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# SILICONES AND PHOSPHAZENES

Silicones and phosphazenes are examples of inorganic Polymers. Inorganic elements can have different valencies Than carbon and therefore different numbers of side groups may be attached to a skeletal atom. This will affect the flexibility of polymers, their ability to react with chemical reagents and interactions with other polymers.

**Among inorganic polymers, silicones and phosphazenes are two important class of polymers with high commercial potential.**

## SILICONES

Silicones are polymeric organosilicone derivative containing containing Si-O-Si linkages. These contain alternate silicon and oxygen atoms in which the silicone atoms are joined to organic groups. these are also called **Polysiloxanes**. These have the general formula  $(R_2SiO)_n$

These may be linear ,cyclic or cross linked polymers .They Have high thermal stability and are also called high Temperature polymers.

## FACTORS AFFECTING THE NATURE OF SILICONE POLYMERS

0. The nature of alkyl and aryl groups.
1. The distribution of organic groups.
2. The type and proportions of structural units.

3. The extent of cross linking.
4. The length of the chain

## **PROPERTIES OF SILICONES**

### **Thermal stability-**

The silicones polymers are

Highly stable towards heat. They exhibit thermal stability up to 200 to 300°C and have low glass transition temperature.

### **Chemical Stability-**

The silicones are stable towards the chemical reagents Some electron deficient salts may result into cleavage of Si-O as well as Si-C bonds. These are quite stable to attack by oxygen

### **Chemical properties-**

**The siloxanes bond in silicones may be cleaved by grignard reagent, alkyl lithium and lithium aluminium hydrides.**

## **SOME OTHER PROPERTIES OF SILICONES**

- . They are water repellants.
- . They are good insulators.
- . They have non stick and anti foaming properties.
- . They have high strength of the Si-C bond.
- . They are resistant to oxidation.

## **USES OF SILICONE POLYMERS**

- . They are used for high temperature oil baths high vacuum pumps.
- . They are used as grease, varnishes and these can be used even at very low temperatures.
- . They are used as lubricants in both high and low temperatures.
- . Their toxicity is low and therefore ,these are used in medicinal and cosmetic implants.

## **SILICON FLUIDS OR OILS**

The silicon fluids are usually linear polysiloxanes of 50 to 200 units having low molecular weight.

They make up about 60% the silicones used. If they are prepared by the hydrolysis of a mixture of  $(\text{CH}_3)_2\text{SiCl}_2$  and  $(\text{CH}_3)_3\text{SiCl}$ , then the chain lengths may vary considerably.

**Commercially, these are prepared by treating a mixture of tetrakis cyclodimethyl siloxane and hexamethyl disiloxane with a small quantity of 100%  $\text{H}_2\text{SO}_4$ .**

## **USES OF SILICON FLUIDS OR OILS**

- . Silicon oils/fluids are used as water repellents for treating building and fabrics.
- . silicones oils are used as heat transfer media in heating belts.
- . B'cos of low surface tensions ,silicon oils can be used as antifoaming agents.
- . Their complete inertness and non toxicity allow

them to be used in cooking oils.

## **SILICONE ELASTOMERS(RUBBERS)**

The silicone rubbers make up about 30% of silicones produced. These are highly useful b'cos they retain their elasticity from -100 to +250°C which is wider range than for natural rubber. These elastomers, may be **vulcanized** to get rubber.

**Vulcanization is a process in which bonds are formed between different chains by cross linking reactions**

### **TYPES OF ELASTOMERS**

- . Room temperature vulcanized elastomers (RTV).
- . Liquid rubbers (LR).
- . High temperature vulcanizing elastomers (HTV) also called heat curing elastomers(HC).

### **USES OF SILICONE ELASTOMERS**

- . The room temperature silicones have good adhesive properties
- . These are also used as sealants for sealing.
- . Liquid rubbers were developed particularly for quick, automated and cheap production of small objects in a high no. of pieces by injecting molding.

- . HTV silicone rubbers are finding wide applications as transparent tubing in food industry medicines, gaskets and rollers etc.

