

## ORGANOMETALLIC COMPOUNDS

Organometallic compounds are those “*compounds in which central metal atoms are directly bonded with the carbon atoms of the hydrocarbon radical or molecule*”.or

An Organometallic compound is defined as *one that posses a metal-carbon bond*. The term “Organometallic” generally denotes compound in which organic groups are directly linked to the metal through at least one carbon atom.

The bonding is ionic or covalent or delocalised between organic groups and a metal atom.

Simple organometallic compounds are one which a metal-carbon bond which is typically similar with respect to the derivative of associated constituent.

Further divided in to

a) Symmetrical: Example: [ Hg (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>] Diethyl mercury

b) Unsymmetrical : Example: CH<sub>3</sub>-Hg-C<sub>2</sub>H<sub>5</sub> Ethyl methyl mercury

A mixed organometallic compounds are those in which a metal atom bonded with more than one identity of organic or inorganic constituent.

Example: C<sub>2</sub>H<sub>5</sub>-Mg-Br Ethylmagnesiumbromide

### Classification of organometallic compounds:

On this basis of nature of metal- carbon bond organometallic compounds are classified in to

#### ✧ **Ionic bonded organometallic compounds:**

The organometallic compounds of alkali, alkaline earth metals, Lanthanides and Actinides are predominantly form ionic compounds. These are generally colourless compounds extremely reactive, non-volatile solids and insoluble in organic solvents.

Examples: Ph<sub>3</sub>C<sup>+</sup>Na<sup>-</sup>, Cp<sub>2</sub>Ca, Cs<sup>+</sup>Me<sup>-</sup>, Na<sup>+</sup>Cp<sup>-</sup>.

#### ✧ **Covalent bonded organometallic compounds:**

##### 1) **σ- bonded organometallic compounds:**

These are the compounds in which carbon atom of the organic ligand is bonded to the metal by a 2 electron, 2 centred ( 2e-2c ) covalent bond. Generally formed by most of the elements with values of electronegativity are higher than 1.

Examples: Ni(CO)<sub>4</sub>, Fe(CO)<sub>5</sub>

##### 2) **π- bonded organometallic compounds:**

These are alkene, alkyne or some other carbon group has a system of electron in π-orbitals overlap of these π- orbitals with vacant orbitals of the metal atom gives rise to arrangement in which the metal atom is bonded to several carbon atom instead of to one.

Examples:[(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe], K[PtCl<sub>3</sub>(η<sup>2</sup>-C<sub>2</sub>H<sub>2</sub>)] (Zeise's salt)

#### ✧ **Multicentre bonded organometallic compounds:**

The compounds in which a loosely bonded electron deficient species exist with the coordination of metal like Li,Be,Al...etc

Examples: MeLi or (CH<sub>3</sub>)<sub>4</sub>Li<sub>4</sub>, Al<sub>2</sub>Me<sub>6</sub>

### Classification of ligands based on hapticity:

In hapto classification organic ligands are classified according to “*number of carbon atoms within a bonding distance of metal atom or the no. of carbon atoms through which an organic ligand is attached to central metal atom*” is known as “hapticity” of the ligand.

This is represented by the symbol “η<sup>n</sup>” appearing before the symbol of the ligand.

Where, n- hapticity of the ligand.

Monohepto ligands (η<sup>1</sup>): Organic ligands attached to the metal through one carbon.Ex: -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>

Dihepto ligands (η<sup>2</sup>) : Example: CH<sub>2</sub>=CH<sub>2</sub>, K[PtCl<sub>3</sub>(η<sup>2</sup>-C<sub>2</sub>H<sub>2</sub>)] (Zeise's salt)

Trihepto ligands (η<sup>3</sup>): Example:Allylic radical CH<sub>2</sub>=CH-CH<sub>2</sub>-

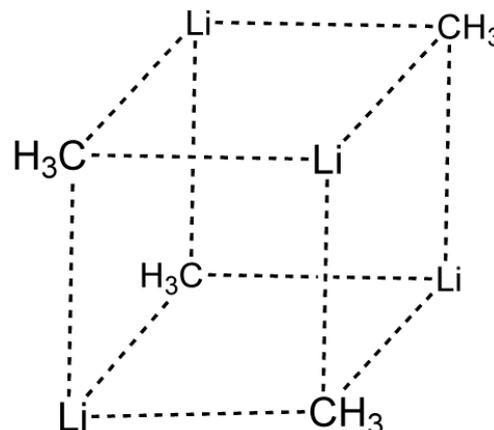
Tetrahepto ligands (η<sup>4</sup>): Example: Butadiene CH<sub>2</sub>=CH-CH= CH<sub>2</sub>

Pentahepto ligands (η<sup>5</sup>): Example: Metallocene M (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>

Hexahepto ligands (η<sup>6</sup>): Example: Dibenzene ChromiumCr(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>

## Structure of Methyl Lithium:

- ❖  $\text{CH}_3\text{Li}$  in nonpolar solvents consists of tetrahedron of Li atoms with each face bridged by a methyl group.
- ❖ The bonding in  $\text{CH}_3\text{Li}$  consists of a set of localized molecular orbitals. The symmetric combination of three Li 2s orbitals on each face of the  $\text{Li}_4$  tetrahedron and one  $\text{sp}^3$  hybrid orbital from  $\text{CH}_3$  gives an orbital that can accommodate a pair of electron to form a 4c-2e bond.
- ❖ The lower energy of the C - orbital compared with the Li orbitals indicates that the bonding pair of electrons will be associated primarily with the  $\text{CH}_3$  group, thus supporting the carbanionic character of the molecule.
- ❖ Some analysis has indicated that about 90% ionic character for the Li- $\text{CH}_3$  interaction.



## Structure of Zeise's salt :

### $\text{K}[\text{PtCl}_3(\eta^2\text{-CH}_2=\text{CH}_2)]$ :-Potassiumtrichloro(ethene)platinate(II)

- 1) Zeise's salt was the first organometallic compound to be isolated in pure form (1825 by William Zeise). It is a square planar complex with 16 electrons.
- 2) The  $\pi$ -acid ligand donates electron density into a metal d-orbital. The metal donates electrons back from a filled d-orbital into the empty  $\pi^*$  antibonding orbital of the ligand (hence the description  $\pi$ -acid ligand). Both of these effects tend to reduce the C-C bond order, leading to an elongated C-C distance.
- 3) The interaction can cause carbon atoms to "rehybridize" from  $\text{sp}^2$  towards  $\text{sp}^3$ , which is indicated by the bending of the hydrogen atoms on the ethylene back away from the metal.
- 4) The Pt-Cl bond trans to the ethylene group is significantly longer than the cis- Pt-Cl bonds.
- 5) The C-C distance, 1.375 Å, is slightly longer than the value found in free ethylene (1.337 Å), indicating some  $\text{d}\pi\text{-p}\pi^*$  back-bonding from the platinum atom to  $\text{C}_2\text{H}_4$ .
- 6) Back-bonding is also indicated by a bending of the four hydrogen atoms away from the Pt atom.

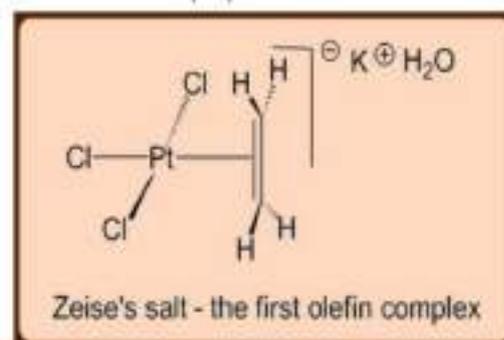
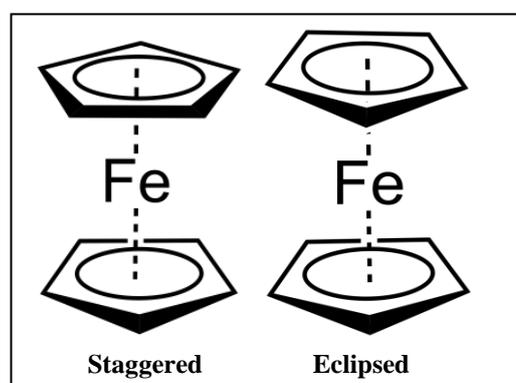


Figure 1. Zeise's salt.

## Structure of ferrocene

### $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$ :- bis( $\eta^5$ -cyclopentadienyl) iron(II)

1. Ferrocene is known as a "sandwich" compound.
2. It occurs as highly stable orange crystals with a melting point of 174° C.
3. In solid state at low temperature, the rings are staggered.
4. The rotational barrier is very small, with free rotation of the rings.
5. Extremely low temperature that is Below 110 K, the Cp rings are ordered and eclipsed.
6. Terms of bonding, the iron center in ferrocene is usually assigned to the +2 oxidation state.
7. Each cyclopentadienyl (Cp) ring is then allocated a single negative charge, bringing the number of  $\pi$ -electrons on each ring to six, and thus making them aromatic.
8. These twelve electrons (six from each ring) are then shared with the metal via covalent bonding. When combined with the six d-electrons on  $\text{Fe}^{2+}$ , the complex attains an 18-electron configuration.



## Metal Carbonyls

Metal Complexes in which Carbon monoxide as a ligand are called metal carbonyls

Example: Cr(CO)<sub>6</sub>, Fe(CO)<sub>5</sub>.

### EAN Rule:

*“The sum of the electrons on the central metal atom or ion and the electrons donated from the ligands in a complex compound is called the effective atomic number (EAN) of the metal and for stable complexes it is generally equal to the atomic number of next incoming noble gas.”*

$$\text{EAN} = \text{No. of electrons in the central metal atom or ion} + \text{No. of electrons donated by ligands}$$

**Note:** An alternative and more general statement can be given instead of EAN rule as follows: *“When the central metal ion or atom of a complex compound acquires noble gas electronic configuration (n-1)d<sup>10</sup> ns<sup>2</sup> np<sup>6</sup> there will be 18 electrons in the valence orbitals (or valence shell) and the electronic configuration will be closed and stable.”* It is known as the 18-electron rule.

The complexes obeying the 18-electron rule are quite stable. 18-Electron rule applied to metal carbonyls. The 18 – electron rule is very useful in predicting stabilities and structures of organometallic compounds.

❖ **There are two conventions for counting electrons in complexes:**

#### a) Neutral atom or covalent model;

According to the covalent model there is covalent bond between Co and H atoms in HCo(CO)<sub>4</sub> and H atom acts as 1e<sup>-</sup> donor ligand. Accordingly, no. of electrons in valence shell of Co in HCo(CO)<sub>4</sub> = 9(Co) + 4x2(CO) + 1x1(H) = 18.

#### b) Oxidation state or ionic model:

According to the ionic model there is ionic bond between (OC)<sub>4</sub>Co<sup>+</sup> and H<sup>-</sup> ions and H<sup>-</sup> ion acts as 2e<sup>-</sup> donor ligand. Accordingly, no. of electrons in valence shell of Co in HCo(CO)<sub>4</sub> = 8(Co<sup>+</sup>) + 4x2(CO) + 1x2(H<sup>-</sup>) = 18

### The steps are generally followed for counting the electrons present in the valence shell of central metal in a metal carbonyl.

- i) The electrons present in the valence shell [i.e., (n-1)d, ns and np orbitals] of the central metal atom are counted and then electrons are added to it or subtracted from it depending upon the nature of charge (negative or positive) present on it in the metal carbonyl.
- ii) Each terminal carbonyl group contributes 2e to the valence shell of the central metal.
- iii) The bridging carbonyl group (M – CO – M) contributes 1e to the valence shell of each metal atom attached by it.
- iv) The metal-metal (M – M) bond contributes 1e to the valence shell of each metal atom.

### Some examples of electron counts in the metal carbonyls:

Sl. No	Compound	EAN		18 e <sup>-</sup>		Stability
		count	No. Of e <sup>-</sup>	Count	No. Of e <sup>-</sup>	
1	Ti(CO) <sub>6</sub>	Total no. of e <sup>-</sup>	22	Total no. Of Valence e <sup>-</sup>	04	Unstable
		6CO×2e <sup>-</sup>	12	6CO×2e <sup>-</sup>	12	
		<b>Total</b>	<b>34</b>	<b>Total</b>	<b>16</b>	
2	V(CO) <sub>6</sub>	Total no. of e <sup>-</sup>	23	Total no. Of Valence e <sup>-</sup>	05	Stable (exception)
		6CO×2e <sup>-</sup>	12	6CO×2e <sup>-</sup>	12	
		<b>Total</b>	<b>35</b>	<b>Total</b>	<b>17</b>	
3	[V(CO) <sub>6</sub> ] <sup>-</sup>	Total no. of e <sup>-</sup>	23	Total no. Of Valence e <sup>-</sup>	05	Stable anion
		6CO×2e <sup>-</sup>	12	6CO×2e <sup>-</sup>	12	
		Charge	01	Charge	01	
		<b>Total</b>	<b>36</b>	<b>Total</b>	<b>18</b>	

4	$\text{Cr}(\text{CO})_6$	Total no. of $e^-$	24	Total no. Of Valence $e^-$	06	Stable
		$6\text{CO} \times 2e^-$	12	$6\text{CO} \times 2e^-$	12	
		<b>Total</b>	<b>36</b>	<b>Total</b>	<b>18</b>	
5	$[\text{Mn}(\text{CO})_5]^-$	Total no. of $e^-$	25	Total no. Of Valence $e^-$	07	Stable anion
		$5\text{CO} \times 2e^-$	10	$5\text{CO} \times 2e^-$	10	
		Charge	01	Charge	01	
		<b>Total</b>	<b>36</b>	<b>Total</b>	<b>18</b>	
6	$\text{Mn}_2(\text{CO})_{10}$ For each Mn	Total no. of $e^-$ $2\text{Mn} \times 25$	50	Total no. Of valence $e^-$ $2\text{Mn} \times 07$	14	Stable
		$10\text{CO} \times 2e^-$	20	$10\text{CO} \times 2e^-$	20	
		$1\text{Mn-Mn bond} \times 2e^-$	02	$1\text{Mn-Mn bond} \times 2e^-$	02	
		<b>Total</b>	<b><math>72/2=36</math></b>	<b>Total</b>	<b><math>36/2=18</math></b>	
7	$[\text{Fe}(\text{CO})_4]^{2-}$	Total no. of $e^-$	26	Total no. Of Valence $e^-$	08	Stable anion
		$4\text{CO} \times 2e^-$	08	$4\text{CO} \times 2e^-$	08	
		Charge	02	Charge	02	
		<b>Total</b>	<b>36</b>	<b>Total</b>	<b>18</b>	
8	$\text{Fe}(\text{CO})_5$	Total no. of $e^-$	26	Total no. Of Valence $e^-$	08	Stable
		$5\text{CO} \times 2e^-$	10	$5\text{CO} \times 2e^-$	10	
		<b>Total</b>	<b>36</b>	<b>Total</b>	<b>18</b>	
9	$\text{Fe}_2(\text{CO})_9$ For each Fe	Total no. of $e^-$ $2\text{Fe} \times 26$	52	Total no. Of Valence $e^-$ $2\text{Fe} \times 08$	16	Stable
		$6\text{CO} \times 2e^-$	12	$6\text{CO} \times 2e^-$	12	
		$3\text{CO (bridge)} \times 2e^-$	06	$3\text{CO (bridge)} \times 2e^-$	06	
		$1\text{Fe-Fe bond} \times 2e^-$	02	$1\text{Fe-Fe bond} \times 2e^-$	02	
		<b>Total</b>	<b><math>72/2=36</math></b>	<b>Total</b>	<b><math>36/2=18</math></b>	
10	$[\text{Co}(\text{CO})_4]^-$	Total no. of $e^-$	27	Total no. Of Valence $e^-$	09	Stable anion
		$4\text{CO} \times 2e^-$	08	$4\text{CO} \times 2e^-$	08	
		Charge	01	Charge	01	
		<b>Total</b>	<b>36</b>	<b>Total</b>	<b>18</b>	
11	$\text{Co}_2(\text{CO})_8$ For each Co	Total no. of $e^-$ $2\text{Co} \times 27$	54	Total no. Of Valence $e^-$ $2\text{Co} \times 09$	18	Stable
		$6\text{CO} \times 2e^-$	12	$6\text{CO} \times 2e^-$	12	
		$1\text{Co-Co bond} \times 2e^-$	02	$1\text{Co-Co bond} \times 2e^-$	02	
		$2\text{CO (bridge)} \times 2e^-$	04	$2\text{CO (bridge)} \times 2e^-$	04	
		<b>Total</b>	<b><math>72/2=36</math></b>	<b>Total</b>	<b><math>36/2=18</math></b>	
12	$\text{Ni}(\text{CO})_4$	Total no. of $e^-$	28	Total no. Of Valence $e^-$	10	Stable
		$4\text{CO} \times 2e^-$	08	$4\text{CO} \times 2e^-$	08	
		<b>Total</b>	<b>36</b>	<b>Total</b>	<b>18</b>	

**Limitation of EAN rule:**

- 1) This rule not obeyed by Square planar organometallic complexes of the late transition metals.
- 2) This rule not obeyed by some organometallic complexes of the early transition metals.
- 3) Some high valent  $d^0$  complexes have a lower electron count.
- 4) Sterically demanding bulky ligands force complexes to have less electrons than EAN.
- 5) The EAN rule fails when bonding of organometallic clusters of moderate to big sizes (6 Metal).
- 6) The rule is not applicable to organometallic compounds of main group metals as well as to those of lanthanide and actinide metals.
- 7) Counting the electrons helps to predict stability of metal carbonyls. But it will not tell you whether a CO is bridging or terminal.

**On the basis of number of metal atoms present per molecule:**

On this basis metal carbonyls are of two types.

a) **Mononuclear metal carbonyls:** The metal carbonyls which contain only one metal atom per molecule are called mononuclear metal carbonyls.

Ex:  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{Fe}(\text{CO})_5]$ ,  $[\text{Cr}(\text{CO})_6]$ , etc.

b) **Polynuclear metal carbonyls:** The metal carbonyls which contain more than one metal atom per molecule are called polynuclear metal carbonyls.

Ex:  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Fe}_2(\text{CO})_9$ ,  $\text{Fe}_3(\text{CO})_{12}$ ,  $\text{Co}_4(\text{CO})_{12}$  etc.

**Physical properties:**

- ❖ **State:** Majority of the metallic carbonyls are liquids or volatile solids.
- ❖ **Colour:** Most of the mononuclear carbonyls are colourless to pale yellow.  $\text{V}(\text{CO})_6$  is a bluish-black solid. Polynuclear carbonyls exhibit dark colour.
- ❖ **Solubility:** Metal carbonyls are soluble in organic solvents like glacial acetic acid, acetone, benzene, carbon tetrachloride and ether.
- ❖ **Magnetic Property:** All the metal carbonyls other than vanadium hexacarbonyl are diamagnetic. The metals with even atomic number form mononuclear carbonyls. Thus, all the electrons in the metal atoms are paired. In case of dinuclear metal carbonyls formed by metals with odd atomic number, the unpaired electrons are utilized for the formation of metal-metal bonds.
- ❖ **Thermal Stability:** Most of the metal carbonyls melt or decompose at low temperatures. Solid carbonyls sublime in vacuum but they undergo some degree of degradation.
- ❖ **Thermodynamic Stability:** Metal carbonyls are thermodynamically unstable. They undergo aerial oxidation with different rates.  $\text{Co}_2(\text{CO})_8$  and  $\text{Fe}_2(\text{CO})_9$  are oxidized by air at room temperature while chromium and molybdenum hexacarbonyls are oxidized in air when heated.

**MONO NUCLEAR CARBONYLS:** **$\text{Ni}(\text{CO})_4$ -Nickel tetracarbonyl:**

**Preparation:** It can be prepared by passing carbon monoxide over nickel in the temperature of  $25^\circ\text{C}$  and 1 atm pressure.



