for yeast during fermentation. If the nitrogen content of the molasses is poor, it may be fortified by the addition of ammonium sulphate or ammonium phosphate.

### iii) Addition of sulphuric acid:

The solution is then made acidic with small amount of sulphuric acid. Acidity is favourable to the growth of yeast but unfavourable to most other bacteria. care should be taken to avoid excess of acid as the yeast may be killed.

### iv) Addition of yeast:

The solution from step (ii) is collected in large fermentation tanks and yeast is added to it. The mixture is kept at about 303K for a few days. During this period the enzymes invertase and zymase present in yeast bring about the conversion of sucrose into ethanol.



The fermented liquid is technically called wash.

### v) Distillation of wash:

The fermented liquid

containing 15 to 18 percent alcohol and the rest of the water is now subjected to fractional distillation. The main fraction drawn is an aqueous solution of ethanol which contains 95.5% of ethanol and 4.5% of water. This is called rectified spirit.

### Manufacture of wine from grapes:

Raw material : Grapes.

Manufacturing Steps:

D) Extraction of juice :

The grapes are crushed by wooden rollers called crushers. The crusher macerates them, but does not crush the seeds. Some of the stems are removed. The juice extracted from the grapes is called must. The grape juice containing glucose, fructose and

to

tartaric acid. The skin of grapes contains tannin various essential oils and there may be colouring matter

### 2) Fermentation:

The must is passed into a large tank and sulphurous acid is added to check the wild yeast. An active culture of selective and cultivated yeast is added. The active fermentation is allowed proceed at the temperature about  $85^{\circ}\text{F}$ . The  $\text{CO}_2$  gas is liberated as a result of conversion of glucose into alcohol. The  $\text{CO}_2$  gas carries the stems and seed to top. This allows extraction of the colour and the tannin from the skin and seeds.

### 3) Clarification:

After the active fermentation the juice is pumped into a loosely large tank. This is prevented the conversion of alcohol to acetic acid. The juice is stored for several month. The yeast ferments the remainder of the sugar and wine is formed.

During this period, yeast settles down tartaric acid, various salts and colouring matters separates out. The wine is allowed to cellar treatment and stand for about 2 month, Hence the suspended matter are removed

An insoluble precipitates with tannin is formed. extra tannin is added and filtered through asbestos. The resulting clarified wine is blended with other wines, sugar, acid and tannin in order to maintain commercial standard.

### Chilling:

Argot or potassium hydrogen tartrate is removed from the wine by chilling method. As a result a more finished wine is obtained

### Ageing:

Good sweet wine is obtained by ageing method in about 4 month.

pasteurization, refrigeration; sunlight, ultraviolet ozone, agitation and aeration are various ageing methods.

### b) freezing:

The wine may be kept at about freezing for 3-4 weeks and oxygen is passed through it. The wine is then racked, clarified and filtered.

Wines are classified as natural wine - alcohol 7-14% fortified wine - alcohol 14-30%. sweet or dry wine and still or sparkling wine

### Manufacture of ethanol from molasses (By distillation)

Molasses is the mother liquor left after the crystallization of cane sugar from the concentrated juice. It is dark coloured thick syrup mass. Molasses contain about 60% cane sugar, mostly sucrose glucose and fructose. It forms an industrial ethyl alcohol. Molasses is converted into alcohol.

### i) Dilution:

Molasses is first diluted with water to bring down the concentration of sugar to about 8 to 10 percent.

### ii) Addition of sulphuric acid:

The solution is then made acidic with a small amount of sulphuric acid. Acidity is favourable to the growth of yeast but unfavourable to most other bacteria. Care should be taken to avoid excess of acid as the yeast may be killed.

### iv) Addition of yeast:

The solution from step (i) is collected in large fermentation tanks and yeast added to it. The mixture is kept at about 30°C for a few days. During this period enzymes Invertase and Zymase present in yeast, bring about the conversion of sucrose into ethanol.



The fermented liquid is technically called wash. It contains 15 to 18 percent alcohol.