## **SILICONE RESINS**

- . Silicone resins are solvent solutions of branched chain siloxanes containing residual hydroxyl groups. Silicone resins are made by dissolving a mixture of phenyl substituted trichlorosilane,  $\text{PhSiCl}_3$  and dichlorosilane in toluene and hydrolysis with water.

## **USES OF SILICONE RESINS**

- . Used as insulating material.
- . Mixed with glass fibers for additional strength.
- . Used as laminates for printed circuit boards.
- . Used for encapsulation of components such as resistors.
- . Used for non stick coating for domestic cooking ware.

## **POLYSILOXANE COPOLYMERS**

Polysiloxane copolymers are obtained by combining polysiloxane structure with organic polymer structure. These are basically of two types

- o Block copolymer

## 1. Craft copolymer

### Block copolymers

- . In which shorter or longer siloxanes are connected by blocks of organic polymers

### Craft copolymers

- . In which there are continuous polysiloxane chains which are either connected or substituted by organic polymers blocks.

## POLY PHOSPHAZENES

- . Inorganic polymers containing alternate phosphorous and nitrogen atoms with two substituent on each phosphorous atom.

## PREPARATIONS OF PHOSPHAZENES

### (A) Methods for polyphosphazene

- $(P_3N_5)_n + nCl_2 \rightarrow (PNCl_2)_n + \text{Other product}$   
 $nP_2Cl_5 + nNH_4Cl \rightarrow (PNCl_2)_n + 4nHCl$   
*phosphonitrilic chloride*
- $S_4N_4 + 6SOCl_2 + 12 PCl_3 \rightarrow 4(PNCl_2)_3 + \text{side product}$
- $5PCl_5 + 3NH_3 \rightarrow (PNCl_2)_3 + 9HCl$
- $(PNCl_2)_3 + 6KSO_2F \rightarrow (PNF_2)_3 + 6KCl + 5SO_2$
- $(PNCl_2)_3 + PbF_2 \rightarrow (PNFCl)_4 + PbCl_2 + \text{other pdt}$

### (B) Methods of other polyphosphazene

*The other type was obtained from trimer*

(hexachlorocyclotriphosphazene) by general scheme summarized in figure. The trimer is obtained by reaction of  $\text{PCl}_5$  and  $\text{NH}_4\text{Cl}$  in an organic solvent (chlorobenzene).

## **(C) Polymerisation of organo or organometallic substituted cyclic phosphazene**

In this method organic substituents are introduced at the Cyclic trimer phosphazene followed by ring opening polymerisation of the substituted cyclic trimer to a high Polymer.

## **PROPERTIES AND STRUCTURES**

Cyclic phosphonitrilic halides,  $(\text{NPCl}_2)_3$  and  $(\text{NPCl}_2)_4$  have been studied

1. **PHYSICAL PROPERTIES** : on heating  $(\text{NPCl}_2)_3$  and  $(\text{NPCl}_2)_4$  polymerise to elastic product of high molecular weight and on heating the product gets depolymerised.
2. **SUBSTITUTION REACTIONS** : The chlorine atom in phosphonitrilic chloride is very reactive and it can be easily replaced by monovalent groups like F, Br, OH, OR, SH, SR, SCN,  $\text{NH}_2$ ,  $\text{NR}_2$  etc
3. **HYDROLYSIS** : The trimer can be hydrolysed to trimetaphosphamic acid which undergoes isomeric change to trimetamido phosphoric acid.
4. **REACTION WITH AMMONIA** :  $(\text{NOCl}_2)_3$  reacts with ammonia to give various substituted products by replacing chlorine. However in presence of excess ammonia  $\text{P}_3\text{N}_5$  formed.

## **USES OF PHOSPHAZENES**

1. The phosphonitrilic halides are used as rigid plastics, fibers because they are water proof and fire proof and are unaffected by oil and petrol.
2. They are used as catalysts in manufacture of silicones.

3. Thin films of poly(aminophosphazene) are used to cover severe burns b'cos they prevent the loss of body fluids and keep germs out.