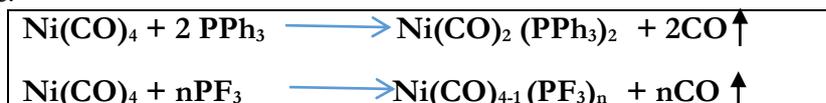
**Properties:** It is a colourless liquid having boiling point  $43^\circ\text{C}$  and decomposition temperature in the range of  $180\text{--}200^\circ\text{C}$ . It is insoluble in water but dissolves in organic solvents.

**Reactions:**

**Action of  $\text{H}_2\text{SO}_4$ :** Nickel tetra carbonyl on treatment with Sulphuric acid undergoes oxidation to form Nickel sulphate.



**Substitution:** Nickel tetra carbonyl undergoes substitution reaction with electron donor ligands like triphenyl phosphine.



**Oxidation:** Bromine oxidises Nickel tetra carbonyl into Nickel Bromide.

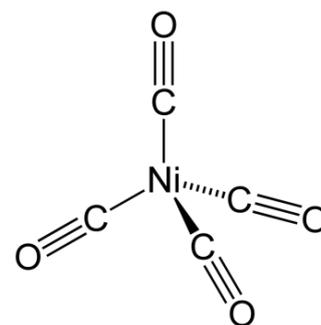


**Structure and bonding:**

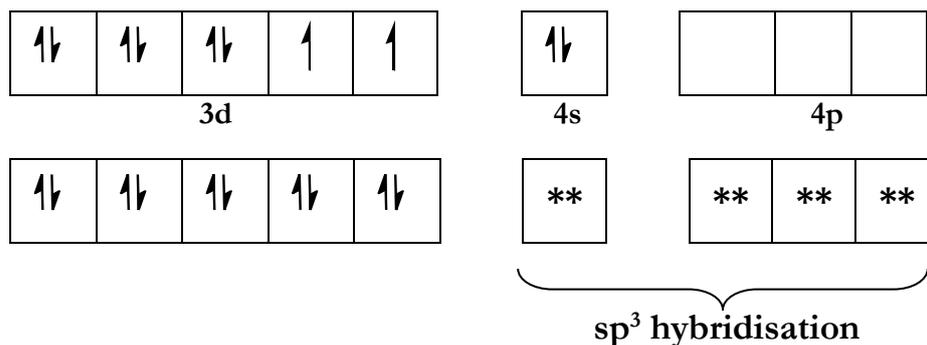
**Structure:** Nickel tetracarbonyl has a tetrahedral geometry. It is also found to be diamagnetic.

The structure of  $\text{Ni}(\text{CO})_4$  can be explained by considering  $sp^3$  hybridization of Ni atom. Since it is diamagnetic, all the ten electrons present in the valence shell of Ni atom ( $\text{Ni} = 3d^8 4s^2$ ) get paired in 3d orbitals. Thus, the valence shell configuration of Ni atom in  $\text{Ni}(\text{CO})_4$  molecule becomes  $3d^{10} 4s^0$ .

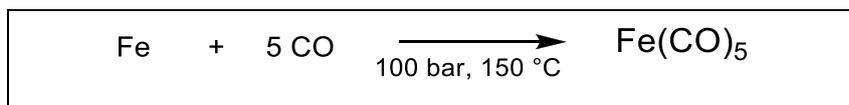
$\text{OC} \rightarrow \text{Ni}$  bond results by the overlap between the empty  $sp^3$  hybrid orbital on Ni atom and the HOMO on C atom in CO molecule as shown below.



(Ni =  $[\text{Ar}] 3d^8 4s^2$ )

 **$\text{Fe}(\text{CO})_5$  -Ironpentacarbonyl:**

**Preparation:** It can be prepared by passing carbon monoxide over iron.



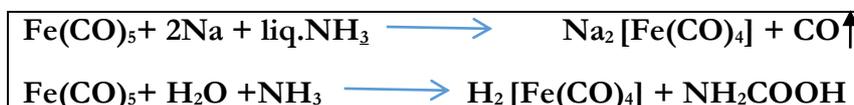
**Properties:** It is a pale yellow liquid having boiling point  $103^\circ \text{C}$  and decomposition temperature around  $250^\circ \text{C}$ . It is insoluble in water but soluble in glacial acetic acid, methanol, diethyl ether, acetone and benzene.

**Reactions:**

**Action of  $\text{H}_2\text{SO}_4$ :** Iron pentacarbonyl on treatment with Sulphuric acid gives Ferrous (II) sulphate.



**Action of  $\text{NH}_3$ :** Reduction of  $\text{Fe}(\text{CO})_5$  with Na gives  $\text{Na}_2\text{Fe}(\text{CO})_4$ , "tetracarbonylferrate" also called Collman's reagent. The dianion is highly nucleophilic.



**Action of Halogen:** Most metal carbonyls can be halogenated. Thus, treatment of  $\text{Fe}(\text{CO})_5$  with halogens gives the ferrous halides  $\text{Fe}(\text{CO})_4\text{X}_2$  ( $\text{X} = \text{I}, \text{Br}, \text{Cl}$ .) These species, upon heating lose CO to give the ferrous halides, such as iron(II) chloride.



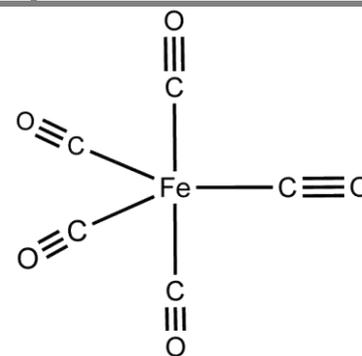
**Action of NO:** Iron pentacarbonyl on treatment with nitric oxide gives nitroso complex.



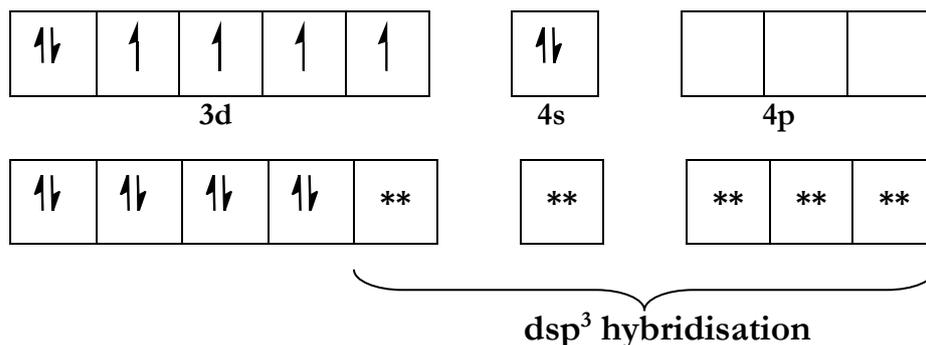
**Structure and bonding:**

**Structure:** The structural studies have suggested trigonal bipyramidal geometry for iron pentacarbonyl. The molecule is also found to be diamagnetic.

The structure can be explained using  $dsp^3$  hybridization in Fe atom. All eight electrons present in the valence shell of Fe atom ( $Fe:3d^6 4s^2$ ) get paired in four 3d orbitals. Thus the valence shell configuration of Fe in  $Fe(CO)_5$  becomes  $3d^8 4s^0$ . The  $OC \rightarrow Fe$  bond results by the overlap between the empty  $dsp^3$  hybrid orbitals on Fe atom and the HOMO on C atom in CO molecule as shown below.



(Fe = [Ar]  $3d^6 4s^2$ )

**Cr(CO)<sub>6</sub> Chromium hexacarbonyl:**

**Preparation:** It can be prepared by on the reaction of chromium chloride with carbon monoxide in presence of  $AlCl_3$  as a catalyst and benzene as a solvent.



**Properties:** It is a white crystalline solid melting above  $150^\circ C$ . It is insoluble in water but soluble in ether, chloroform, carbon tetrachloride and benzene. It is not attacked by air, bromine, cold aqueous alkalis, dilute acids and concentrated hydrochloric acid as well as sulphuric acid.

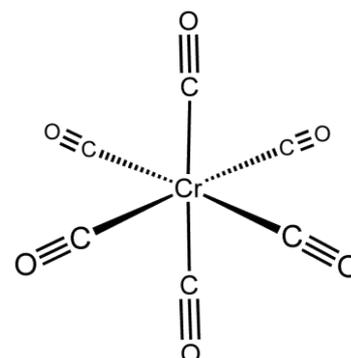
**Reactions:**

**Action of  $NH_3$ :** Chromium hexacarbonyl undergoes reduction with sodium metal in presence of liq.ammonia.

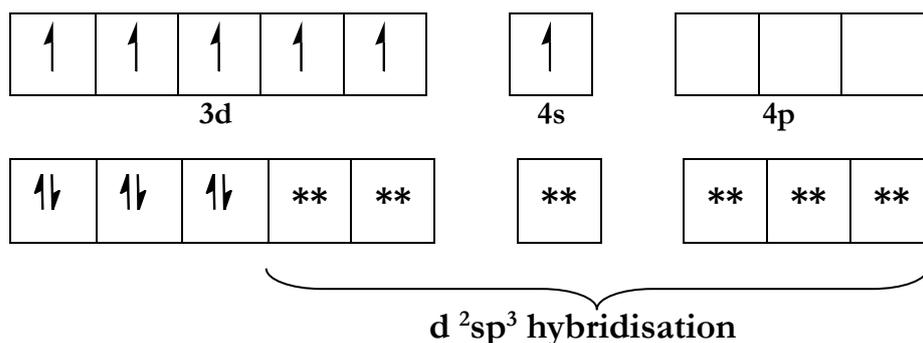
**Structure and bonding:**

**Structure:** The structural studies have suggested an octahedral geometry for chromium hexacarbonyl. The molecule is also found to be diamagnetic.

The structure can be explained using  $d^2 sp^3$  hybridization in Cr atom. All six electrons present in the valence shell of Cr atom ( $Cr: 3d^5 4s^1$ ) get paired in three 3d orbitals. Thus the valence shell configuration of Cr in  $Cr(CO)_6$  becomes  $3d^6 4s^0$ . The  $OC \rightarrow Cr$  bond results by the overlap between the empty  $d^2 sp^3$  hybrid orbitals on Fe atom and the HOMO on C atom in CO molecule as shown below.



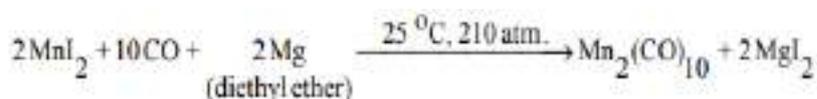
(Cr = [Ar] 3d<sup>5</sup> 4s<sup>1</sup>)



## POLYNUCLEAR CARBONYLS :

### Mn<sub>2</sub>(CO)<sub>10</sub>, Dimanganese decacarbonyl:

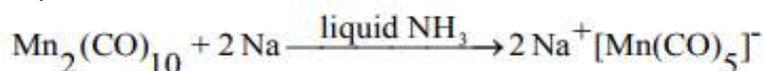
**Preparation:** It can be prepared by carbonylation of manganese iodide with carbon monoxide using magnesium as a reducing agent.



**Properties:** It forms stable golden yellow crystals having melting point of 155 °C. soluble in Organic solvents. It is oxidized by trace amount of oxygen in solution. Hence, the solution must be stored in inert atmosphere.

#### Reactions:

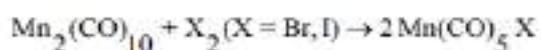
**Reaction with metals:** Dimanganese decacarbonyl on treatment metals undergoes reduction to form manganese pentacarbonyl anion.



**Reduction:** At 200 atm and 200<sup>o</sup> C on treatment with hydrogen gas gives respective hydrido complex.

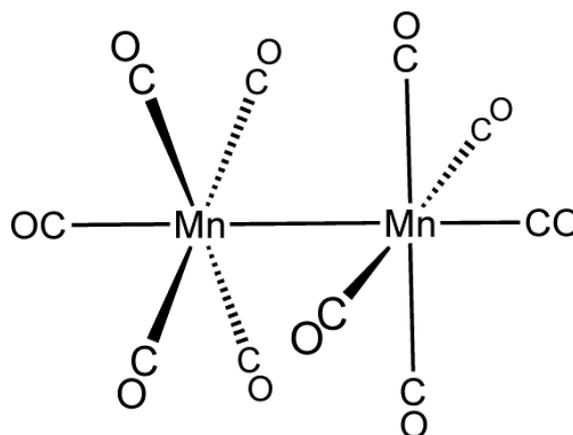


**Reaction with Halogen:** Halogenation of Mn<sub>2</sub>(CO)<sub>10</sub> proceeds with scission of the Mn-Mn bond to give respective manganese pentacarbonyl halide.

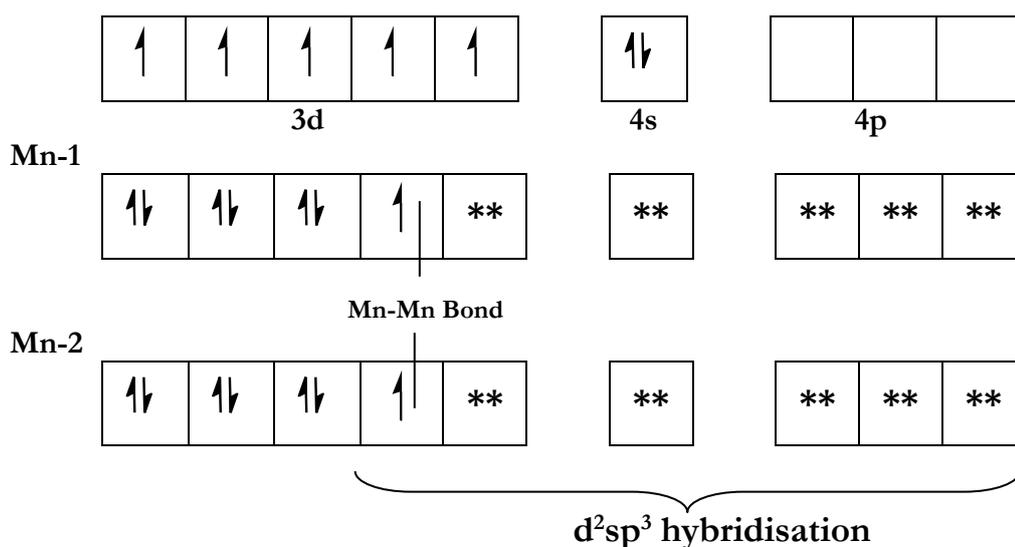


### Structure and bonding:

Manganese pentacarbonyl does not exist as Mn (Z=25) has an odd atomic number. However, the structure of dimanganese decacarbonyl consists of two manganese penta carbonyl groups joined through a Mn-Mn bond. The formation of this inter metallic bond effectively adds one electron to each of the manganese atoms. Thus, manganese, an element with odd atomic number forms a binuclear carbonyl. Since, the molecule does not have any unpaired electrons, it is diamagnetic. In Mn<sub>2</sub>(CO)<sub>10</sub>, the Mn – Mn bond is formed by the linear overlapping of singly occupied d<sup>2</sup> sp<sup>3</sup> hybrid orbitals of two Mn atoms.



(Mn = [Ar] 3d<sup>5</sup> 4s<sup>2</sup>)



### Co<sub>2</sub>(CO)<sub>8</sub>, Dicobalt octacarbonyl:

#### Preparation:

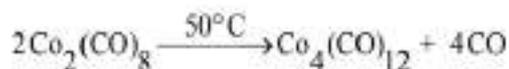
It can be prepared by direct combination of carbon monoxide with cobalt metal.



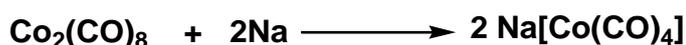
**Properties:** It is an orange crystalline substance having melting point 51°C, soluble in alcohol, ether, and CCl<sub>4</sub>, turns deep violet upon exposure to air.

#### Reactions:

**Action of heat:** Upon heating at 50 °C it forms tetracobalt dodecacarbonyl.



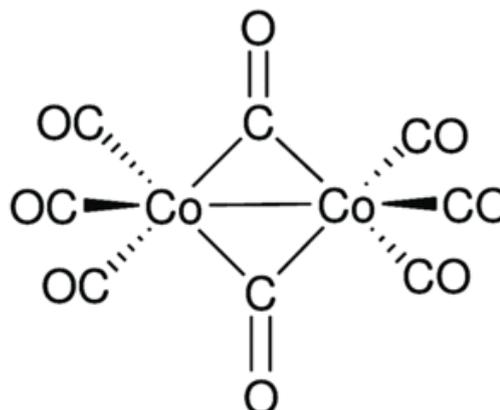
**Reduction:** Dicobalt octacarbonyl with sodium metal undergoes reduction to give tetracarbonyl cobalt anion (tetracarbonyl cobaltate).



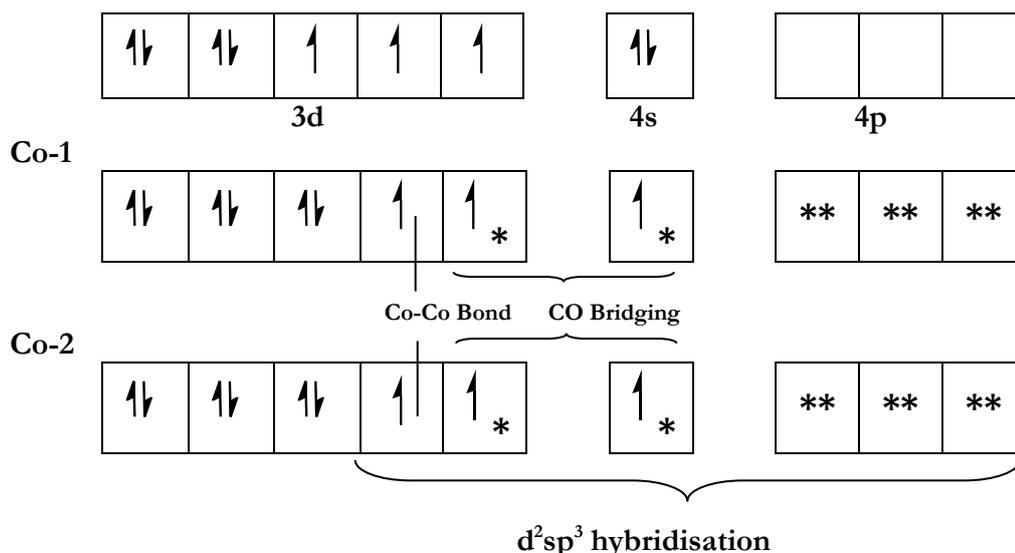
#### Structure and bonding:

Dicobalt octacarbonyl is known to exist in two isomeric forms. A bridged structure of this molecule is observed in the solid state as well as solution state at a very low temperature.

❖ In the bridged structure, the cobalt atoms are in d<sup>2</sup> sp<sup>3</sup> hybrid state. Three such hybrid orbitals on each cobalt atom accept lone pair of electrons from three carbon monoxide molecules to form total six Co←CO coordinate bonds. A Co-Co bond is formed by the overlapping of two half-filled d<sup>2</sup> sp<sup>3</sup> hybrid orbitals on the cobalt atoms. Remaining two half-filled hybrid orbitals on each Co atom overlap with appropriate orbital on carbon atom of the carbonyl to form two bridging CO groups. Thus, all electrons in this molecule are paired and it is diamagnetic.