### V) Distillation of wash:

The wash is distilled in a specially designed continuous still called Coffey still. It consists of two tall fractionating columns. These are analyser and rectifier. These are provided with perforated horizontal plates and valves opening upwards. The Coffey still works on the counter current principle. The steam and alcohol travel in opposite direction through the still.

The wash is pumped to the Coffey still and then it is passed into heat exchanger. A current steam is passed from the lower end of the analyser. Steam moves up the analyser and takes the vapours of alcohol from the down coming wash.

The mixture of alcohol and vapours leaves the analyser at the top end. It enters into the rectifier. Here the steam is condensed because of higher boiling point ( $100^{\circ}\text{C}$ ) than that of ethanol ( $78.3^{\circ}\text{C}$ ). The uncondensed vapours escape near the top. It is condensed with the help of a condenser. The 90% pure alcohol is obtained. It is subjected to fractional distillation.

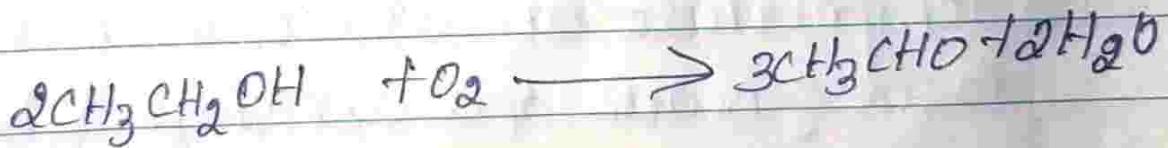
The fractions are given below

- i) The first fractions contain low boiling liquids like acetaldehyde.
- ii) The second fraction contains 95% ethanol called rectified spirit or industrial alcohol. This mixture is heated under reflux over quick lime for about 5 to 6 hours and then allowed to stand for 12 hours. On distillation of this mixture pure alcohol ( $100\%$ ) is obtained and called absolute alcohol.

iii) The last high boiling fraction (125-145°C) contain fusel oil. It consists mainly in amyl alcohol.

Manufacture of vinegar by Quick vinegar process:

Quick vinegar process is limited to production of vinegar for food industry. Vinegar is 4-6% acetic acid. It is obtained from fermented liquor containing 12-15% ethanol. The aqueous solution of ethanol in contact with air and under influence of bacterium acetic produces acetic acid.



Manufacturing steps:

D In the Quick vinegar process large wooden vats filled with wood shavings impregnated with old vinegar (bacterium)

are used in series.

- 2) The vats are fitted with a perforated cover. ethanol is introduced at the top of the first vat and allowed to trickle down the shaving.
- 3) Air is drawn in through the holes in the lower walls of the vessel and passes up in the opposite direction to the trickling liquid.
- 4) The heat generated in the oxidation of ethanol to acetic acid maintains the temperature at  $35^{\circ}\text{C}$  which is favourable to the growth and activity of bacteria.
- 5) The liquor leaving the bottom of each vat is introduced at top of the next vat.
- 6) The maximum concentration of acetic acid obtained by the method is 10%. The process requires 8-10 days for completion.

- 3) Balrampur chini mills Ltd. West bengal
- 4) Banmi amman Spining mill's Ltd west bengal
- 5) Palmia bharat sugar & Industries Ltd

Match Industries:

Manufacture of matches:

Raw materials:

- i) White pine or aspen woods
- ii) Ammonium phosphate
- iii) paraffin wax
- iv) potassium chlorate
- v) animal glue
- vi) antimony tri sulphide
- vii) Sulphur
- viii) powdered glass
- ix) Inert fillers
- x Red phosphorus, white
- xi adhesives such as gum arabic or urea formaldehyde

## Manufacture of Match stick:

### i) cutting the match sticks:

Logs of white pine or aspen are cut into short length about 0.5m by the debarking machine. The stripped log is placed in a peeler it cut into a sheet about 0.1 inch thick called veneer. The veneer glassed into chopper. it cuts into small sticks.

### 2) Treating of match sticks:

The cut match sticks are soaked with a dilute solution of ammonium phosphate for several days retardant. the dried stick are stored in large tank.

