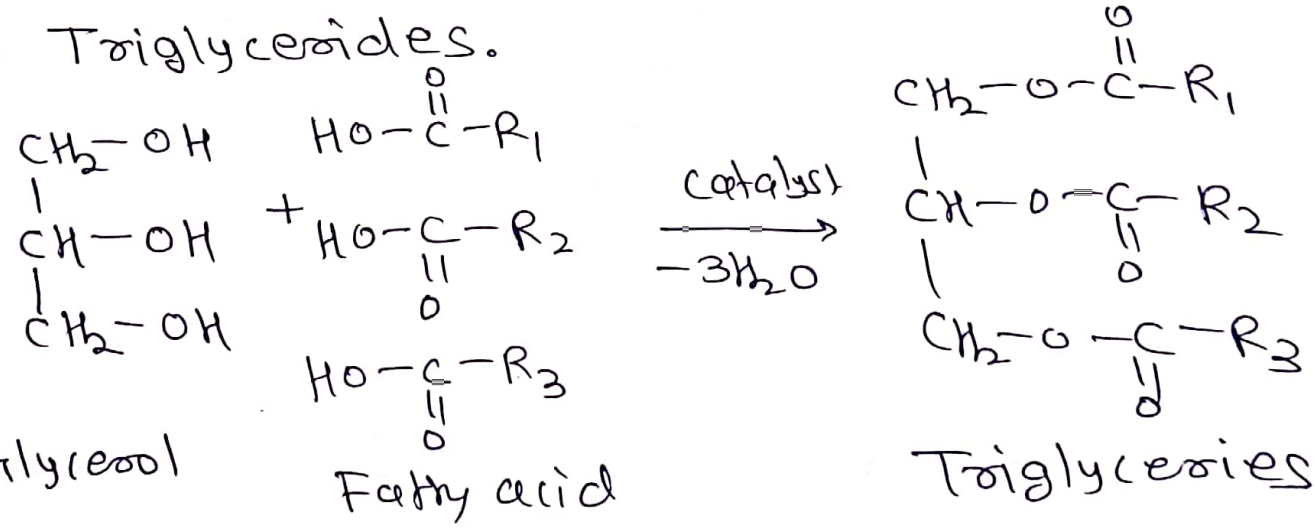
* Oils, Fats, Soap & Detergents

- Fats & oils are reffered as Lipids.
- Lipds are constitutes of plants & animals that are insoluble in water but soluble in organic solvents (ether, hexane, benzene)
- Ex:→ Vegetable oils – groundnut oil, coconut oil, soyabeen oil sunflower oil
- Fats – butter, beeftallow, lard animal fats.

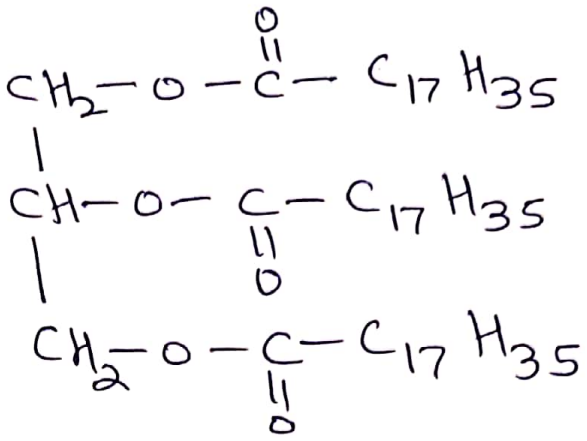
* chemical Nature :-

Natural fats & oils are the triesters of glycerol with long chain carboxylic acid (C_{12} to C_{22}) are called as Triglycerides.



- If all three hydroxyl groups (-OH) are esterified with same fatty acids, the resulting ester is called a simple triglycerides.

- Ex:-

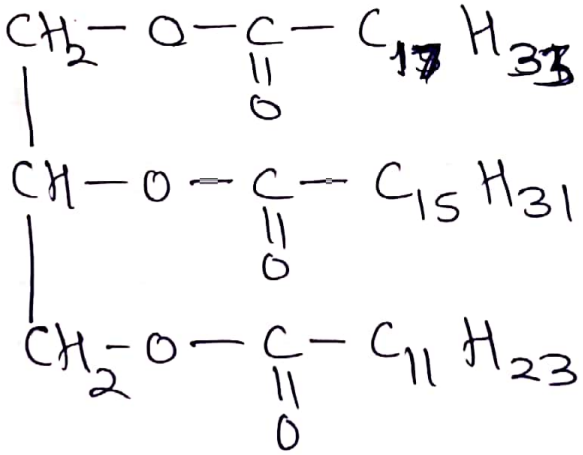


Glycerol Stearate

fats (m.p. 71 °C)

- Naturally occurring fats & oils contains two or three different fatty acids are called mixed triglycerides.

Ex:→



Glyceryl auropalmito-oleate.

- These triglycerides are Further classified on the basis of physical State at room temp.
- It is fats, it solid at 25 °C.
- It is oils if liquid at room temp.
- Fats contains greater proportion of saturated fatty acid.
- oils contain greater proportion of unsaturated fatty acids.

Ex:→ ① Glyceryl tristearate having saturated acid moiety ($R = C_{17}H_{35}$) is a fats (solid, M.P. 71 °C)

② Trilinolein having unsaturated acid moiety ($R = C_{17}H_{31}$) is a oil.
(liquid at R.T. M.P. = 09 °C)

- oils contains short chain saturated & unsaturated acid residues.
- fats contains more long chain saturated acids residues.