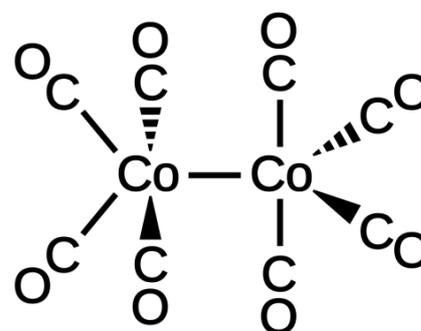


(Co = [Ar] 3d<sup>7</sup> 4s<sup>2</sup>)

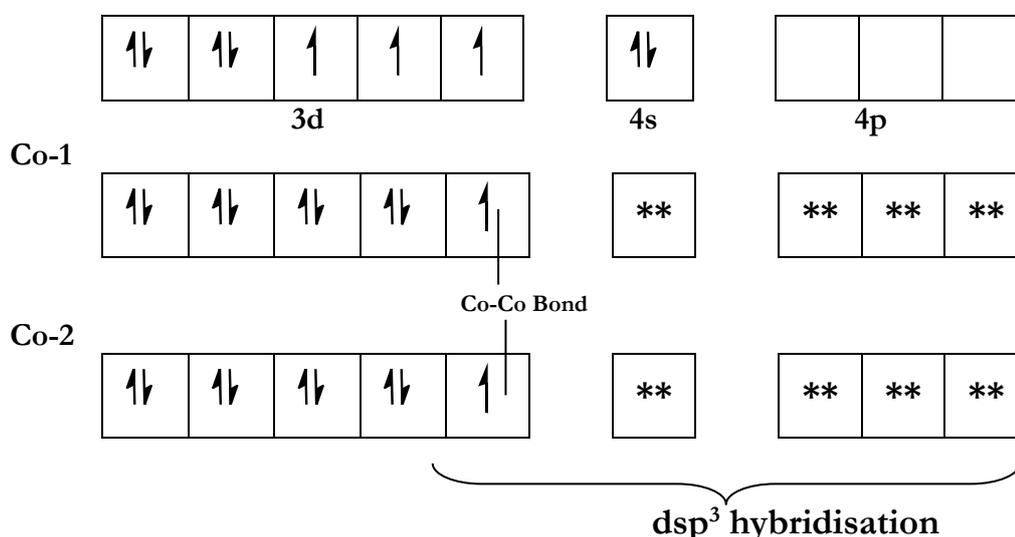


❖ A non - bridged structure predominates in a solution at temperatures above ambience.

In the non-bridged structure, the cobalt atoms are in d sp<sup>3</sup> hybrid state. Four such hybrid orbitals on each cobalt atom accept lone pair of electrons from Four carbon monoxide molecules to form total Four Co←CO coordinate bonds. A Co-Co bond is formed by the overlapping of two half -filled d sp<sup>3</sup> hybrid orbitals on the cobalt atoms. Thus, all electrons in this molecule are paired and it is diamagnetic.

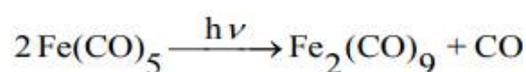


(Co = [Ar] 3d<sup>7</sup> 4s<sup>2</sup>)



## Fe<sub>2</sub> (CO)<sub>9</sub>, Diiron nonacarbonyl:

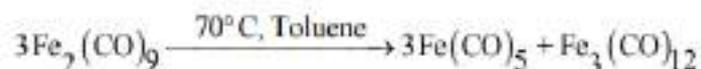
**Preparation:** Cold solution of iron pentacarbonyl in glacial acetic acid undergoes dimerization under the influence of ultra-violet light to give golden yellow crystals.



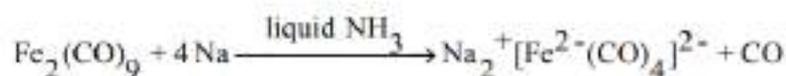
**Properties:** Diiron nonacarbonyl forms golden yellow triclinic crystals melting at 100 ° C. It is insoluble in water but soluble in toluene and pyridine.

**Reactions:**

**Action of heat:**

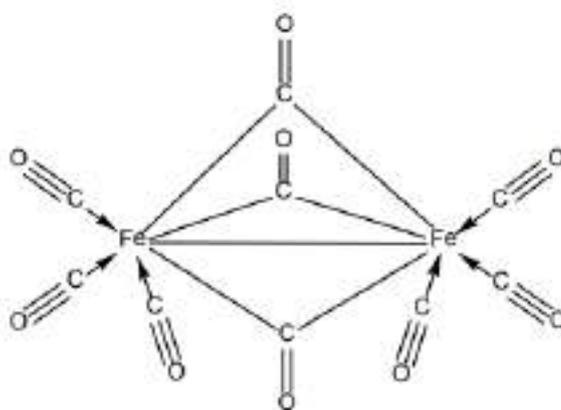


**Action of metal:** Diironnonacarbonyl on treatment with sodium metal in presence of liq.ammonia gives tetracarbonyl ferrate with loss of CO.

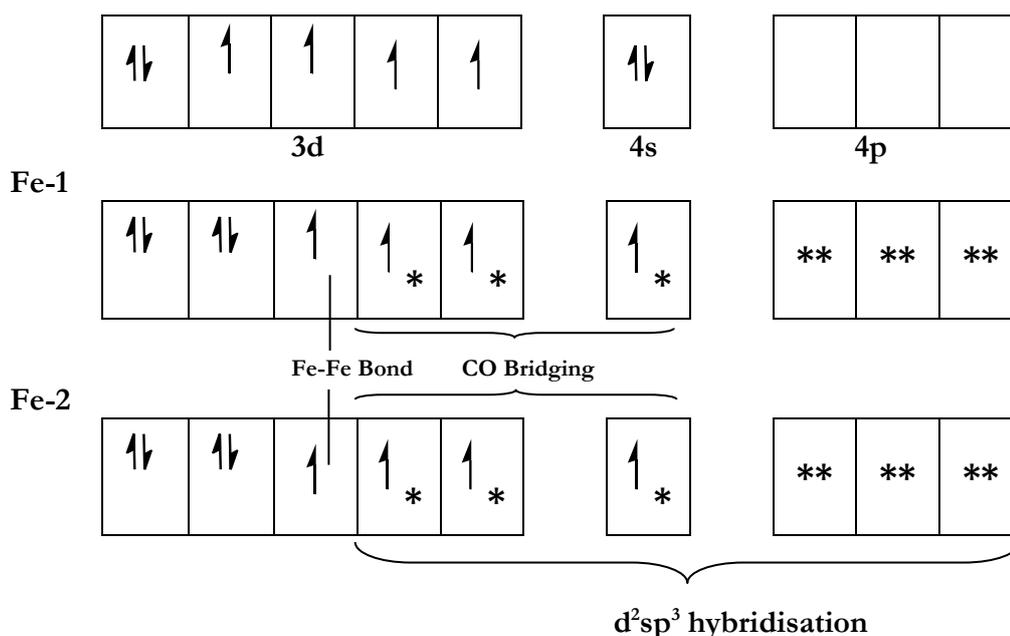


**Structure and bonding:**

Each of the iron atoms in diiron nonacarbonyl has three terminal carbonyl groups. The remaining three carbon monoxide ligands act as  $\mu^2$ -CO groups. In addition to this, there is a weak Fe-Fe bond formed by sharing of two unpaired electrons present in the 3d orbitals of iron atoms. Thus, both the iron atoms in the molecule are identical with coordination number seven. Since, the molecule does not have any unpaired electron, it is diamagnetic. The structure of this molecule can be explained using  $d^2sp^3$  hybridization in Fe atoms as shown in the figure.



(Fe = [Ar] 3d<sup>6</sup> 4s<sup>2</sup>)

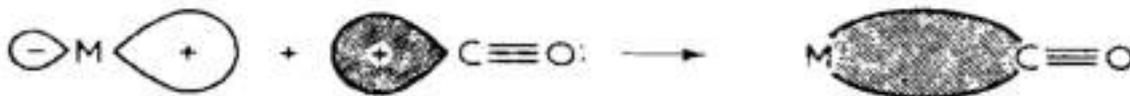


## Bonding in metal carbonyls:

The nature of M-C bond formation Illustrated as follows.

### Formation of M-C $\sigma$ -bond:-

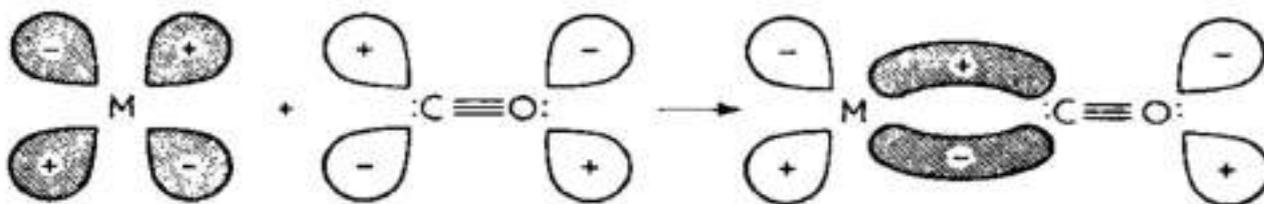
First there is dative overlap of filled carbon  $\sigma$ -orbital with the vacant metal orbital to form  $\sigma$ -bond



*The formation of the  $C \rightarrow M$   $\sigma$ -bond using an unshared pair of electrons on the carbon atom of CO*

### Formation of M-C $\pi$ -bond:-

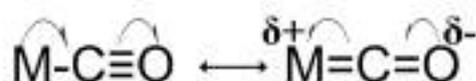
overlap of filled d-orbital of metal with the vacant  $\pi^*$  orbital of CO form  $\pi$ -bond



*Formation of the  $M \rightarrow C$   $\pi$ -bond by donation of metal d  $\pi$  electrons into the  $\pi^*$  antibonding orbitals of CO.*

This bonding mechanism is synergic. The effect of  $\sigma$ -bond formation strengthens the  $\pi$ -bond, vice versa. The movement of metal electrons into CO orbitals will make CO as a whole negative and hence, will increase its basicity. Which accounts for the greater strength via  $\sigma$ -orbitals of carbon. Also the movement of electrons into metal in the  $\sigma$ -bond tends to make the CO positive. Thus, enhancing the acceptor strength of  $\pi^*$  orbital of CO.

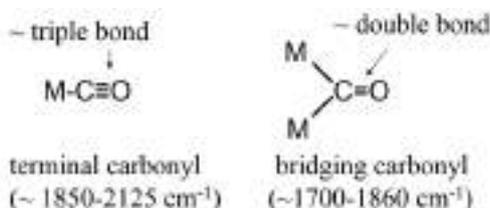
**The carbonyl ligand is a  $\pi$ -acid:** This is an acid in the Lewis sense, where it receives electrons from the metal ion, and it is a  $\pi$ -acid because this involves  $\pi$  bonding. The  $\pi$ -bonding involves overlap of the  $\pi^*$  orbitals of the CO with d orbitals from the metal and so is  $d\pi-p\pi$  bonding. The canonical structures involved in the  $\pi$ -acid nature of CO are:



## IR spectra and bridging versus terminal carbonyls:

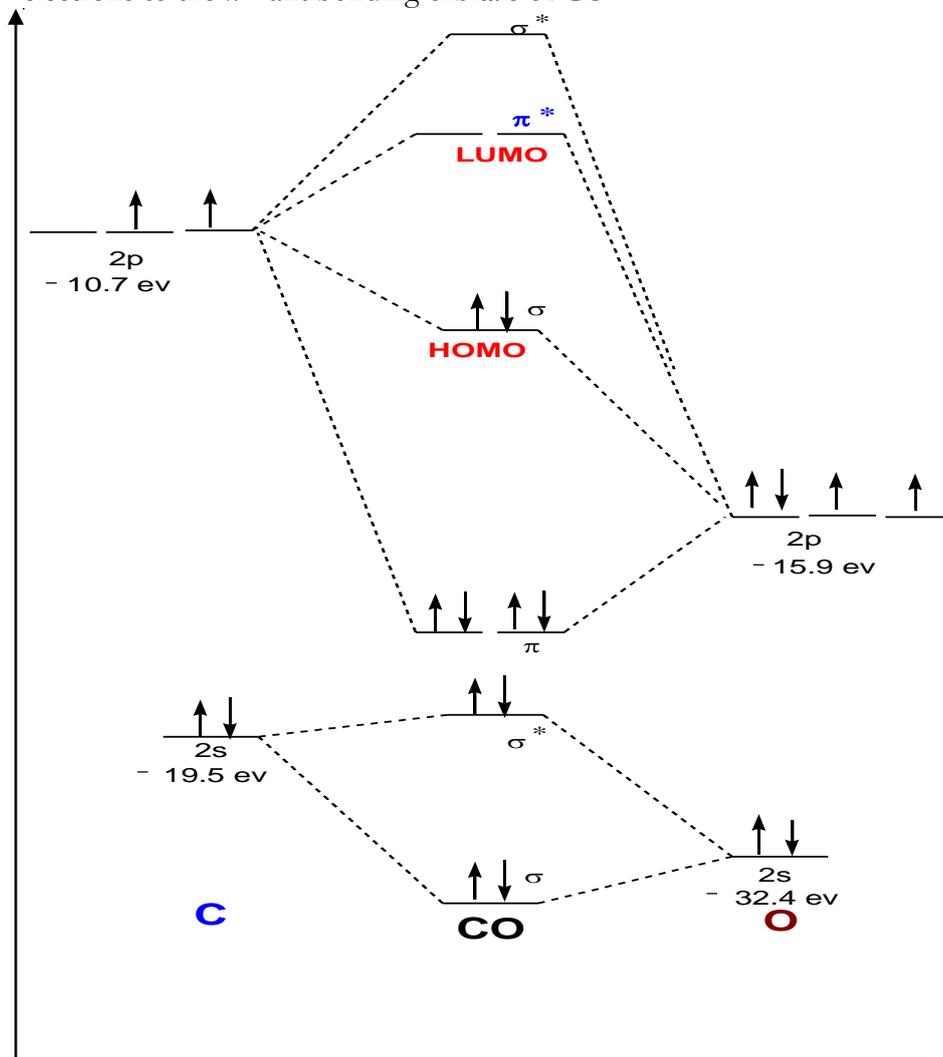
Bridging CO groups can be regarded as having a double bond C=O group, as compared to a terminal C $\equiv$ O, which is more like a triple bond:

The  $\nu_{\text{CO}}$  stretching frequency of the coordinated CO is very informative as to the nature of the bonding. Recall that the stronger a bond gets, the higher its stretching frequency. Thus, the more important the M=C=O (C=O is a double bond) canonical structure, the lower the  $\nu_{\text{CO}}$  stretching frequency as compared to the M-C $\equiv$ O structure (C $\equiv$ O is a triple bond):

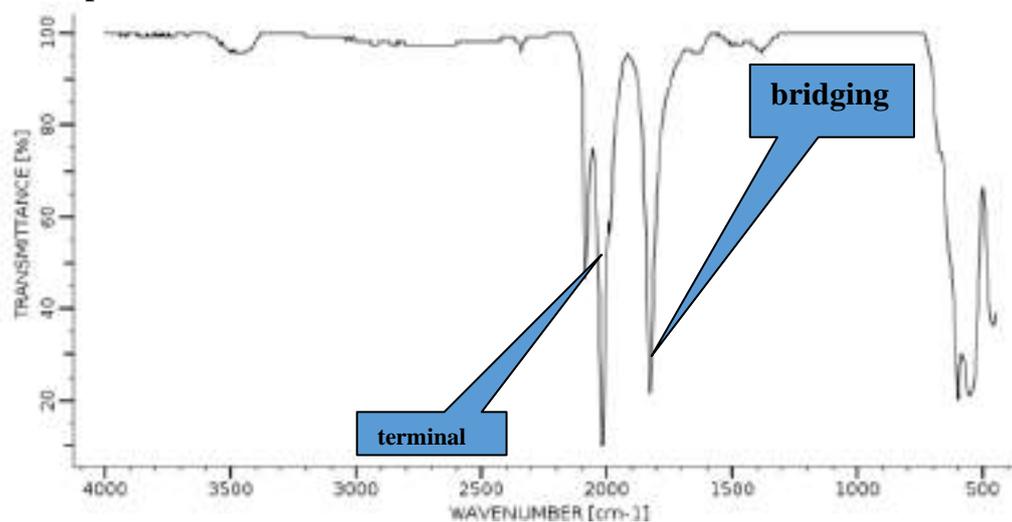


## Molecular Orbital diagram of CO :

The highest occupied molecular orbital (HOMO) of CO is weakly antibonding (compared with the O atomic orbitals) and is an MO which is carbon based. Secondly, the  $\pi^*$  antibonding orbital which is the lowest unoccupied molecular orbital (LUMO) is also of comparatively lower energy which makes it possible to interact with metal d orbitals for bonding. There exists a strong back bonding of metal electrons to the  $\pi^*$  antibonding orbitals of CO.



Example of IR spectrum:



## FERTILIZERS

Fertilizers are “*The products that improve the levels of the available plant nutrients and/or the chemical and physical properties of the soil, thereby directly or indirectly enhancing the growth, yield and quality of the plant*”.

### Fertility of soil:

- a) **Virgin Soil:** It is the portion of the soil or land in which plants have not grown since long time. It is always fertile and good crop may be yielded due to elements present in it have not been used up by the plants as food.
- b) **Exhausted Soil:** It is the soil on which crop and after crop, especially of the same variety has been raised. The plants keep on absorbing the same elements for the soil and hence the soil becomes impoverished or an unproductive soil. Factors affecting the fertility of soil are as follows
  - ✓ Nitrogen, phosphorus, potassium and other mineral salts
  - ✓ The amount of fixed nitrogen
  - ✓ pH value of the soil (7-8)

### Characteristic features of good fertilizer

- a. Must be soluble in water.
- b. The element present in the compound must be easily available to the plant Should be cheap.
- c. Should not be toxic to plant .
- d. Should be stable for long time .
- e. Should maintain the pH of the soil in the vicinity of 7 to 8.

### Benefits of Fertilizer

- a) Farming efficiency improvement
- b) Improvement of soil quality with adequate fertilization.
- c) Crop quality improvement
- d) Water conservation

### Classification of fertilizers:

Inorganic fertilizers are further classified in to

**Indirect fertilizers:** These fertilizers which are added to soil to improve its biological, chemical, or mechanical properties.

Example: limestone, ground dolomite (decreases soil acidity) and gypsum (increases salt content)

**Direct fertilizers:** These are fertilizers which contain the nutrient elements in the form of compounds which are directly taken up by the plants. These are further classified as nitrogenous, phosphatic, potash, magnesium,..etc.

**N-type (Nitrogenous fertilizer):** Those fertilizers which mainly supply nitrogen to the plants are called nitrogenous fertilizers.

Ex: Urea( $\text{H}_2\text{NCONH}_2$ ), Ammonium sulphate [ $(\text{NH}_4)_2\text{SO}_4$ ] and Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ).

**P-type (Phosphatic fertilizers):** Those fertilizers which mainly supply phosphorus to the plants are called phosphatic fertilizer.

Ex: Super phosphate of lime [ $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{CaSO}_4$ ], Mono potassium phosphate( $\text{KH}_2\text{PO}_4$ (0-52-35)).

**K-type(Potash fertilizer):** These are the fertilizers which supply K to plants.

Ex: Potassium nitrate ( $\text{KNO}_3$ ), Potassium chloride (KCl), Potassium sulphate ( $\text{K}_2\text{SO}_4$ ).

**Mixed fertilizer:** Fertilizers containing more than one plant nutrient are called mixed fertilizers. Now a day instead of using a single fertilizer, a mixture of fertilizers containing N, P, and K are used.