### 3) forming of match heads:

The stored sticks are transferred into holes on a long, continuous perforated steel belt. The perforated belt

wax and dried. paraffin provides a fuel to the match stick.

This fuel transfers the flame from the burning chemicals to the match stick. further the match sticks are dipped in solution of match head base chemicals. The base solution contains a mixture of potassium chlorate and small amount of phosphorus sesquisulphide. it also contains sulphur, rosin and a small amount of paraffin wax. A water soluble dye may be added to give the base ~~of~~ a colour such as red or blue.

Further the match sticks are dipped in tip solution. These increase the friction and control burning rate. Zinc oxide may be added and coated the matches are dried slowly.

## pyrotechnics:

Pyrotechnics refers to making fire by chemical reaction. It produces light, heat, noise or gases. It is done by combustion of a fuel and an oxidiser. In pyrotechnics the combustion process is instantaneous.

### uses:

- 1) Crackers and sparklers are used for commercial purposes
- 2) Coloured bombs are used for military signals.

## Unit - V

### ADHESIVES, ENAMELS AND EXPLOSIVES

#### Adhesives:-

An adhesive can be defined as any substance capable of holding materials together by surface attachment.

Classification of adhesives:- The broad classes of adhesives and their brief description are given below.

#### Animal glue:- Preparation:-

(1) Animal glue is prepared from the bones of dead animals, wastes of animals, wastes of Slaughter-houses and scrapes from leather industry.

(2) The waste is first purified by lime. It is degreased by adding benzene.

(3) It is treated with acid to remove Calcium phosphate.

(4) The product is hydrolysed by hot water to get liquor glue.

(5) The liquor glue is filtered and then bleached with  $\text{SO}_2$ .

(6) It is mixed with borax, formaldehyde (preservative) and concentrated.

(7) The concentrated liquor is allowed to cool.

(8) cakes of glue are precipitated.

(9) The cakes are dried and cut into flakes or powdered.

(10) For using, cakes or flakes or powder is boiled with water to get a jelly-like mass, which is then applied.

Uses:- (1) Animal glues are used in manufacturing furniture.  
(2) It is used in radio-cabinets and card-boxes etc.

Protein adhesives:-

Preparation:- Protein adhesives are prepared from soyabean, corn, casein albumin, Peanut etc..

(1) Soyabean glue:- Dry soya beans are crushed to extract oil. The left over material is then mixed with milk of lime ( $\text{Ca(OH)}_2$ ) and caustic soda ( $\text{NaOH}$ ) to form jelly like adhesive Paste.

(2) Casein glue:- Skinned milk is curdled with dilute acid. The solid casein is precipitated and dried and mixed with lime and preservative. The casein is powdered. It mixed with water to form jelly-like adhesive Paste.

Uses:- (1) Casein adhesives are used in wood work industry.

(2) Casein adhesives are used in the manufacture of drinking cups, straws and ice cream containers.

(3) Soyabean adhesives are used in combination in veneer field.

Starch adhesives:-

Preparation

Required Materials:-

- (i) Starch - 100 Parts
- (ii) water - 200 Parts
- (iii) caustic lye - 25 Parts

(iv) Borax - 0.14 parts

(v) HCl - 5 parts.

Starch is boiled with hot water and caustic lye is added slowly. After one and a half hours borax as well as acid is added slowly. Now the paste is placed in slightly alkaline urea to lower the viscosity of the paste. The pH of the liquor is adjusted by adding monosodium phosphate.

Uses:-  
1) It is used for manufacturing of envelopes and stamps.

2) It is used for manufacturing of note books, binding books and other paper goods.

3) It is used for sealing of wrappes, wood bonding wall paper etc.

### Enamels:- INTRODUCTION:

Enamel is hard and glossy coating applied on wares for decorative and protective purposes. The enamels used to coat the metal surface are known as porcelain enamel. Porcelain enamel is a ceramic mixture containing a large proportion of fluxes. All porcelain enamels are opaque. They are either white or coloured. It is fused on the metal surface at moderate red heat. Opaque and white or coloured metal surface is formed. The enamelled metal is easy to clean and resist corrosion.