Ex: Nitro phosphate containing murate of potash  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{Ca}(\text{NO}_3)_2 + \text{KCl}$

**Examples for NP, PK, KN, NPK fertilizers:**

**NP:** Ammonium dihydrogen phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ), Ammonium hydrogen phosphate [ $(\text{NH}_4)_2\text{HPO}_4$ ]

**PK:** mixture of triple super Phosphate and Potassium sulphate.

**NK:** fertilizers containing both N and K (potassium nitrate)

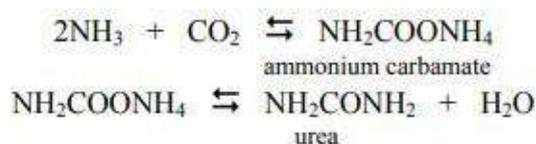
**NPK:** fertilizers containing N, P, and K. Nitro phosphate with Potash

**Based on physical nature fertilizers classified in to:**

- **Granular Fertilizer:** Solid material that is formed into particles of a predetermined mean size.
- **Coated Fertilizer:** Granular fertilizer that is covered with a thin of a different material in order to improve the behavior and/ or modify the characteristics of the fertilizer.
- **Liquid Fertilizer:** A term used for fertilizers in suspension or solution and for liquefied ammonia.
- **Powder Fertilizer:** A solid substance in the form of very fine particles. Powder is also referred to as “no granular fertilizer” and is sometimes defined as a fertilizer containing fine particles, usually with some upper limit such as 3 mm but no lower limit.

**Preparation / manufacture of some fertilizers:****❖ Manufacture of Urea:**

Urea is produced from ammonia and carbon dioxide in two equilibrium reactions:



The urea manufacturing process as shown below,

**Step 1 - Synthesis**

A mixture of compressed  $\text{CO}_2$  and ammonia at 240 barg pressure reacted to form ammonium carbamate. This is an exothermic reaction, and which is readily decompose to give urea.

**Step 2 - Purification**

The major impurities in the mixture at this stage are water from the urea production reaction and unconsumed reactants (ammonia, carbon dioxide and ammonium carbamate). The unconsumed reactants are removed.

**Step 3 - Concentration**

Urea solution is heated under vacuum, which evaporates off some of the water, increasing the urea concentration. In the evaporation stage molten urea is produced at  $140^\circ\text{C}$ .

**Step 4 - Granulation**

Urea is sold for fertilizer as 2 - 4 mm diameter granules. These granules are formed by spraying molten urea onto seed granules which are supported on a bed of air. The final product is cooled in air, weighed and conveyed to bulk storage ready for sale.

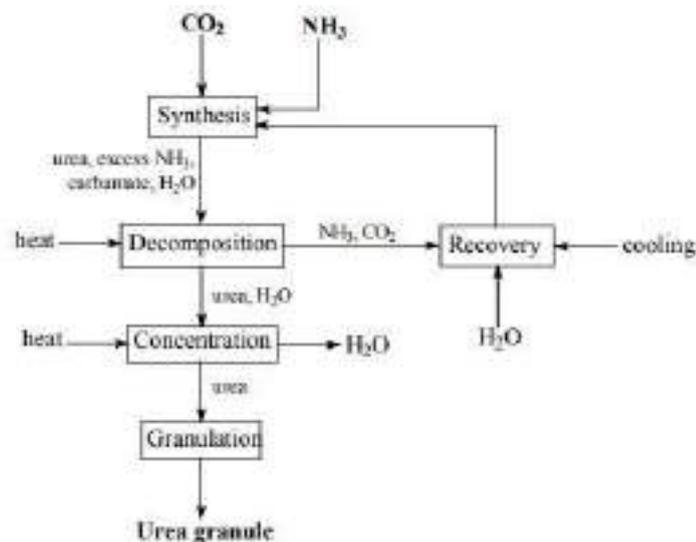
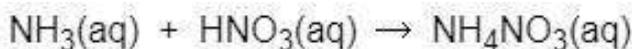


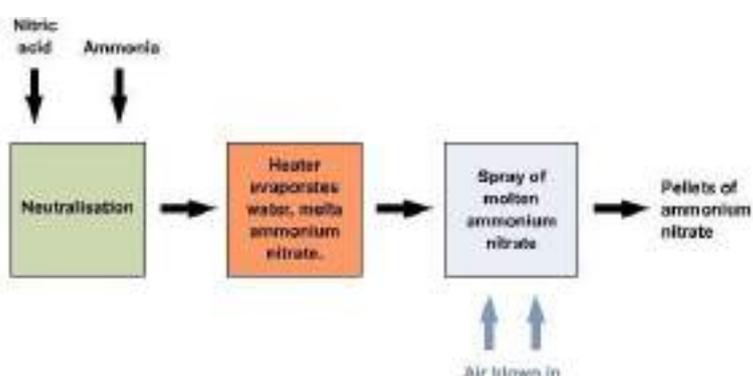
Figure 2 – Schematic representation of urea synthesis

### ❖ Manufacture of Ammonium nitrate:

Nitric acid and ammonia react to form the important fertilizer, ammonium nitrate, in a neutralization reaction:



1. Solutions of nitric acid and ammonia are pumped in to mixing vessel.
2. The nitric acid is neutralised to form ammonium nitrate.
3. Ammonium nitrate solution is heated, water evaporates off leaving heavy molten ammonium nitrate.
4. Molten ammonium nitrate is sprayed to cooling chamber. Air is blown in to bottom of the cooling chamber to cool ammonium nitrate.



### ❖ Manufacture of Calcium ammonium nitrate:

Ammonium nitrate is first prepared by the reaction of ammonia and nitric acid. Ammonium nitrate so obtained contains some un-reacted nitric acid which is neutralized by adding calcium carbonate on cooling grains of calcium ammonium nitrate separates out.

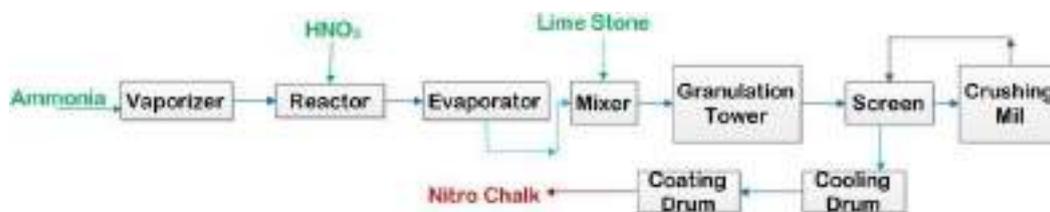


Figure: Manufacturing of Calcium Ammonium Nitrate

CAN is produced by mixing quickly concentrated ammonium nitrate solution with ground or powdered calcitic or dolomitic limestone. granulation technology is used to produce CAN.

#### Granulation process:

1. Calcium ammonium nitrate is produced by granulating concentrated ammonium nitrate solution with pulverized limestone or dolomite in a granulator. Ammonium nitrate solution is prepared by reacting preheated ammonia with nitric acid in a neutralizer.
2. Concentrated ammonium nitrate is pumped and sprayed into the granulator which is fed with weighed quantity of limestone powder and recycle fines from the screens. The hot granules are dried in a rotary drier by hot air.
3. Dried hot granules are screened and fines and oversize recycled. Granules of proper size are cooled in a rotary cooler by air and coated with soapstone dust in a coating drum. The final product is sent to storage.

### ❖ Manufacture of Ammonium phosphate:

There are two major types of ammonium phosphate which are mono ammonium phosphate (MAP,  $\text{NH}_4\text{H}_2\text{PO}_4$ ) and di ammonium phosphate (DAP,  $(\text{NH}_4)_2\text{HPO}_4$ ).

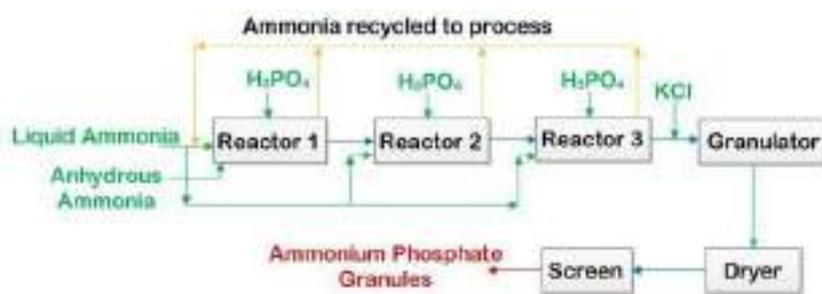
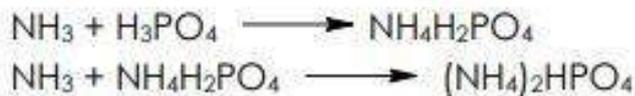


Figure: Manufacturing of Ammonium Phosphate

### Neutralization

- Quantities of phosphoric acid and ammonia in the neutralization step are different from mono ammonium phosphate (MAP) and diammonium phosphate (DAP).
- To manufacture mono ammonium phosphate, ammonia to phosphoric acid ratio is 0.6 in the neutralizer and then 1.0 in the granulator.
- While for di ammonium phosphate, the ratios are 1.4 and 1.0 in the neutralizer and granulator respectively.
- Phosphoric and ammonia are added to the first of three continuous mixed reactors, anhydrous ammonia is added to the first neutralizer.
- Further ammonia is added in the 2<sup>nd</sup> and 3<sup>rd</sup> tanks to obtain conversion to the diammonium salt if a higher nitrogen containing fertilizer is needed.

### Granulation

- Slurry from the third neutralized is mixed with KCl and absorbed in a bed of dry recycle fertilizer moving through a rotating drum granulator.
- Dried product is separated into three fractions on a double deck screen.

### ❖ Preparation of sodium ammonium phosphate:

It is prepared by dissolving molecular proportions of disodium hydrogen phosphate and ammonium chloride in little hot water, sodium ammonium phosphate formed.



### ❖ Preparation of poly phosphate:

When  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$  is heated to  $105^\circ\text{C}$ , it loses water and becomes anhydrous on further heating to  $800^\circ\text{C}$ , it is converted into  $\text{Mg}_2\text{P}_2\text{O}_7$ .



### ❖ Manufacture of Calcium super phosphate:

Finely ground phosphate rock is mixed with sulfuric acid to form calcium superphosphate.



Figure: Manufacturing of Superphosphate

Acti  
Gric

### Continuous-den process

1. Finely ground phosphate rock is mixed with sulfuric acid. The acid and water are fed into the cone mixer to provide the necessary mixing with the phosphate rock.
2. The fresh superphosphate is discharged from the cone mixer into a pug mill, where additional mixing takes place and the reaction starts. From the pug mill the superphosphate drops onto the den conveyor.
3. The conveyor den is enclosed so that fumes do not escape into the working area. These fumes are scrubbed with water sprays to remove acid and fluoride before being exhausted to the atmosphere. Scrubber water is neutralized by passing through the limestone bed.
4. The powdered superphosphate enters the rotary drum granulator, where it is mixed and granulated with recycled fines.
5. Final curing of the product occurs during storage.

### ❖ Manufacture of Potassium chloride:

In the process the ore is crushed to +10 mesh size then washed to remove clay slimes. To render it inert to amines, washed crushed ore is treated first with starch or mannogalactan gums and then with an amine acetate which selectively coats KCl particles. Air is then bubbled through the slurry. The air bubbles attach themselves to the coated particles and float them to the surface while the uncoated particles sink. The floated KCl is centrifuged, dried and packed.

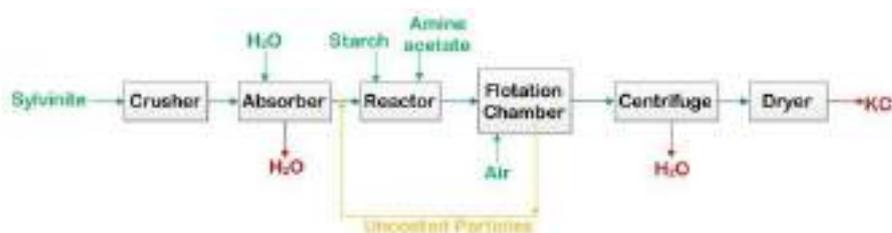


Figure: Manufacturing of Potassium Chloride by Flotation Process

### ❖ Manufacture of Potassium sulphate:

Potassium chloride reacts with sulfuric acid during the slow mixing of the ingredients in the gas heated Mannheim furnace consisting of cast iron muffle with rotating plough which helps to agitate the mixture. Hydrochloric acid produced during the reaction is cooled and absorbed into water to produce 33% hydrochloric acid as a byproduct. The precipitated potassium sulfate fertilizer is cooled, filtered and the lumps are crushed and granulated.

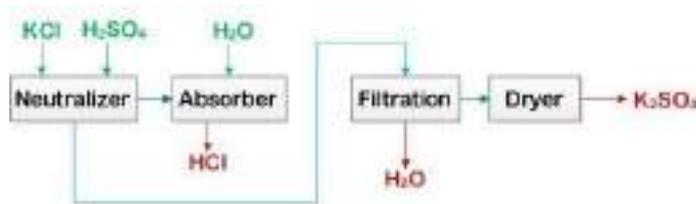
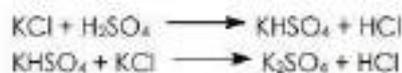


Figure: Manufacturing of Potassium Sulfate

### Compound Fertilizers:

The production and marketing of compound fertilizers are unique compared with commodity type fertilizers such as urea, ammonium phosphates and potash. Unlike commodity type fertilizers, **compound fertilizers are usually manufactured (formulated) to meet local or regional crop requirements. Often, in addition to containing various ratios of the primary nutrients (N+P<sub>2</sub>O<sub>5</sub>+K<sub>2</sub>O), they contain certain secondary and micronutrients specific to the crop needs in a particular agro-climatic region.**

#### Role of Compound fertilizer:

The decision to use compound fertilizers is usually driven by one or more of the following factors:

1. Convenience.
2. Crop nutrient needs.
3. Government policy objectives.
4. Economics.

#### Mixed fertilizer:

**Mixed fertilizer typically refers to a fertilizer containing two or more of the elements of nitrogen, phosphorus and potassium (NPK) which are essential for promoting plant growth and high crop yields.** They are obtained by thoroughly mixing the ingredients either manually or mechanically. NPK mixture fertilizers are formulated and recommended by agricultural scientists to enhance the output of crops by giving it specific and exclusive blend of plant nutrients. They are slow releasing by nature and remain in the field for a long time. They are made as per the soil and are crop specific.

Ex: Nitro phosphate containing murate of potash  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{Ca}(\text{NO}_3)_2 + \text{KCl}$

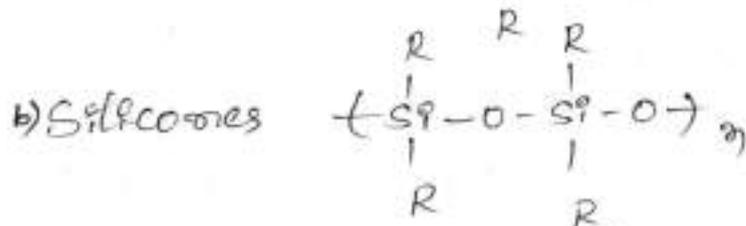
**Mixed fertilizers have a number of advantages, a few of them being:**

- Use of mixed fertilizers results in reduction of labour costs.
- This facilitates uniform soil application of plant nutrients.
- The use of a fertilizer mixture leads to balanced manuring. It results in higher crop yield.
- Being in granulated form, mixtures have a better physical condition and hence their application is easier.

## Inorganic polymers.

Inorganic polymers are giant molecules composed of atoms other than carbon. The atoms are linked together mainly by covalent bonds.

example: a) polyphosphazines  $\left( \begin{array}{c} R \\ | \\ P=N \\ | \end{array} \right)_n$ ,



General properties of inorganic polymers:

- (\*) With few exceptions, inorganic polymers do not burn. They only soften or melt at higher temperature.
- (\*) Inorganic polymers which have cross-linked structures with a high density of covalent bonds
- (\*) These polymers generally stiffer and harder than organic polymers.
- (\*) The chain segments between cross links in polymers having cross linked structures are usually short and stiff.
- (\*) Inorganic polymers are built up of highly polar repeat units. These polymers would therefore, dissolve only in polar solvents.
- (\*) Inorganic polymers are generally much less ductile than the organic polymers.
- (\*) Inorganic polymers are generally obtained in pure crystalline as well as pure amorphous forms.
- (\*) Inorganic polymers, in general are stronger, harder and more brittle than the organic polymers.
- (\*) They are highly branched has complex structure.
- (\*) Not environmental friendly as they are non-biodegradable.

## Glass transition temperature ( $T_g$ )

The glass transition temperature is defined as "the temperature at which internal energy of polymer molecules increases to such an extent that the chain segments of the polymer molecules are just ready to leave their lattice positions".

or

"The temperature at which the higher molecular weight materials transform from glassy state to a viscous or rubbery state".

Factors affecting glass transition temperature:

- (1) molecular weight:  $T_g$  is directly proportional to the molecular weight of the polymer.
- (2) Cross-linkage: Glass transition temperature is directly proportional to the degree of cross linkage.
- (3) chain flexibility: glass transition temperature is inversely proportional to the chain flexibility.
- (4) Substituents: Glass transition temperature is directly proportional to number of side groups.
- (5) Intramolecular force: glass transition temperature is directly proportional to the intramolecular force.
- (6) plasticizer:  $T_g$  is inversely proportional to the proportion of plasticization.
- (7) polar groups: presence of polar groups increases the intermolecular forces. Inter chain attraction leading to increase in the  $T_g$ .
- (8) molecular structure: Insertion of bulky, inflexible side groups increases  $T_g$  of material due to decrease in mobility.

## Significance of glass transition temperature:

The glass transition temperature is an important property of the polymer it provides the following information.

- ① It is used to know whether a polymer molecule is flexible or rigid and brittle.
- ②  $T_g$  is used to measure type of response of polymer.
- ③  $T_g$  gives an idea about the polymeric material whether it will behave like plastic or rubber.
- ④  $T_g$  value provides an indication of the temperature region at which a polymer transform from solid rigid state to soft viscous state.
- ⑤  $T_g$  informed about a right processing temperature.

## Important Inorganic polymers.

there is a wide variety of inorganic polymers, important among are

- (1) phosphorus-based polymers.
- (2) Boron-based polymers
- (3) Sulphur-based polymers
- (4) Silicon-based polymers.

### ⇒ phosphorus-based inorganic polymer:

The phosphorus-based polymers can be divided into two categories (i) chain polymers and (ii) network polymers depending upon the type of linkage involved between their atoms.

ex: polyphosphazenes, phosphonitrilic chlorides.

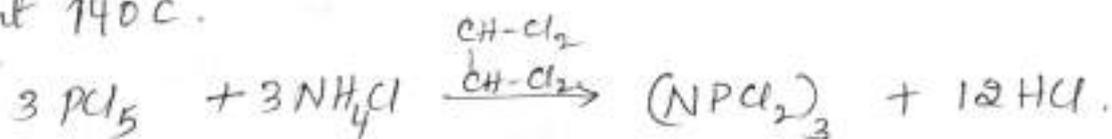
### Phosphonitrilic chlorides

The polymer having the general formula  $\left[ \underset{\text{Cl}}{\overset{\text{Cl}}{\text{P}}} = \text{N} \right]_n$

This polymer is known as "inorganic rubber". It undergoes degradation under normal conditions more rapidly than do the

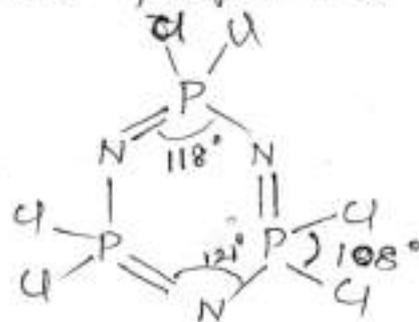
organic polymers (rubbers) hence, the polymer do not find much commercial use.

preparation:  $[\text{NPCl}_2]_3$  is obtained by heating phosphorus pentachloride with small excess of ammonium chloride in an inert solvent like tetrachloroethane (chloroform) at  $140^\circ\text{C}$ .



Structure of  $[\text{NPCl}_2]_3$ :

- ① It is a planar with hexagonal ring with alternate phosphorous and nitrogen.
- ② Two chlorine atoms are attached to each phosphorous atom.
- ③ The angle between P-N-P is  $121^\circ$  and Cl-P-Cl is  $108^\circ$ .
- ④ Each nitrogen atom is  $\text{sp}^2$  hybridized and phosphorous atom is  $\text{sp}^3$  hybridized.
- ⑤ The lone pair of electron on nitrogen atom makes  $[\text{NPCl}_2]_3$  molecule to show basic properties.
- ⑥ It is stable at boat form.
- ⑦ angle between N-P-N  $\rightarrow 118^\circ$  and P-N-P is  $121^\circ$ .



Applications:

- ① used as water proof and fire proof material.
- ② It is used as plasticizer.
- ③ Also used as catalyst in manufacture of silicones.
- ④ The polymer thin films are used in hospitals to cover severe burns and other extensive wounds.
- ⑤ Fluorinated compounds useful for fuel and gaskets, ... since, they retain elasticity at low temp.

⇒ Boron-based polymers.

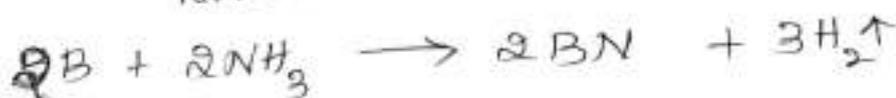
Boron based polymers constitute an important class of inorganic polymers. Among these most important ones are polycarboranes and polymeric Boron nitride.

Boron nitride:  $(BN)_n$

Polymeric Boron nitride exists in two forms i.e. as a layer polymer and as a three dimensional network polymer.

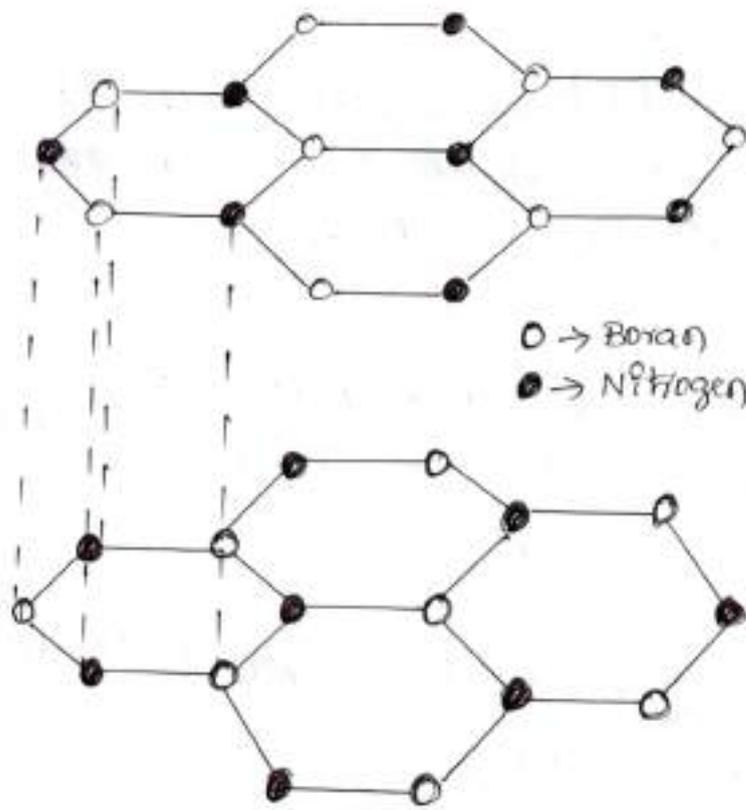
Preparation:

It is formed by heating boron to a white heat in an atmospheric nitrogen, NO or  $NH_3$ .

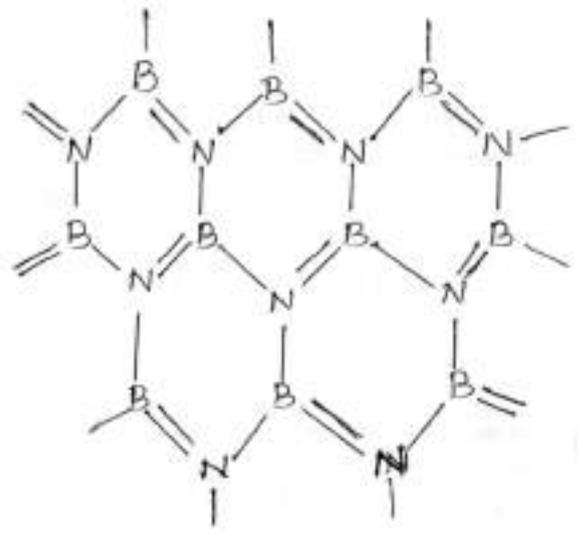


Structure:

- ① The polymeric solid has a graphite like structure containing alternate Boron and nitrogen atoms. The B-N bond distance 145 pm.
- ② The bonds are formed by  $sp^2$  hybrid orbitals on boron and nitrogen atoms.
- ③ The remaining two  $e^-$  on nitrogen are used for forming  $\pi$ -bonds by donation from N to B.
- ④ As in graphite there are alternative single and double bonds between B and N atoms.
- ⑤ Alternate sheets are located such that Boron atoms are directly over nitrogen atoms.
- ⑥ This structure leads to easily sliding of planes relative to each lending Boron nitride lubricant properties. Comparable to graphite.
- ⑦ Unlike graphite, it is electrical insulator. since, there is large band gap b/w valence band & conduction band.



Layer structure of Boron nitride



One layer structure of Boron nitride.

### Applications of Boron nitride:

- ⊗ used as solid lubricant for high temperature bearings.
- ⊗ mould release agent for die casting of glass and metals.
- ⊗ ultra-high pressure transmitting agent.
- ⊗ Coating for erosion resistant plants.
- ⊗ Embedding medium for heating wires.
- ⊗ Coating for graphite hot pressing moulds.
- ⊗ Boron nitride is the source for preparation of ceramic composite.
- ⊗ protective and insulating sleeves for thermocouples.
- ⊗ Crucibles for melting glass and metals.
- ⊗ Neutron absorber and shields for nuclear reactors.

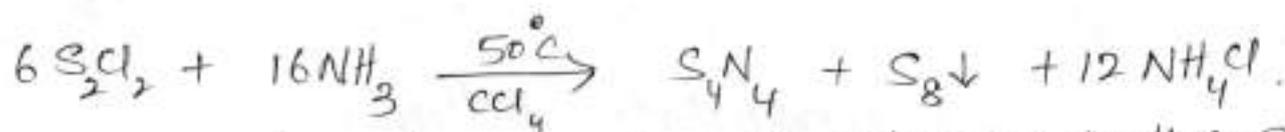
## ⇒ Sulphur-Based polymers

A large number of sulphur based polymers are known. These includes linear as well as network polymers. The most important linear chain polymers are polymeric sulphur and polymeric sulphur nitride.

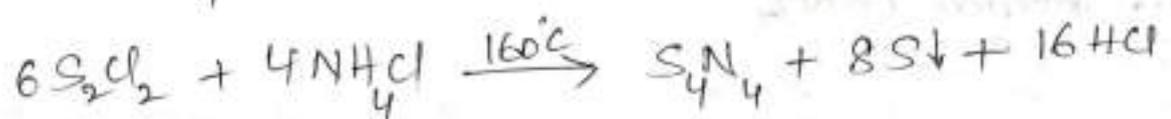
### Sulphur nitride $(SN)_4$

#### Preparation:

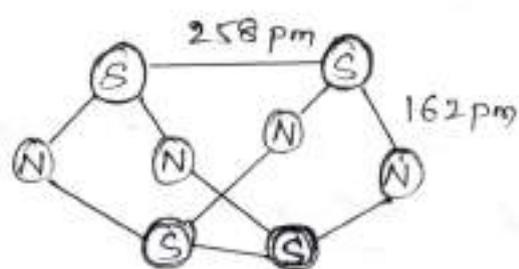
It is prepared by passing  $NH_3$  gas into a warm solution of  $S_2Cl_2$  (sulphur monochloride) in  $CCl_4$ .



Alternatively it can also be prepared from heating  $S_2Cl_2$  and  $NH_4Cl$  at  $160^\circ C$ .

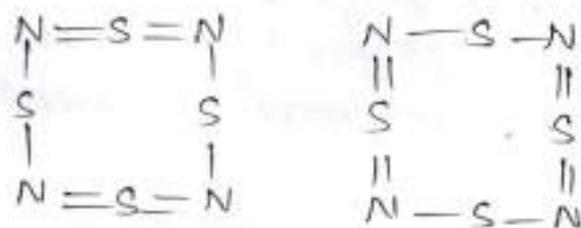


#### Structure:



- ⊗  $S_4N_4$  has an eight membered cage-shaped heterocycle.
- ⊗ The S-N distance 162 pm and S-S bond distance is 258 pm.
- ⊗ In terms of VBT several resonance structures are drawn for  $S_4N_4$ .
- ⊗ All S-N distances are equal and suggest that some electron delocalisation.

## Resonance structures:



## Applications:

- ① It is used as finger print developing material.
- ② It is used in light emitting diodes (LEDs)
- ③ It is also used in solar cells.
- ④ used as superconducting material below 1K.
- ⑤ It is the first conducting polymer.

## ⇒ Silicon-based polymers

Silicon based polymers constitute the most important class of inorganic polymers. These include organopolysiloxanes commonly known as "silicones".

## Silicones:

The polymeric organo-silicon compounds containing Si-O-Si linkage are called silicones.

There are two major types of silicones.

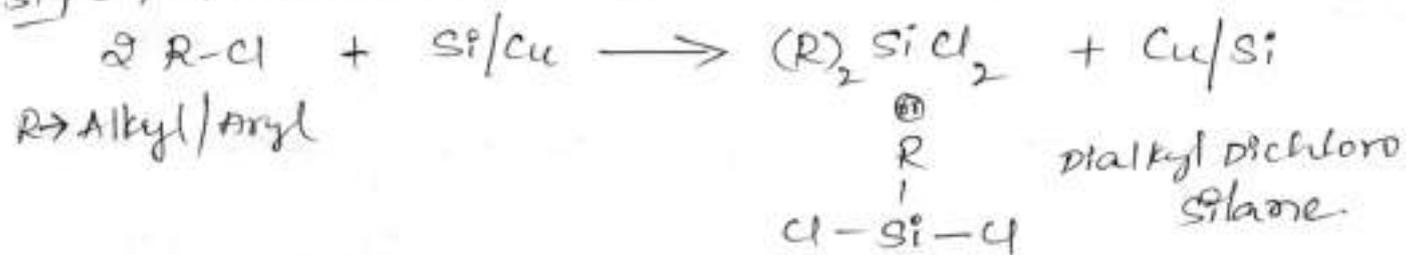
(\*) Linear silicones

(\*) Cyclic or cross linked silicones.

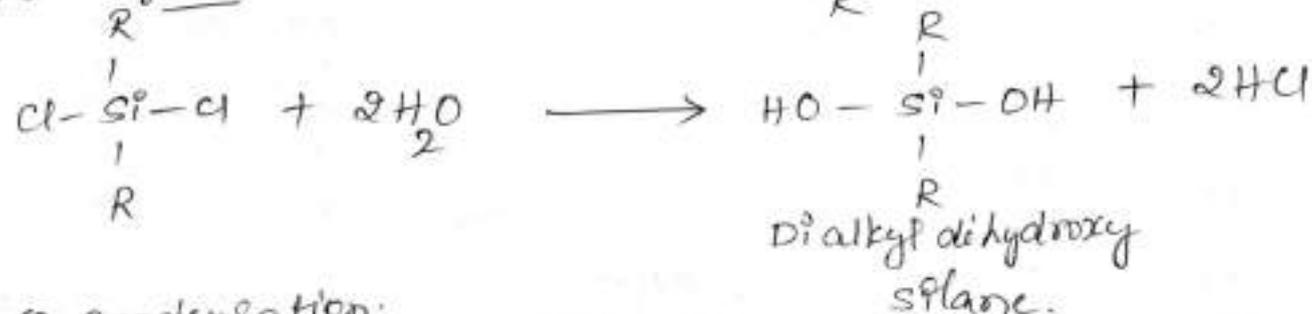
## Preparation:

Silicones are prepared by hydrolysis of alkyl or aryl substituted silicon halides. These compounds are initially synthesised by passing alkyl or aryl halides over Cu/Si catalyst at about 300°C.

Step 1 preparation of dialkyl dichloro silane

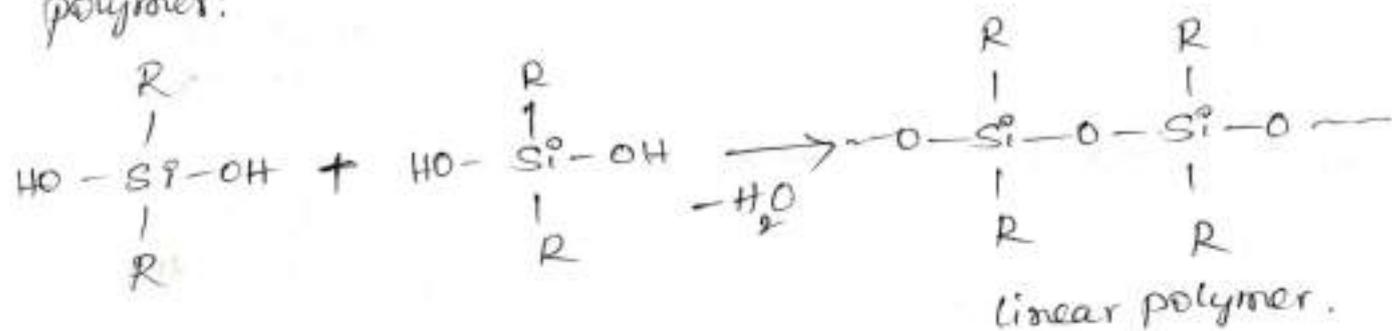


Step 2 Hydrolysis:



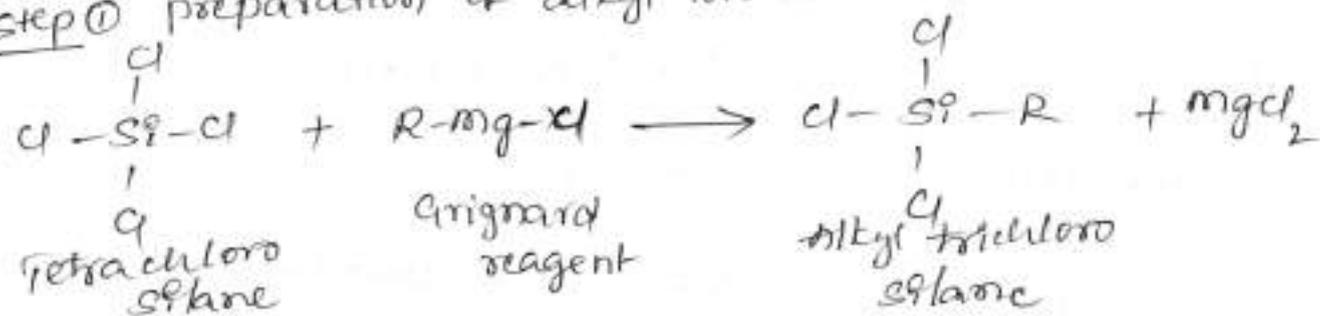
Step 3 Condensation:

polymerization of dialkyl dihydroxy silane: leads to linear polymer.

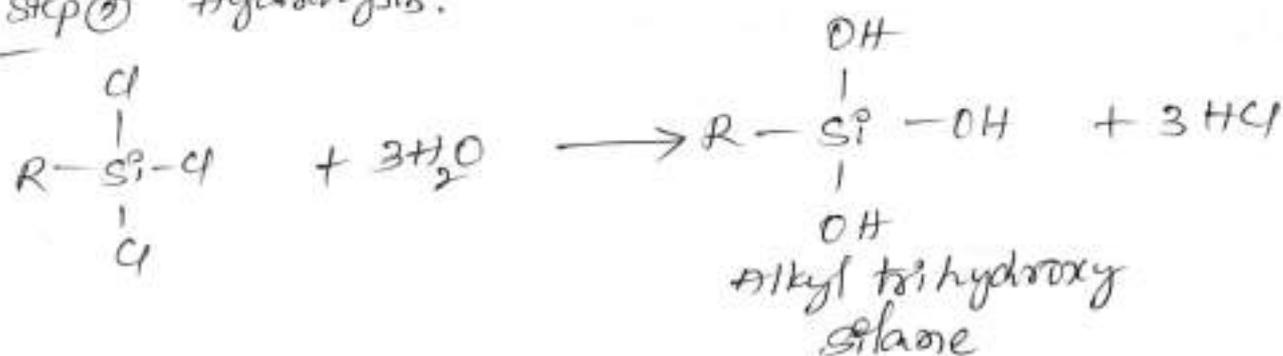


⇒ preparation of cross linked polymer:

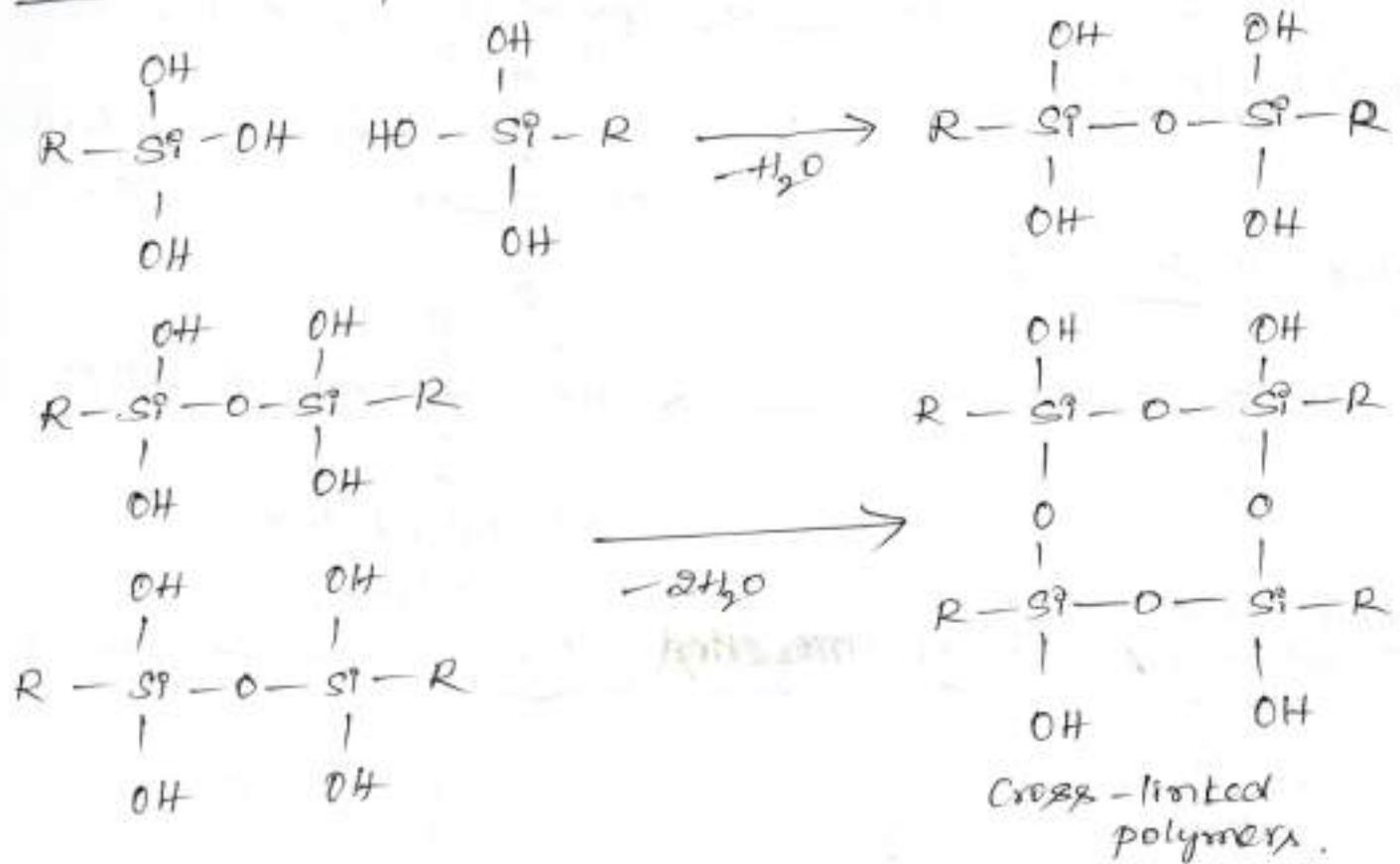
Step 1 preparation of alkyl trichloro silane.