### Raw Materials:-

Raw materials used in enamels may be six types. These are

(1) Refractories:- Refractories contribute to acidic part of the melt. It gives body to glass. clay, feldspars & quartz are used for this purpose.

(2) fluxes:- Fluxes are basic in character. They react with acidic refractories to form the glass. They decrease the fusion temperature of the enamels. Example:- borax, soda ash, eniolite and fluorspar.

(3) opacifiers:- opacifiers are compounds which are added to the glass to give white appearance. Insoluble opacifiers -  $TiO_2$ ,  $SnO_2$  and  $ZnO$ ; Delustrification opacifiers - eniolite and feldspar.

(4) colours:- Metal oxides, elements, salts and salts are used as colouring materials.

(5) floating agent:- The clay has a dual role.

It acts as a floating agent to suspend the enamel in water or as the body forming agent.

(6) electrolytes:- Borax, Soda ash, magnesium sulphate, Magnesium carbonate are used as electrolytes. It peptizes the clay and keeps suspended in the enamel.

Application:-

The enamel is applied on the metal surface in two coats by dry or wet process. Before the liquid enamel is applied to the metal, the surface is cleaned thoroughly.

In the Wet Process, the surface with single coating is again slip coated, dried and refined.

In dry process, a ground mixture of frit, clay, opacifiers and colours is poured uniformly on the hot first coating. The article is refined finally after applying the mixture of ingredients.

After drying, the slip coated articles are fired. Hence the enamel melts on the ware into a smooth continuous and glossy layer. The requirements for a successful firing of good enamel are:

1. Proper support of the ware
2. Uniform cooling and heating of the ware.
3. Proper firing temperature -  
160 to 850°C.
4. Proper time of firing - 1 to 15 min
5. An atmosphere free from dust.

Uses:- Enamel wares are applied in the field of refrigerators, dairy equipments, food processing equipments, hospital furniture, mobile cars, stationary wares etc.,

### Explosives:-

Definition:- An explosive is defined as a material which under the influence of thermal or mechanical shock decomposes rapidly and spontaneously with the evolution of a great amount of heat and large volume of gases.

## Classification of explosives:-

Explosives are classified into three types. These are primary explosives, low explosives & high explosives.

### Primary or Initiating explosives:-

- (1) These are inorganic salts.
- (2) They are highly sensitive.
- (3) It explodes on receiving a small shock or fire.
- (4) They should be handled with the utmost care.
- (5) It is used to initiate the explosion of the main explosives.
- (6) It is less sensitive compared to the main explosives.
- (7) Example: lead azide, mercury fulminate, diazodinitrophenol, picromannite.

### (b) Low explosives or Propellants:-

- (1) They burn and do not explode.
- (2) The action of low explosive is less shattering.
- (3) They evolve large volume of gas on combustion in a definite and controlled manner.
- (4) These are used in the cartridge cases of rifles, pistols etc.

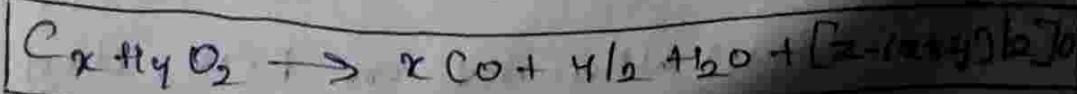
- (5) Example: colloidal cellulose nitrate.

### (c) Secondary or high explosives:-

- (1) These are organic materials.
- (2) These are quite insensitive to flame and mechanical shock.
- (3) They explode violently.
- (4) The action of high explosive is rapid shattering.
- (5) Example:- TNT, Picric acid, dinitramine.