Step 2 Hydrolysis.



### Step (3) condensation polymerisation



### Applications of Silicones:

- ① silicone oils are highly stable and non-volatile on heating so, they are used for high temperature oil bath, high vacuum pump.
- ② they are used as low temperature lubricants.
- ③ They are used for waterproofing material.
- ④ They are used in electrical condensers (Insulator).
- ⑤ silicon fluids are non-toxic are used in antifoaming agents.
- ⑥ they are used as plasticizers in paints.
- ⑦ they are used as fire resistance materials.

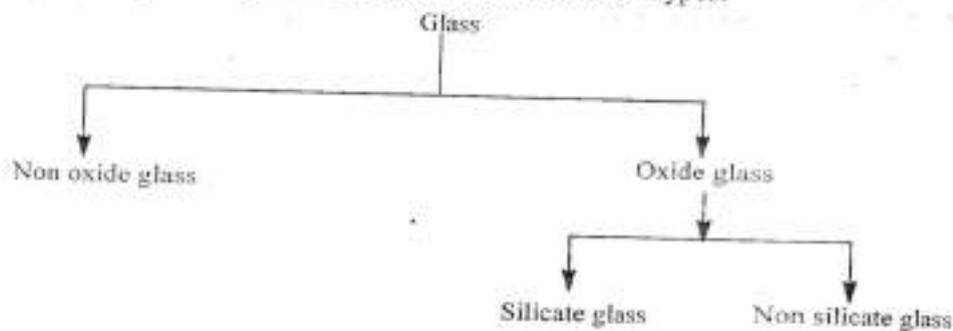
3

## Silicates

**Glass:** Glass is an amorphous, hard, brittle, transparent or translucent super cooled liquid of infinite viscosity having no definite melting point. It is obtained by fusing a mixture of number of metal silicates.

Normally glass is formed upon cooling of a molten liquid in such a manner that there is no regular (ordered) arrangement of atom.

Based on the composition glasses are classified into different types.



### Non-oxide glasses:

Glasses not containing oxygen.

1) **Heavy metal fluorides:** Fluorides of Zr, Ba, La, Al, Na (ZBLAN)  
They are used in telecommunication fibers (since they have relatively low optical loss)  
They are extremely difficult to form and have poor chemical durability.

2) **Glassy metals (no oxide metals):** They are formed by high speed quenching of fluid metals.

Most studied glass metal is, compound of iron, nickel, phosphorus and boron.  
It is used in flexible magnetic shielding and power transformer.

3) **Semiconducting solids (Chalcogenised):**

They are formed by melting together the S, Se, or Te (16-group) with elements of group 15 and 14 (As, Sb, Ge).

They are used in threshold and memory switching devices and in xerography.

Amorphous silicon (Si) and amorphous germanium (Ge)

Used in photovoltaic application, solar cells, calculator.

### Oxide glasses:

1) **Non silicate glasses:** Glasses not containing silica ( $\text{SiO}_2$ ) are called non silicate glasses.  
They are generally phosphates, borates

2) **Silicate glasses:** Glass based on  $\text{SiO}_2$  are called silicate glasses.

Silica glasses are the most commercially important glasses.

Glass made of exclusively  $\text{SiO}_2$  is called silicate glass or **Vitreous silica**.

Silica glasses are used in high service temperature.

Very high thermal shock resistance

High chemical durability  
Very low electrical conductivity  
Good UV transparency.

3) **Soda-lime-silica based glasses:** are low cost, good durability, used in containers, window planes, light bulbs and tubes, Table wares etc.,

### Properties of glass

More or less random arrangement of atoms is responsible for many of the properties that distinguish glass from other solids. one unique property of glass is its **isotropicity**, that is properties such as tensile strength, electrical resistance, refractive index, thermal expansion etc., are of equal magnitude in any direction through the material.

#### Density:

In the random atomic order of a glassy solid, the atoms are packed less densely than in a crystalline solid. This random arrangement leaving large interstitial spaces or holes between the atoms.

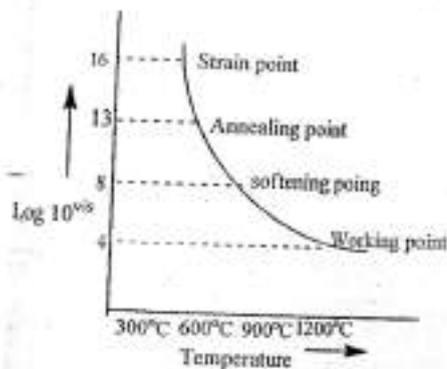
The density of glass depends on the composition.

#### Elasticity and plasticity:

Elasticity is the measure of ability of a solid to recover its original dimensions after being subjected to lengthwise tension or compression. Glasses have high elasticity.

### Thermal Properties:

#### Viscosity:



Viscosity of glass depends on temperature, Viscosity of glass decreases with raise in temperature. It is measured in poise (cm g s)

Transformation of glass from liquid state to solid state is gradual, the transition takes place over a range of temperature called the glass transformation range this is called **glass transition temperature (T<sub>g</sub>)**.

Addition of amount of alkali (network modifying atoms -NWM) lower the transformation temperature.

**Thermal Expansion:**

Glass normally expands when heated and shrink when cooled. When hot glass is suddenly cooled, the outer layer shrink relative to the inner layer, great tension may develop in the outer layer, this tension may leads to cracking.

Resistance to such thermal shock is known as **thermal endurance of glass**. It is inversely related to the thermal expansion coefficient and thickness of the glass.

Eg: Soda-lime silicates, alkali-lead-silicates have high thermal expansion coefficient.

Pyrex-type sodium borosilicates, vitreous silica have low thermal expansion coefficient.

Silica glass containing 7.5%  $\text{TiO}_2$  has zero thermal expansion coefficient.

**Thermal conductivity:**

Thermal conductivity is due to atomic vibrations(Phonon mechanism). Atomic vibrations does not increases appreciably with temperature hence glass have low thermal conductivity.

**Chemical properties:**

Chemical durability in glass depends on ion exchange reaction in which alkali ions in the glass are exchanged with hydrogen atom or hydronium ion present in the atmospheric humidity or water. The alkali metal ions thus leached out of the glass react with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the atmosphere to produce alkali carbonates and bicarbonates.(which deposit on the glass surface)

Vitreous silica, borosilicate, aluminosilicates are excellent weathering resistance.

Small amount of alumina in glass improve the chemical durability of glass.

**Electrical properties:****Electrical conductivity:**

Although most glasses contains charged metal ion(Capable of conducting electric current), the high viscosity of the glass prevent their movements and prevent the electrical conductivity.

Thus glass is efficient electrical insulator.

High voltage lamps require low electrical conductivity glass.

**Dielectric Constant:**

Glasses have high dielectric constant. The dielectric constant of glass generally increases with the concentration of (NWM)ions. Most soda-lime-silicate glasses have high dielectric constant.

They are used in separating plates of capacitors, and in IC's.

Vitreous silica has lowest dielectric constant.

**Optical properties:****Transparency:**

Electrons in glass molecules are confined to particular energy levels, they cannot absorb and reemit photons(No electronic transition) as a result light energy travels through the glass without absorption and reflection, so glass is transparent.

Molecular units in glass are smaller than the wavelength of ordinary light hence the absorption of light is negligible.

**Opacity:**

Radiation of some wavelength can cause glass molecule to vibrate, making the glass opaque.  
Eg: Most oxide glasses are opaque to UV radiations (<350 nm).

**Colour:**

Glass with certain metallic oxide absorb wavelength of certain colour and let other wavelengths pass, thus glass appears coloured.

Eg: Cobalt oxide give- blue colour to the glass. Chromium oxide give green colour, Manganese oxides give purple colour.

**Photosensitivity:**

Glass containing small amount of cerium oxide and ions of copper, silver or gold when exposed to UV radiation causes the oxidation of cerium and reduction of copper, silver or gold ions to metallic state, upon subsequent heating, the metal nuclei grow to colloidal state and develop colour. (Red for copper and gold, yellow for silver)

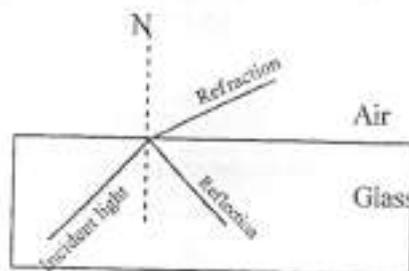
Photochromic eye glasses are generally alkali-boroaluminosilicates with 0.01 to 0.1% of silver halide and small amount of copper.

Upon absorption of light the silver ion reduces to metallic silver and form colloid about  $120\text{\AA}$  in size, the colloid make the glass gray or brown. The darkening is removed by the removal of light (optical bleach) or by raising the temperature (thermal bleaching)

**Refraction and Reflection of Light:**

If the light ray strikes the boundary between the two medium at an angle other than the normal angle, then light will be partially reflected back into the first medium and partially refracted or deflected in its path through the second medium.

The effect of light reflected or refracted depends on the relative densities of the two medium (glass and air) and also depends on the angle of incidence.



If  $\theta_i < \theta_c$  most of the light is refracted and small amount of light is reflected

If  $\theta_i > \theta_c$  all the light is reflected back to the glass.

Refractive index depends on the type of glass and wave length of the light.

## Manufacture of Glass:

Raw materials used in the manufacture are classified into following groups

- 1) Network formers(NWF)
- 2) Network modifiers(NWM)
- 3) Oxidising agents
- 4) Refining agents
- 5) Cullets
- 6) Colouring agents.

**Network formers:** There are the oxides of elements which are surrounded by four oxygen atoms in the tetrahedral chain forming highly cross linked network of chemical bond.

Eg: Sand or quartz ( $\text{SiO}_2$ ),  $\text{B}_2\text{O}_3$ ,  $\text{GeO}_2$ ,  $\text{P}_2\text{O}_5$  etc.,

### Network Modifiers:

These are the large diameter elements having high coordination number, they alter the network structure, usually present as ions, bonded to non bridging oxygen atoms.

Eg: Oxides of alkali metals  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$   
Oxides of alkaline earth metals,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$   
Oxides of lead, Oxides of zinc.

### Oxidising agents:

Materials like  $\text{NaNO}_3$  or certain peroxides are used to reduce the colour of impurities like iron oxide and manganese oxide.

### Refining agents:

Salt cake ( $\text{Na}_2\text{SO}_4$ ) is used to remove impurities in the form of scum.

To reduce or to eliminate quantity of air bubbles from molten glass, refining agents like  $\text{As}_2\text{O}_3$  and small amount of feldspar is added to the glass.

### Cullets:

Waste or broken glass pieces are called cullets. Cullets lower the cost of production and helps in the fusion of glass batch.

### Coluring agents:

During the manufacture of coloured glass, some metal oxides are used as colouring agents.

Eg: Oxides of chromium and iron gives green glass

Oxides of copper and cobalt gives blue glass

Oxides of Mn gives violet glass

Oxides of Ce and Ti gives yellow glass.

**Manufacture process of glass consists of the following four steps:**

- I. Preparation of glass batch and Melting of glass batch.
- II. Fabrication of the articles.

- III. Annealing of article formed
- IV. Finishing treatment.

**Preparation of glass batch and Melting of glass batch:**

The calculated amount of raw materials are ground separately and mixed in the batch mixer to get homogeneous mixture called glass batch. The dry glass batch is charged into the furnace.

Two types of furnace are used for glass melting. 1) Tank furnace and 2) Pot furnace

**Tank furnace:**

It consists of a large rectangular tank built of fire clay blocks. The batch material is fed into the tank and charge is heated at 1400 -1500°C by burning producer gas for about 10 – 12 hours, The Collets melt first and helps the melting of rest of the charge.

The following reaction takes place in the furnace.



Silica also combines with silicate of calcium and sodium to form glass.

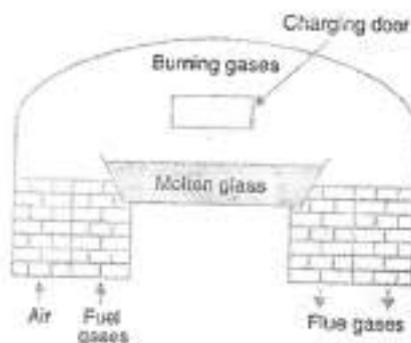


During melting lot of frothing is formed due to evolution of the gases like CO<sub>2</sub>, SO<sub>2</sub>, O<sub>2</sub> etc..

Temperature is maintained to reduce the viscosity and to get homogeneous liquid. Heating is continued till the glass is free from gas bubbles. Impurities form a scum called glass gall which is skimmed off (Na<sub>2</sub>SO<sub>4</sub> is added to remove scum and ready escape of gases, little As<sub>2</sub>O<sub>3</sub> is added to remove bubbles).

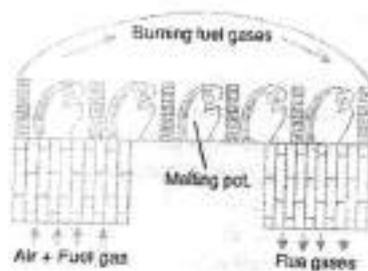
The required colouring agent is added to the colour less molten glass and it is allowed to cool(700 to 1200°C) so that it will have the proper viscosity for shaping.

*Note: Tank furnace is a continuous process used for the production of large quantity of only one variety of glass at a time.*



**Pot Furnace:** In this furnace, the charge is fused in fire clay pots. The pots may be opened or closed. The pots are placed in the furnace and heated by burning producer gas. When the fusion is complete the pots are removed from the furnace and the fused mass is taken out for shaping.

*Note: Pot furnace is employed for the production of high quality glass, since the charge remains protected from the product of combustion.*



**Shaping:** The Plastic glass formed in the furnace is next shaped into the desired articles such as sheets, tubes, rods, bottles etc., either by blowing from mouth or by means of a machine or hand mould or by machines.

**Annealing:**

After shaping the glass articles need to be cooled slowly. Rapid cooling causes fracture of the glass articles (brittle) due to internal strain. If the glass articles are cooled too slowly leads to crystallization of glass, so that glass articles are cooled in controlled rate is called annealing of glass. Annealing of glass is done in a special chamber of about 50 – 60 foot long, the temperature of the chamber is gradually reduced to room temperature.

**Finishing:**

After annealing, the glass articles are subjected to finishing such that cleaning, grinding, polishing, cutting, etc., to bringing them to usable form.

**Composition and properties of silicate glasses:**

1) **Soda lime glass:**

The approximate composition of soda lime glass is  $\text{SiO}_2$ (75%),  $\text{Na}_2\text{O}$ (15%),  $\text{CaO}$ (12%).

About 90% of all glasses produced belong to soda lime glass.

It is low cost, Low melting point, It is resistance to devitrification (Crystallisation), resistance to water but less resistance to acids.

Uses: It is used in Window glass, electric bulbs, plate glass, bottles, jars, building blocks, table wares etc.,

2) **Lead Glass or Flint Glass:**

The approximate composition of lead glass is  $\text{SiO}_2$ (50%),  $\text{PbO}$ (45%), little  $\text{K}_2\text{O}$ .

It is more expensive than soda-lime glass, it has low softening temperature, it has high refractive index.

It is bright lustrous and high specific gravity (3 to 3.3)

Uses: High quality table wares, optical lenses, neon sign tubing, Cathode ray tubes, Prisms, Window shields for X-ray in medical fields and  $\gamma$ -rays shield in atomic energy fields.

3) **Safety glass:**

a) **Laminated Glass:**

A thin layer of vinyl plastic is introduced between the two or three sheets of glass.

It is tough, when the glass breaks it does not fly into pieces as the inner plastic layer tends to hold back the broken pieces of the glass.

Uses: Used as window shields of automobiles and aeroplane.

b) **Armoured glass (Bullet Proof glass):**

It is obtained by pressing together several layers of glass with vinyl resins in alternate layers.

It is very tough, not allow bullets to penetrate.

Uses: Safety glass in aircrafts, helicopters, submarines, automobile window screens.

c) **Tough glass or Tempered glass:**

It is made by dipping the hot glass in an oil bath, so that the outer layer of glass shrink and acquire a state of compression, while the inner layer in a state of tension.

It is more elastic, it withstand thermal and mechanical shocks. When such glass breaks it shatters into many small pieces, the pieces will not have sharp edges and do not cause injury.

Uses: such type of glass is used in making doors and windows of automobile glass.

4) **Borosilicate glass:**

The approximate composition of the glass is  $\text{SiO}_2$ (80%),  $\text{B}_2\text{O}_3$ (15%),  $\text{Na}_2\text{O}$ (4%),  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$  are in trace quantity.

It has low thermal coefficient of expansion, High chemical resistance, very high softening temperature, excellent resistance to shocks.

Uses: It is used in laboratory apparatus, kitchen wares, television tubes, electrical insulators, pipe lines for corrosive liquids.

5) **Fluorosilicate glass:**

The glass made up of fluorine, silicon and oxygen is called fluorosilicate glass, it has low-K dielectric.

Uses: Fluorosilicate glass is used between copper metal layers during silicon integrated circuits fabrication process(Computer chips) it is widely used by semiconductor fabrication where it forms insulating dielectric.

6) **Coloured glass:** Coloured glasses are made by the addition of appropriate amount of a colouring agent to the batch. Various transition metal oxides are used get coloured glass.

Green : Iron chromate

Blue: Cupric oxide, cobalt oxide, ceric oxide

Yellow: Cerium oxide, titanium oxide

Pink: Selenium oxide

Violet: Manganese oxide.

7) **Photochromic Or Photosensitive glass:**

Photochromic glasses are those which darken when exposed to solar radiation or any other radiations having UV component and undergoing bleaching as the exposer is stopped.

They are dark in bright sunlight but clear in low ambient light conditions.

Composition: alkali borosilicate contains small concentration of silver halides(0.2-0.7%) ( $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ )

A reversible photo darkening phenomenon appears due to precipitation of minute grains of silver metal with the absorption of visible light.



$\text{AgCl}$  is sensitive to UV and violet light

$\text{AgBr}$  and  $\text{AgI}$  are sensitive to longer wavelengths

Uses: They are used in ophthalmic lenses, building and automobile windows.

**Crooke glass** is a special optical glass contains  $\text{SiO}_2$ ,  $\text{PbO}$ ,  $\text{K}_2\text{O}$ , and little  $\text{CeO}_2$ (ceric oxide) it cuts off harm full UV radiations so it is used in spectacles.



## CERAMICS ( Keramose-in Greek)

Ceramic refers to clay products such as porcelain wares, potteries, refractories, building bricks, insulators, etc.,

"All materials made from clay, moulded to desired shape and fired to make them hard are known as ceramics"

### Classification:

Ceramics are broadly classified into two class:

- 1) Heavy clay products: Eg: Bricks, roof tiles, drain tiles, Hollow tiles, Stone wares, and refractories.
- 2) Pottery products: Eg: China ware, wall and floor tiles Electric insulators,

Ceramic may also classified as **porous**, and **non-porous**. The porosity is depends on particle size, moulding process and temperature of vitrification.

Further ceramic may be classified based on the method of production and its uses into following classes.

- 1) White ware: Tiles, China dish, utensils, Jars, Decorative articles, ceramic insulators, spark plugs.
- 2) Structural clay product: Bricks, roof tiles, Hollow tiles
- 3) Refractory material: Crucibles, Lining for furnace and Killen

**Raw materials:** The basic raw materials required for the manufacture of ceramics are

- 1) Clay, 2) Feldspar, 3) Sand or quartz

**Clay:** Finely grained rock which gain plasticity when wet, hard when dried and rock like permanent mass when fired.

Clays are impure hydrated aluminosilicates

Eg: i) Kaolinite or China clay:  $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$

ii) Illite:  $K_2O, MgO, Al_2O_3, SiO_2 \cdot H_2O$

If the clay remains at its original location is called primary clay, which contains low iron content.

Eg: Kaolinite or China clay.

If in the course of geological changes, the clay has been transported to another location is called secondary clay, which contains relatively large iron oxide content.

**Feldspar:** Aluminosilicates of sodium potassium and calcium are called feldspar. They have low fusion temperature. They serve as a flux and a binder in ceramic articles.

Eg: i) Potash feldspar ( $K_2O, Al_2O_3, 6SiO_2$ )

ii) Soda feldspar ( $Na_2O, Al_2O_3, 6SiO_2$ )

iii) Lime feldspar ( $CaO, Al_2O_3, 6SiO_2$ ).

**Sand(Quartz):** Sand is silicon dioxide exist in the form of quartz, flint etc. Sand provides skeletal structure to ceramic ware. It reduces shrinkage and induces rigidity.

**Other ingredients:** very small quantity of certain substances such as borax, sodium nitrate, soda ash, oxides of iron, lead, aluminium, magnesium are also added to improve the properties.

#### **Manufacture of ceramic ware:**

Ceramic ware can be produced by wet process or dry process or cast process.

In wet process involves the following stages.

1. **Preparation of slip:** The raw material are ground to a fine powder separately. They are mixed in proper proportion in a mixer tank. A cream like paste is obtained which is called the 'slip'.
2. **Filtering:** The paste is then passed through a filters press to remove excess of water.
3.  **Casting:** The soft mass obtained is kneaded well to get off air bubbles. This is then cast into desired shape using moulds or hand press etc. the articles are then dried slowly and fired in a oven to get a hard, porous ware called 'bisque'.

4. **Glazing:** The ceramic ware obtained above is hard, translucent and porous.

"Glazing is process of providing non-porous, hard, glassy surface to the bisque."

The ingredients require for glazing are quartz, feldspar, a little boric acid and metal oxides of zinc, lead and tin. These raw materials are finely powdered and mixed in required proportion. A homogeneous paste is made with water which is called slurry. The slurry is applied on the ceramic ware by dipping or spraying or by using brush. The ceramic ware is then dried. The dried articles are fired to high temperature under controlled conditions, depending on the temperature of firing the pores are covered up.

**Purpose of glazing:** Glazing is carried out

- i) to produce decorative look.
- ii) to make the surface impervious to water, liquids etc.,
- iii) to increase the durability of ceramic ware.
- iv) to protect the surface from any atmospheric action.
- v) to provide smooth glassy surface.

#### **Special ceramic products:**

- i) **Ceramic composites:** Composite materials made from metal and ceramics. A metallic substrate material is reinforced with ceramic hardened particles, this make it possible to combine the low weight of metal with the heat resistance ceramic.  
Ceramic fibers embedded in ceramic matrix, (silicon carbide fibers)  
Uses: Reinforcing engine cylinder sleeves, piston rings, break disks.  
Jet engine, turbine blades, jet Engine blades.

- ii) **Ferroelectric ceramics:**
- a) **Piezoelectric ceramics:** When mechanical stress is applied between two surfaces of a solid dielectric part, generate voltage between the surface.  
 Eg: Lead zirconates and titanate. Barium titanate, Bismuth titanate  
 Uses: transducers, actuators, sensors like hydrophones, sonar, strain guards, medical ultrasound equipments.
- iii) **Ferromagnetic ceramic: (Ferrite):** Made of iron oxide and barium and strontium carbonate with small amount of other metal oxides. They have magnetic property.  
 Uses: Ferritic antennas, permanent magnet, motors, loudspeakers magnets, TV deflection yoke cores and convergence coil cores, Magnetic resonance imaging(MRI), audio-visual reading heads.
- iv) **Ceramic biomaterials:** they are light weight, wear resistant, and not attacked by the enzymes)  
 Uses, Artificial teeth, bone joints, filling gaps in damaged bones
- v) **High alumina ceramic:** mechanically strong, wear resistant, corrosion resistant  
 Uses: insulator for electrostatic precipitators.
- vi) **Sensors:**
- a) **Humidity sensors;** made of titanium oxide and magnesium chromates.  
 b) **Gas sensors:** made of oxides of titanium, iron, tin, silver and zinc.
- vii) **Superconducting Ceramics:** Lanthanum-barium-copperoxide( $\text{LaBa}_2\text{Cu}_3\text{O}_{6+x}$ ) and Yttrium-Barium-Copperoxide( $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ ) are super conducting ceramics.  
 ( $\text{LaBa}_2\text{Cu}_3\text{O}_{6+x}$ ) is high temperature superconductor ( 138K).  
 Uses: Electricity transmission, Levitation trains, MRI imaging.
- Viii) **Semiconducting ceramics:** Ceramic based on ZnO doped with suitable dopent.have super conducting properties.  
 Uses: Varsistors, which are used for overvoltage protection, and positive temperature coefficient resistors.
- ix) **Silicon nitrides( $\text{Si}_3\text{N}_4$ ):** High thermal stability.  
 Uses: Tiles used as outside coating for space shuttles(It withstand over  $1500^\circ\text{C}$  during re-entry into the Earth's atmosphere) Gas burner nozzles, Ballestic protection, nuclear fuel uranium oxide pellets, Missile nose cones, Rocket nozzles, jet engine turbine blades.
- x) **Vitreous enamel:** It is opaque seldom transparent, coloured or colourless flux, it is easily fusible.  
 Uses: It is used as protective or decorative agent to coat the surface of glass, porcelain and metals(iron sheets).

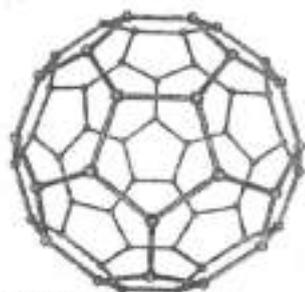
## Fullerenes:

Fullerenes are allotropic forms of carbon. These were discovered in 1985 by *Smalley* and *Kroto*. These are named after the famous American architect *Richard Buckminster Fuller*. Fullerenes are prepared by the evaporation of graphite electrode. Fullarene are found in chimney and in candle flame.

There are two important types of fullerenes: 1) fullerene- $C_{60}$  and 2) fullerene- $C_{70}$

Fullerenes are brown coloured solids. They are soluble in organic solvents like  $CS_2$  and aromatic liquids, they are insoluble in water and ether.

### Fullerene- $C_{60}$ :



Fullerene- $C_{60}$  has a cage like structure made up of 60 carbon atoms containing 20 hexagons and 12 pentagon rings. In fullerene each carbon atom has  $sp^2$  hybridisation. There are 30 double bonds present in alternate positions, however no delocalisation of electrons because of non planar structure. The shape of the fullerene is spherical, it resembles the soccer ball with diameter of 710 pm

### Fullerene- $C_{70}$ :

It is a polygon, made up of 25 hexagon and 12 pentagon rings. It has a structure similar to *Rugby ball* with the diameter of 780pm and 690 pm. Fullerenes are cannot be considered as aromatic compound because there is no hydrogen atoms in the molecules, they behave highly unsaturated and give addition reaction similar to alkenes.

### Uses:

Fullerenes are used as lubricants. They are used as super conductors. Fullerene coated glasses are used in working with high intensity laser beams

### Carbon Nanotubes:



Carbon nanotubes are allotropes of carbon with a cylindrical nanostructure. They have hollow structure with the walls formed by one atom thickness sheet of carbon.

Carbon nanotubes are formed by plasma arcing of graphite.

The cylindrical nanotubes have unusual properties, which are valuable for nanotechnology, electronics, optics, and in material science and technology.

Properties of nanotubes depends on the rolling angle and radius.

Application: Bulk carbon nanotubes have been used as composite fibers in polymers to improve the mechanical, thermal and electrical properties of the bulk product.

**Application of Carbon nanotubes:**

- 1) Bicycle components.
- 2) Construction of aircraft
- 3) Carbon nanoepoxy resin
- 4) Environmental monitoring products
- 5) Tennis and Badminton rackets.

**Carbon fibers:** carbon fibers are the fibers about 5 – 10 micrometer in diameter. Carbon fibers have high stiffness, high tensile strength, low weight, high chemical resistance, high temperature tolerance and low thermal expansion.

Uses Composite materials, Graphite reinforced polymers.

In metal matrix composite, Fibers in the filtration of high temperature gases,

Electrodes as it has high surface area and corrosion resistance.

Motorcycle racing gloves, Micro electrodes,

## Cement

Cement is a powdered material, which initially have a plastic flow when mixed with water, it set into hard solid structure in several hours.

**Type of cements:**

- 1) **High alumina cement:** it is a calcium aluminate, prepared by heating lime stone and bauxite(containing iron oxide, magnesia, silica and other impurities)  
It has very rapid rate of development of strength and resistance to sea and salt water.
- 2) **Hydraulic hydrate lime:** It consists of calcium hydroxide a major component, dicalcium silicate( $C_2S$ ) and tricalcium silicate( $C_3S$ ) are the minor components.  
It is low price and have good strength. It is used for brick mortar composition.
- 3) **Pozzolan cement:** This cement is made by grinding 3 part of pozzolan(volcanic ash) with 1 part of hydrated lime in presence of some burnt clay.  
It is mixed with Portland cement as a cheap extender.

Portland cement is one of the most important building material at present time.

“Portland cement is a mixture of calcium aluminate and silicates of varying composition, which hydrate when mixed with water to form a rigid solid structure with good compressive strength.”

The Portland cement is a mixture of the following composition.

- i) Dicalcium silicate ( $2\text{CaO SiO}_2$ )
- ii) Tricalcium silicate ( $3\text{CaO SiO}_2$ )
- iii) Tricalcium aluminate ( $3\text{CaO Al}_2\text{O}_3$ )
- iv) Tetracalcium alominao ferrite ( $4\text{CaO Al}_2\text{O}_3 \text{Fe}_2\text{O}_3$ )
- v) Magnesium oxide ( $\text{MgO}$ )
- vi) Calcium oxide( $\text{CaO}$ )

**Types of Portland cement:**

Varying the composition of the constituent present in the cement, it is possible to vary the rate of setting, heat evolved and strength characteristics.

Based on the above characteristics the Portland cement is classified into five types.

- 1) **Regular Portland cement:** They contain 40-60% of tricalcium silicate( $\text{C}_3\text{S}$ ), 10-30% of dicalcium alumino silicate( $\text{C}_2\text{AS}$ ) and 7-13% of tricalcium aluminate ( $\text{C}_3\text{A}$ ) It is white cement. Quick setting cement. It harden to full strength in about 28 – 30 days
- 2) **Modified Portland cement:** They have high  $\text{C}_2\text{S} / \text{C}_3\text{S}$  ratio. They are sulphate resistant cement. Heat evolved not exceeds 70- 80 cal/g
- 3) **High early setting Portland cement:** These cements contain high percentage of  $\text{C}_3\text{S}$  and  $\text{C}_3\text{A}$ . It is quick setting cement, it attain strength in 3 days. Uses, road construction.
- 4) **Low heat Portland cement:** These cements contains lower percentage of  $\text{C}_3\text{S}$  and  $\text{C}_3\text{A}$ . Heat evolved not exceed 60 – 70 cal/g use in massive structure work
- 5) **Sulphate resistant Portland cement:** they have low  $\text{C}_3\text{A}$  and high  $\text{C}_4\text{AF}$ . Resist sulphates. Good for sea water contact.

**Manufacture of Cement:**

**Raw materials:** 1) Lime stone, 2) Silica, 3) Alumina, 4) Iron oxide and 5) Gypsum

Clay provides all ingredients(silica, alumina and iron oxide) required..

**Lime:** is the principal ingredient, it provides strength to the cement. Its proportion is must be properly regulated. Both excess and lesser amount of lime reduces the strength of the cement.

**Silica:** Imparts strength to cement.

**Alumina:** Reduces setting time of cement.

**Iron oxide:** Provide strength, hardness and colour to the cement.

**Gypsum(CaSO<sub>4</sub>.2H<sub>2</sub>O):** It prevent early setting(quick setting) of cement.

There are two methods of manufacture of Portland cement;

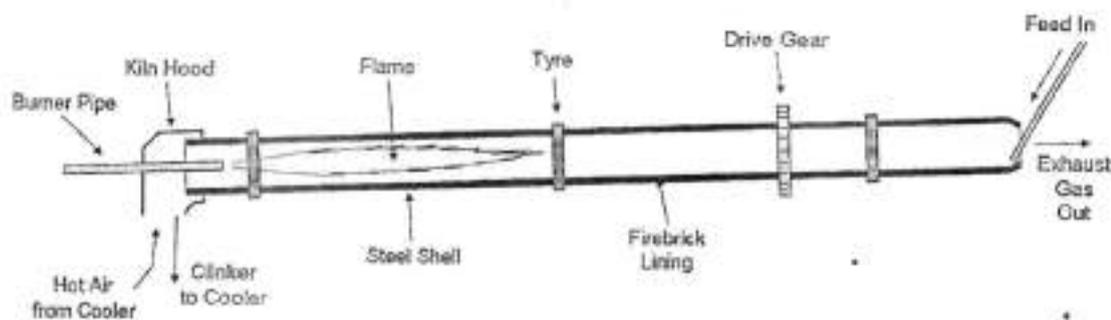
I. Wet process

II. Dry process. (Dry process require less fuel consumption and provides accurate control).

**Dry process:**

**Grinding:** The raw material are separately ground to a fine powder in a ball mills. The powdered materials are then mixed in proper proportions to obtain a homogeneous mixture called "dry meal"

**Burning:**



The dry meal is introduced into a rotary kiln, This is steel tube lined inside with refractory bricks and kept in a slanting position. The charge moves down slowly. A blast of burning saw dust is sent in from the other end. A maximum temperature of 1750°C is reached here.

At this temperature lime and clay undergo chemical fusion to form calcium aluminate and silicates.

The following chemical reaction takes place in the kiln.



The product formed is called "cement clinker". The cement clinker is very hot(1000°C) is allowed to cool by blowing air in the opposite direction.

**Grinding of clinker:** The clinker is ground to a fine powder in ball mills. During grinding process 2-3% of gypsum is added to reduce setting time of cement. The powdered cement is packed in air tight bags.

**Setting of cement:** On mixing cement with water to get a plastic mass called cement paste; a process of hydration sets in. A gel like substance is formed which is finally sets to a hard stone like mass.

The process of solidification is due to (i) Setting and (ii) Hardening.

Setting is defined as stiffening of original plastic mass due to initial gel formation.

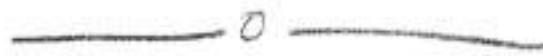
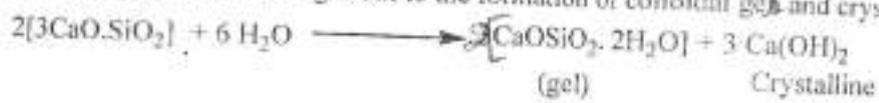
Hardening occurs due to gradual dehydration followed by crystallization and provides strength to the material.

The strength developed by cement depends on the amount of gel formed and the extent of crystallization. It requires about 28 days.

Initial setting is due to hydration



Final setting and hardening is due to the formation of colloidal gel and crystallization.



# SURFACE COATINGS:



## Objectives of coating surfaces:

A coating is a covering that is applied to the surface of an object, referred as substrate.

The purpose of applying coating may be decorative, functional or both.

propriate → Functional coatings are applied to change the surface properties of the substrate, such as adhesion, wettability, corrosion resistance, or wear resistance.

ns the → Protective coatings are used to protect the surface of the substrate.

## Ex: Paints:

→ Magnetic coatings such as for cassette tapes, floppy disks.

→ Insulating coatings on magnet wires used in transformers.

## Preliminary treatment of surface:

Preliminary treatment has to be done to make a surface resistant against oxidation, corrosion etc.

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Surface coatings: Any mixture of film forming materials plus pigments, solvents and other additives, which when applied to a surface and dried, yields a thin film that is functional and decorative.

## Properties of coatings:

- > It is water resistant. It is important since all coatings will come in contact with moisture.
- > It should be corrosion resistant.
- > Proper adhesion: A corrosion resistant coating must also be highly adherent.
- > Chemical resistance: It is the ability of the coating, and particularly the resins from which it is formulated, to resist breakdown by the action of chemicals to which it is exposed.

Paints: It may be defined as a homogeneous fluid containing suspension of finely divided solids that dries up when applied on a surface. The drying up of paint may be due to oxidation or evaporation and polymerisation.

Requisites of a good paint:

1. It should be inert to the atmosphere to which it is being exposed and then be able to protect the painted surface from environmental effects.
2. It should have a high covering (or hiding) power.
3. It should form a thin, uniform, tough, adhesive and impervious film.
4. It should provide a glossy appearance.
5. The film produced by the paint should be washable.

Purpose of painting:

- (i) Protection: Protection of surface (metal or wood) from destructive influence of the surroundings. Painting also improves wear and tear, resistance to oxidation etc.
- (ii) Decoration: Give an attractive look to the surface.
- (iii) Functional: In marking roads, traffic signs etc.

Constituents / composition of a paint:

The chief constituents of a paint are:

- (i) Pigments
- (ii) Binder
- (iii) thinner
- (iv) drier
- (v) others like pigment extenders, anti-skinning agents, colouring agents, defoamers, preserving agents etc.

(i) Pigments:

Pigments are solid coloured substances which is bound to a surface with the help of a binder. Both inorganic and organic substances can be used as pigments.

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### Functions of a pigment:

1. To provide colour and to impart an aesthetic appeal to the film.
2. To protect the paint film by reflecting the destructive ultraviolet radiations.
3. To strengthen the paint film.
4. To reduce gloss and weathering property.

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### Properties of a pigment:

(i) A good hiding power or covering power:

The ability of a pigment to cover the surface is called hiding or covering power.

It is expressed as number of  $m^2$  of surface covered by one litre of the paint. This depends on the difference in the refractive index of the pigment and that of the vehicle.

(ii) Chemically inert and be non-toxic.

The pigment should be chemically inert, so that film formed is stable. It should not have any adverse effect on the painter and others, i.e., be non-toxic.

(iii) Should freely mix with film-forming constituent i.e., oil.

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### Classification of pigments:

Pigments may be classified as:

- (i) Natural or synthetic.
- (ii) Organic or inorganic and
- (iii) On the basis of colour.

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- (i) (a) Natural or mineral: talc, mica, chalk, clays, iron ores,
- (b) Synthetic or chemical pigments: white lead, zinc oxide, lithopone, titanium oxide,
- (c) Reactive pigments: Titanium dioxide, red lead, zinc oxide etc.

## List of coloured and white pigments.

Colours	Examples
1. Red	Red lead $Pb_3O_4$ , Red oxide $Fe_3O_4$ , Chrome red $Pb(OH)_2 \cdot PbCrO_4$ , Umbers (Hydrated $Fe_2O_3$ + Clay + certain other materials) (ii)
2. Green	Chromium oxide $Cr_2O_3$ , Emerald green $CrO_3 \cdot 2H_2O$
3. Yellow	Chrome yellow $PbCrO_4$ , Zinc chrome $ZnCrO_4$
4. Blue	Prussian blue $KFe [Fe(CN)_6]$
5. Black	Carbon black, graphite.
6. White	Zinc oxide $ZnO$ , Lithopone - $ZnS + BaSO_4$ , White lead $3PbCO_3 \cdot Pb(OH)_2$ , Titanium white ( $TiO_2$ ), Basic lead sulphate $Pb(OH)_2 \cdot PbSO_4$ .