### Characteristics of an explosive:-

- (1) The rate of decomposition should be fast. It should produce a large volume of gaseous products exothermically.
- (2) It should be cheap and stable under normal condition. Stability of an explosive is determined by its decomposition point by DTA.
- (3) It should have lower energy of dissociation. Usually, explosive molecules contain N-N, N-O, N-Cl and O-O bonds. The difference in electronegativities in this case is zero or very small.
- (4) It should have a positive oxygen balance. The oxygen balance indicates the oxygen present in the molecule. This oxygen is utilised to oxidise the C and H to form  $H_2O$  respectively. Percentage of oxygen in  $C_xH_yO_z$  molecules is given below.

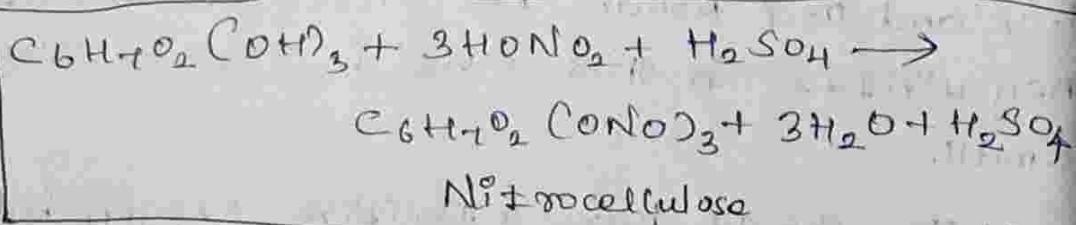


$$\% \text{ of Oxygen balance} = \frac{[2 - (x + y/2)] \times 16 \times 100}{\text{Mol. wt. of } C_x H_y O_z}$$

### Nitrocellulose or cellulose nitrate:

#### Preparation:-

Cellulose nitrate is prepared from cotton linters which are purified by boiling in kiers with a dilute solution of caustic soda. Now the cotton linters are free from dust, natural oil and non-cellulose. It is bleached with  $Ca(OH)_2$ . The bleached linters are dried and weighed. The bleached and dried cotton linters are heated with the mixes of 21.1.  $HNO_3$ , 63.1.  $H_2SO_4$ , 0.5 %  $N_2O_4$  and 5.5 l. of water at  $30^\circ C$  for about 2-2.5 hours in a mechanical dipper nitrator. The excess of nitrating mixture is centrifuged from nitrated cotton. The nitrated cotton is washed and boiled with  $H_2O$ . This gives a more stable nitrocellulose.



The nitrocellulose contains about 12.6%. nitrogen is called pyrocotton. Cotton nitrated to contain 13.2-1.0% more nitrogen is known as gun cotton.

#### Properties:-

- (1) When set on fire, dry gun-

cotton explodes rapidly.

(2) When wet, it is set-off by a small amount of another explosive. Mercury fulminate is commonly employed.

(3) Dry gun-cotton is ignited by shock.

(4) Military smokeless powders are prepared from a blend of Pyrodinitro and gun cotton. It contains about 13.15% nitrogen.

Uses:-

(1) Dry gun-cotton in fibre form is used in torpedoes and submarine mines.

(2) It is used as propellant in rifles or artillery shells.

(3) It is used for forming granules of particular shape and size.

(4) Nitrocellulose is used for the preparation of military smokeless powder.

Dinitro acid:-

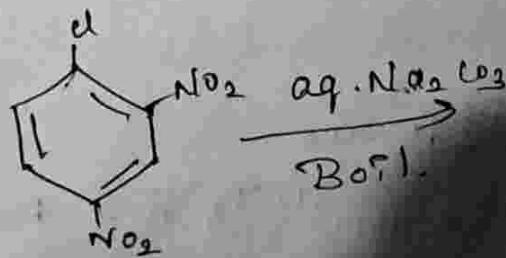
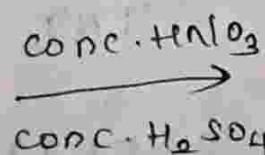
Preparation:-

Chlorobenzene is treated with a mixture of conc.  $\text{HNO}_3$  and conc.  $\text{H}_2\text{SO}_4$ .

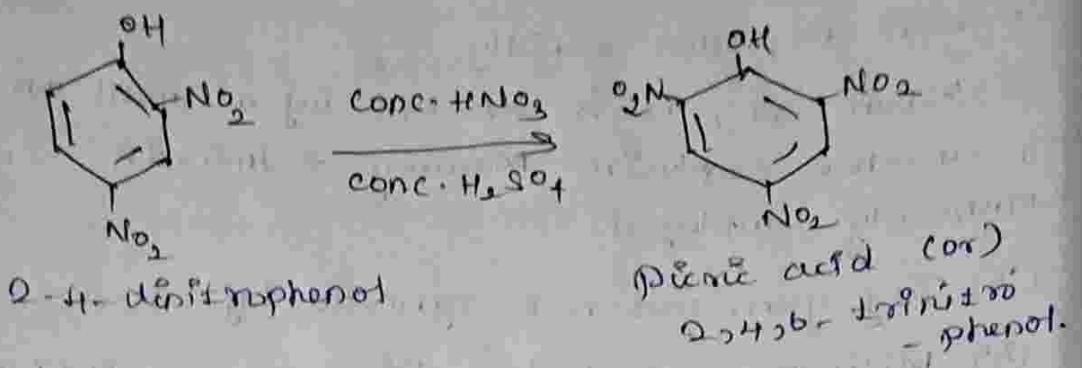
2,4-dinitrochlorobenzene is formed. It is boiled with aqueous sodium carbonate solution. 2,4-dinitrophenol is formed. It is treated with conc.  $\text{HNO}_3$  and conc.  $\text{H}_2\text{SO}_4$  to give Dinitro acid.



Chlorobenzene



2,4-dinitrobenzene



### Properties:-

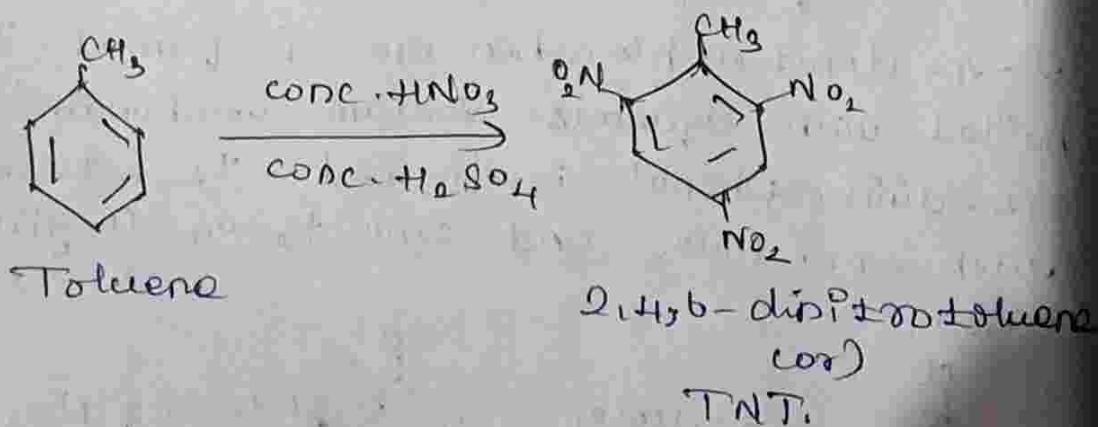
(1) Picric acid is a high explosive.

(2) It explodes violently.

Trinitrotoluene (TNT) or 2,4,6-trinitrotoluene

### Preparation:-

TNT is prepared by the nitration of toluene using a nitrating mixture of conc.  $\text{HNO}_3$  and conc.  $\text{H}_2\text{SO}_4$  in 1:1 ratio in tank reactor. These contents are stirred continuously. Liquid TNT is formed. It is washed with ammonical solution of sodium sulphide. It is passed into cold water. TNT crystallizes out. Crystals of TNT are filtered and purified by melting. The melt is dried and poured in containers.