## (ii) Binders or Film forming materials.

The film-forming constituent of a paint which is the non-volatile liquid portion of the paint is called a binder. This helps to bind the pigment to a surface. (iv)

The binders are generally fatty oils of vegetable origin. Examples include linseed oil, soyabean oil, tung oil etc.

### Functions of a binder:

1. Serve to hold the pigment on the surface.
2. Give adhesion to the surface. (i)
3. Provide moisture-proofness. (ii)
4. Form protective film through oxidation, evaporation or polymerisation.

### Mechanism of film formation:

The oil generally contains double bonds. Oxygen is absorbed at these double bonds resulting in the formation of peroxide free radicals. The peroxides on condensation and polymerisation, giving rise to a film having three dimensional cross links stabilised by the pigments. The paint (v)  
(a)

film is hence tough and adherent.

### (iii) Thinners:

It is necessary to have a thin concentration of the paint for easy and uniform application.

Thinners are the volatile liquid part of the paint.

Function: Thinners lower the viscosity of the paint.

The type of thinner used depends on the binder.

Commonly used thinners are water, turpentine, benzene, xylene, ether, dipentene, alcohol etc.

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Vehicle: The liquid part of the paint i.e., a mixture of the binder and the thinner is called a medium or vehicle.

The pigment is dispersed in the vehicle.

### (iv) Driers: Driers are substances added to accelerate the drying of the film.

Certain antioxidants present in some oils prevent oxidative drying of oils. This results in a delay in the process of drying and film-forming of the paint.

Functions of the drier:

(i) Suppress the action of antioxidants.

(ii) Catalyse the drying of the film through oxidation, polymerisation process.

Commonly used driers are naphthalene, resins and linoleates of heavy metals like Mn, Pb, Co, Zn etc.

The drier should be used only in small quantities (1%).

### (v) Other ingredients are:

(a) Pigment extenders: which are white or colourless pigments. They do not add to colour or opacity. They are added to improve the quality and durability of the paints. Clay,

gypsum, chalk, talc, barium sulphate are some of the common pigment extenders.

(b) Plasticizers: help in improving the elasticity of paint film and prevents its cracking. Examples are tophenyl phosphate, dibutyl phthalate etc.

(c) Anti-skinning agents: prevent gelling and skinning of paint film. These substances prevent chalking of the dispersed pigment particles and improve the stability of the paint during storage.



Polyhydroxy phenols like tert-butylphenol serve as anti-skinning agent. (C<sub>11</sub>H<sub>16</sub>O)

### OIL PAINTS:

Oil paint is a type of slow-drying paint that consists of particles of pigment suspended in a drying oil, commonly linseed oil.

The viscosity of the paint may be modified by the addition of a solvent such as turpentine or white spirit.

Vehicle: Oils are used as vehicle for paints.

Oils contain a considerable portion of glycerine, which is a hygroscopic fat, and prevents unprepared oils from drying.

### Modified oils:

Oil modified alkyd resins or polymers forming vehicle with the drying oil is used as a binder. These may be oxidising alkyd resins (which are used for house paints, interior paints, air drying under coats etc), alkyd and cellulose resins (which are used for making low temp. backing under coats) and alkyd and silicone resins (which are used for superior chemical and heat resistant coats).

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Pigment toners:it film  
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Insoluble organic dyes are known as toners and can be used as pigments. They are quite durable and have high colouring power.

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Ex: para red, Hansa yellow G (lemon yellow), toluidine toner etc. are the various dyes that have been used as toners in pigment industry.

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\* Para red can be prepared by diazotisation of p-nitroaniline and coupling it with  $\beta$ -naphthol.

\* Hansa yellow G can be prepared by diazotisation of m-nitro ~~p~~-toluidine and coupling it with acetoacetanilide.

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\* Toluidine toner, which is a red pigment, is made by coupling the diazotised m-nitro-p-toluidine with  $\beta$ -naphthol.

addition

Lakes pigments: Lakes are the organic dyes on an inorganic adsorbent (such as clay).

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Ex: Para red, Hansa yellow G etc are important lakes. Clay, barite, aluminium hydroxide etc are well known inorganic adsorbents.

Both toners and lakes are ground in oil or applied like any other pigment.

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Extenders or fillers: The extenders or fillers are added to the paint in order to decrease the cost of the paint and to supplement the pigment in increasing the covering and weathering power of the film.

Extenders improve consistency, levelling and setting of the paint.

Various fillers used are talc, china clay, gypsum, silica, glass flakes, asbestos and anhydrite etc.

Thinners: Thinner is added to the paint to dissolve film forming material and to thin concentrated paints for better handling. It is also used to suspend pigments.

- \* After adding thinner, the paint may be applied more easily on the surface by brushing, spraying or dipping.
- \* Diluents or thinners may be including aliphatic or aromatic naphtha fractions or many contain turpentine.
- \* Turpentine being less volatile, maintains the fluidity of the freshly applied film for a certain period of time.

### Enamels or Gloss Finishes

Pigmented varnishes are usually known as enamels.

[Varnish: Varnishes are transparent viscous liquids and contain no pigments. It is a homogeneous colloidal dispersion of resins in drying oils and volatile solvents].

The purpose of preparing enamels is to get a good gloss, because after drying, the enamels form a very good lustrous and glossy finish. Pigments, vehicles, driers, thinners are the various ingredients used in the preparation of enamel. They make use of pigments having fine texture and easily dispersible capacity.

For example, Titanium dioxide ( $\text{TiO}_2$ ), calcium sulphate are used for white enamel while coloured enamels are formed by replacing some or whole of the white pigment.

The vehicle used is either oleoresinous (oil plus resin) or only resin.

Oleoresinous vehicle is prepared by cooking together one or more resins (such as phenolic resins, linoxyn etc) with one or more drying oils (such as linseed oil, tung oil, fish oil, soyabean oil, dehydrated castor oil etc). The resin is used as a solution of resin in a solvent and

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drying oil.

Alkyd resins are most commonly used in the manufacture of enamels because these resins are capable of providing many desired properties such as high gloss, permanence, washability, good levelling, good initial colour.

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Emulsifying agents:

Emulsifying agents help to form an emulsion. Depending on the type of pigments and vehicles used, different emulsifying agents are chosen. Tetrasodium phosphate, sodium lauryl sulphate, ammonia are the examples of emulsifying agents.

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SPECIAL PAINTS:

Heat retardant / heat resistant paints:

The paints which are capable of resisting heat even up to red heat are called heat resistant paints.

\* These paints generally contain base of metallic powder like tin, zinc, graphite, aluminium etc. Some paints also contain polyphenyl silicones.

\* These paints are generally used in furnaces, oil stills.

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Fire retardant paints:

These paints contain such type of materials (called Binders) which breakdown at high temperatures and produce non-inflammable gases such as  $HCl$ ,  $HBr$ ,  $CO_2$ ,  $NH_3$ , water vapour etc.

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ing oil,  
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\* These gases serve to dilute the inflammable gases produced by breakdown of the other components of the paint.

Chlorinated rubber, PVC, alkyds and epoxides etc. breakdown to produce corresponding non-inflammable hydrogen halides. Carbonate pigment yield carbon dioxide, water base paints yield water vapour and urea formaldehyde.

resins yield  $\text{NH}_3$ .

Paints containing magnesium phosphate, zinc ammonium pyrophosphate, calcium ammonium phosphate or zinc ammonium tungstate etc. form a glass like melt at elevated temperatures. Thus

\* This melt prevents combustion by serving a barrier between air and inflammable substance.

### Eco-friendly paints:

Eco-friendly paints which are having low or minimal VOC (volatile organic compounds)

In paints VOCs tend to be solvents such as white spirit, which evaporate as paint dries, releasing pollutants into the environment. They also contain heavy metals such as arsenic, lead and chromium.

Once these enter into the air we inhale, they can go into our lungs and create a toxic effect on our bodies. These paints not only harm the human body, but also the environment.

Eco-friendly paints can be classified into three types.

1. Zero-VOC paints: total VOC content less than 5gram per liter of paint.
2. Low-VOC paints: VOC content from 5 to 200gram per liter of paint.
3. Natural paints: Made of natural compounds such as tree resins, water, plant oil, essential oil and natural dyes, do not contain any VOCs.

Plastic paints: Plastic emulsion paint is water based wall paint. It is based on acrylic and provide a smooth matt finish to the walls.

These paints have gained popularity because of their ease of application, quick drying properties, non-

objectionable odour and good washability.

Composition: The material shall consist of pigments and if required suitable extenders in appropriate proportion in a medium consisting of any stable synthetic polymer emulsion in water.

Dyes: A dye is a coloured substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber.

Both dyes and pigments are colored, because they absorb only some wavelengths of visible light. Dyes are usually soluble in water whereas pigments are insoluble.

Some dyes can be rendered insoluble with the addition of salt to produce a lake pigment.

Wax polishing:

Polishing is the process of creating a smooth and shiny surface by rubbing it or using a chemical action leaving a surface with a significant specular reflection.

Waxes are a diverse class of organic compounds that are lipophilic, malleable solids near ambient temperatures.

They are insoluble in water but soluble in organic, non-polar solvents. They include higher alkanes and lipids typically with melting points above  $40^{\circ}\text{C}$ , melting to give low viscosity liquids.

Mainly polyethylene and polypropylene waxes are used in the formulation of coatings.

They are also used in paints as they confer matting effects and wear resistance.

They are also employed as release agents, find use as slip agents in furniture and confer corrosion resistance.

### Water and oil paints:

Water paints are the paints used in a painting method in which the paints are made of pigments suspended in a water-based solution.

Oil paints are a type of slow-drying paint that consists of particles of pigment suspended in a drying oil, commonly linseed oil. The viscosity of the paint may be modified by the addition of a solvent such as turpentine or white spirit and varnish may be added to increase the glossiness of the dried oil paint film.

Oil painting is the process of painting with pigments with a medium of drying oil as the binder.

### Applications of oil painting:

- (i) In finishing and protection of wood in buildings and exposed metal structures such as ships and bridges.
- (ii) Used for both interior and exterior surfaces of wood and metal because of hard wearing properties.
- (iii) Due to slow drying properties, it has been recently used in paint-on-glass animation.

Characteristics: The oil paints that require an oil that hardens, forming a stable, impervious film. They are called siccative or drying oils. They have high levels of polyunsaturated fatty acids. Oils with an iodine number greater than 130 are considered drying, those with an iodine number of 115-130 are semi-drying and those with an iodine number less than 115 are non-drying.

Linseed oil is a drying oil.

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Preliminary treatment of a surface:

We need to ~~prelimine~~ carry out preliminary treatment :-

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- To prepare the surface for subsequent process, i.e. coating  
→ To remove the contaminants as it may react with the surface coating materials.

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The principle contaminants are:

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- (i) oils & greases (ii) Oxide films & rust (iii) Solid particles such as metal chips & abrasive, dust etc

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Preliminary treatment involves two methods:

- 1) Mechanical 2) Chemical.

ments.

Mechanical: In this method, the physical removal of oils, oxide films, dust from the work surface by means of abrasives or mechanical action is done.

Ex: Blast finishing.

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Chemical: In this method, the surfaces can be cleared chemically to remove dirt and contaminants.

It involves:

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- (i) Alkaline cleaning: An alkali is used to remove oils, grease, wax and metal chips, silica from a metal surface.

Method: Spraying or immersing at high temperatures of 50-95°C followed by water rinse to remove residue.

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- (ii) Solvent cleaning: The organic soils such as oils & grease are removed by means of chemicals that dissolve these soils.

Method/technique: Hand wiping, immersion/spraying.

- (iii) Acid cleaning: To remove oils and oxide films from

metal surfaces using acid solutions combined with water miscible solvents.

Ex.  $HCl$ ,  $H_2SO_4$ ,  $HNO_3$  etc.

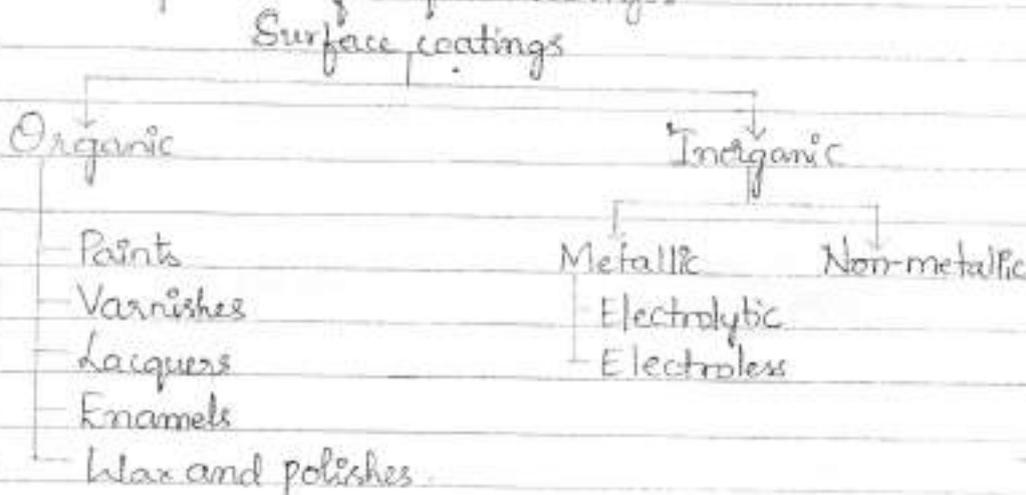
Technique: Soaking, spraying.

During this cleaning process, the substrate material is critically constant of the substrate material. Shouldn't undergo any damaging reactions which are caused by cleaning chemicals.

Because: \* Aluminium is dissolved by most acids & bases

\* Steel are resistant to alkali but react with acids.

Classification of surface coatings:



(A) Metallic coatings: In this method, the metallic article which is to be protected is known as base metal. The metal which is used for coating is known as coat metal. Therefore metallic coatings are applied over the base metal surface is done by two methods.

(i) Electroless (ii) Electroplating

Electroless plating: It is a process of plating which is done entirely by chemical reaction.

\* No external source of electric current is required in this case.



with material which is exposed to acids

It involves:

- Deposition of metal onto the part of the surface occurs in an aqueous solution containing ions of the coat metal.
- The process uses a reducing agent and work part of the surface. Catalyst reduces metal to ions.
- Nickel and Nickel alloys are used for this plating. Others are iron, aluminium, Titanium etc.

Autocatalytic immersion of steel in an aqueous solution of coat metal to get an uniform coating.

### Hot dipping:

- \* The base metal/article to be coated is dipped in a bath of molten coat metal or its alloy for sufficient time to get a uniform coating.
- \* The base metal must be very clean so that it will be wetted by the molten metal and a uniform coating will result.
- \* This method is used for producing a coating of low melting metals such as zinc, tin or lead on iron, steel and copper which have higher melting points.

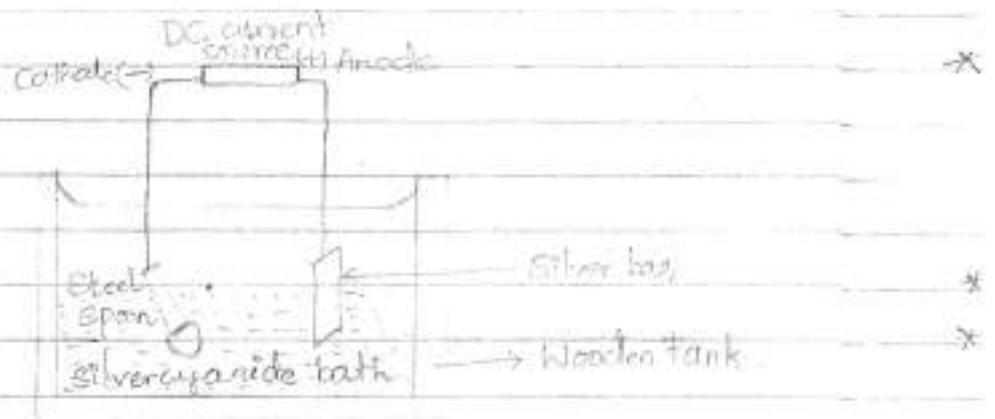
The hot dipping involves the galvanisation method.

- The process of coating a base metal (iron/steel) with a thin coat of zinc to prevent it from rusting.
- This method involves:
- \* Iron/steel cleaned by pickling it in dil. HCl and removing all the impurities and rust from the surface.
  - \* It is washed well, dried & immersed in a bath containing molten zinc and ammonium chloride flux.
  - \* Temperature of bath is maintained at  $430^{\circ}\text{C}$ .
  - \* Coating occurs and then the coated metal is passed through a pair of rollers to remove the excess of molten metal and to obtain a thin uniform coating.
  - \* It is cooled slowly.

Uses: Protection of iron pipes, roofing sheets.  
protection of screws and bolts from atmospheric corrosion.

Electroplating: It is also known as electrodepositing.

- \* It is based on the principle of electrolysis.
- \* A process by which, the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution containing a soluble salt of coat metal.



- \* In the actual process, the metal which is to be electroplated (base metal) is taken as cathode and coat metal is taken as anode.
  - \* A solution of the coat metal salt is used as electrolyte.
  - \* Now the anode and cathode are dipped in the electrolyte the electrodes are connected to a battery and current is passed.
  - \* Electrolysis takes place and a thin layer of the coat metal is obtained.
- The thickness of electroplating depends on;
- The current density.
  - Time of deposition.
  - Temperature of electrolytic bath.
  - Concentration of bath electrolyte.

This method is most important & most commonly employed method for producing metallic coatings and it

corrosion. → gives a fine coating.  
It is also used in making jewellery and finely fancy articles.

siting.

### Metal spraying:

ited on \* The surface to be coated must be clean and rough  
ough an so that the coat metal in the molten state is sprayed  
coat on to the rough surface of the base metal by means of  
a spray gun.

\* The coating may be applied to a particular area of the article and thickness can be controlled.

### Advantages:

- \* Irregular objects can be easily given a uniform coat.
- \* Coatings can be applied on a non-metallic base made of glass, wood or plastic.

### (B) Non-Metallic coatings:

- \* Here non-metals are used as coating material.
- \* Common types of such coatings plastic or rubber coating.
- \* It involves application of layers of the given polymer on to a substrate material.

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electrolytic  
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Different coatings of such type are known:

(i) Wire and cable coatings: In this case, whole length of conducting wire or electrical cable is coated with plastic or polymer to provide thermal or electrical insulation.

(ii) Planar coatings: It involves coating of a flat film over a flat surface.

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(iii) Conformal coating: It is applied over a 3-dimensional

## ANODIZING:

- \* It is a process of deposition of oxide film on a metal surface with the help of an anode and oxidation phenomenon.
- \* The aluminium coated surfaces requires oxidation to convert the metal to its inert oxide.
- \* It is carried out by using amalgam aluminium coated article as the anode in a bath of 10-15%  $H_2SO_4$  and electrolyzing.
- \* Any inert material can be cathode.
- \* When current is passed, chromic acid oxidises aluminium to its oxide which is porous.
- \* After electrolysis, the article is kept in a boiling water bath which results in the formation of  $Al_2O_3 \cdot H_2O$ .
- \* The formation of oxide leads to the expansion of the film thus reducing the porosity.
- \* Coloured coats can be obtained by adding dyes to the electrolytic bath.

## Application:

Aircraft parts, pistons and machine parts are anodised using this method.

The anodised coatings provides

- High electrical insulation and
- Resistance to abrasion and corrosion.