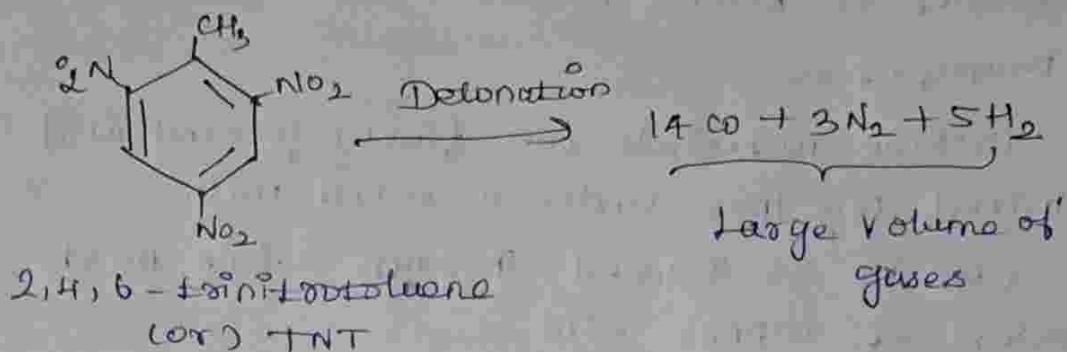


### Properties:-

(1) It is a faint yellow crystalline solid.

(2) It is a high explosive.  
(3) TNT is superior to picric acid because of its low melting point ( $81^{\circ}\text{C}$ )

(4) TNT has enough Oxygen for internal combustion. Hence, it explodes violently on detonation and liberates large volume of gases.



(5) It is safe explosives, requiring strong detonation to set it off.

Uses:-

(1) It is used in shell firing and under water explosions.

(2) It is used for filling bomb shells, hand grenades and torpedoes alone or with other explosives.

(3) TNT is mixed with ammonium nitrate, it forms the blasting material amatol which is used for demolishing old buildings and rocks.

(4) It is used for demolishing loading in containers because of its low boiling point.

(5) It is important in military because

(i). It is safe explosive in manufacture, transportation and storage.

(ii) It is non-hygroscopic.

(iii) It is a violent disruptive explosive.

(iv) It does not react with metals to form unstable compounds.

### Gun Powder or black powder:-

An intimate mixture of  $KNO_3$ , Charcoal and sulphur is known as gun powder or black powder.

#### Manufacture:-

- (1) Raw materials are finely ground and mixed together under a wheel mill.
- (2) It is passed through a fine mesh sieve of copper wire.
- (3) The mixture is converted to moist state in a mill under heavy edge pressure.
  - (A) The cake is obtained. It is broken up into small pieces which are subjected to a pressure of about 400 psi.
  - (B) A hard mass is obtained. It is granulated by rollers. The resulting grains are polished in rotating wooden drums and added small amount of graphite.
  - (C) The obtained gun powder is dried at  $40^\circ C$ .

#### Properties:-

- (1) It is very cheap.
- (2) It is high lifting power and produces large blocks on quarrying.
- (3) Destructive power of gun powder is low compared to dynamite.

(i) Efficiency of gun powder is comparatively lower than dynamite.

Uses:- It is used in quarrying stones.

Cordite:-

Cordite is prepared by mixing a paste of 65.1 Nitrocellulose, 30.1 Nitroglycerin and 5.1 Vaseline with acetone. The mixture is forced by hydraulic pressure and formed a thread or cord like material. Hence the name is cordite. Acetone is evaporated from cordite to form the horny cordite.

Properties:-

- (1) cordite is very sensitive to shock.
- (2) It is easy to handle.

Uses:- It is excellent propellant for large calibre naval guns.

Dynamite:-

Original dynamite is a mixture of 15.1 nitroglycerin and 25.1 kieselguhr. Modern dynamites use wood flour, ammonium nitrate or sodium nitrate as the absorbing agents of nitroglycerin. An oxidizer is added sometimes.

Dynamite is easy to handle.

Properties:- (1) It is a high explosive.

(2) It is costlier than gun powder.

(3) It has high shattering power and produces small blocks on quarrying.

- (4) Destructive Power of dynamite is high compared to gun powder.
- (5) Efficiency of dynamite is comparatively larger than gun powder.
- uses:- It is used for rock blasting and gold mining.