Occurrences ⇒ Oil & fats are occur in plant and animals.

→ In plants ÷ plant stored large quantities of fats in their seeds, root & fruits. cotton, beans, peanuts, coconuts & olives have high fat content.

→ In Animals ÷ Fats found in under skin, around intestine & kidneys, Lard & tallow

* General properties of oils ÷

① Oils & fats are solid or liquids.
- They are odourless & testless when pure.
- They are lighter than water
- Insoluble in water but soluble in organic solvent like benzene, ether etc.
- They foom emulsions when agitated with water in presence of soap, gelatin

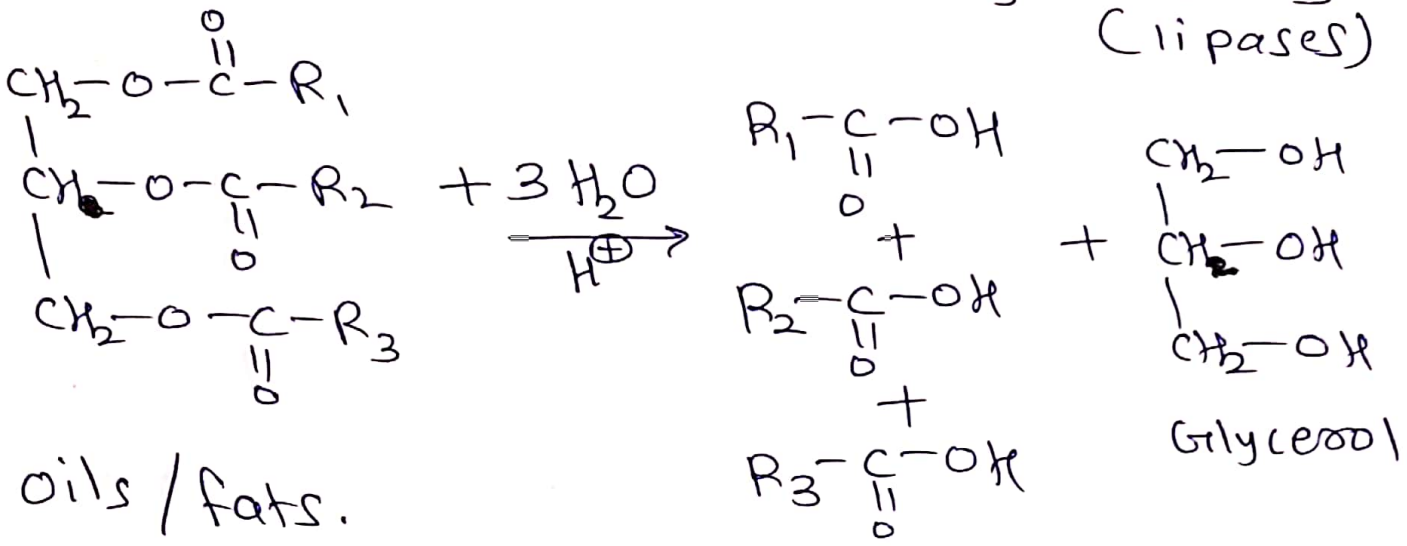
* chemical properties of oils & fats.

1] Hydrolysis ⇒

oils & fats undergo hydrolysis when heated with steam or mineral acids or alkali. It can also done by enzymes (lipases)

Ex

(1)

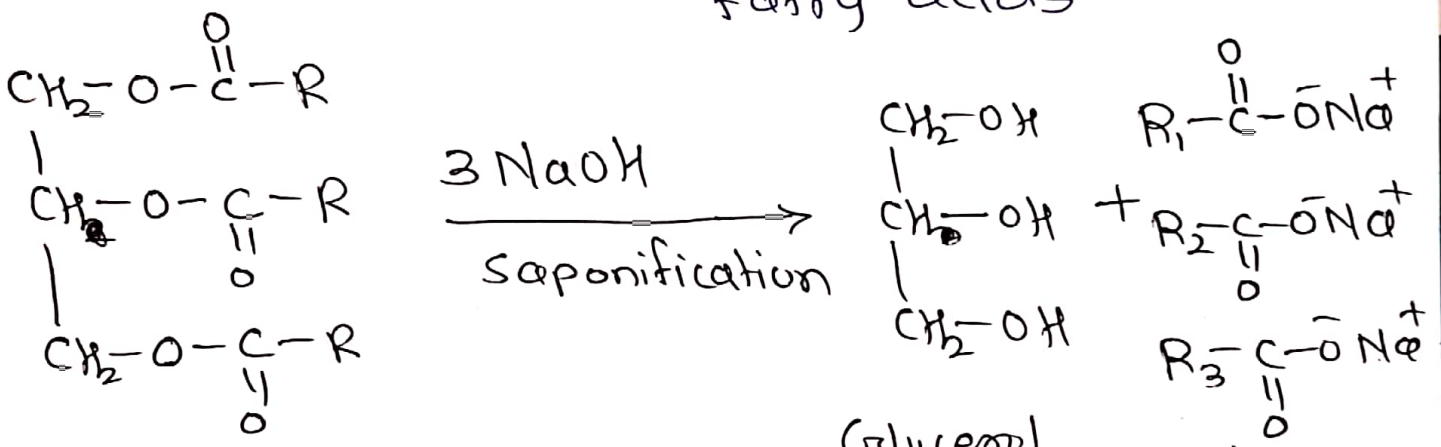


oils / fats.

fatty acids

Glycerol

(2)



oils or fats.

Glycerol

Sodium salt of fatty acid (Soap)

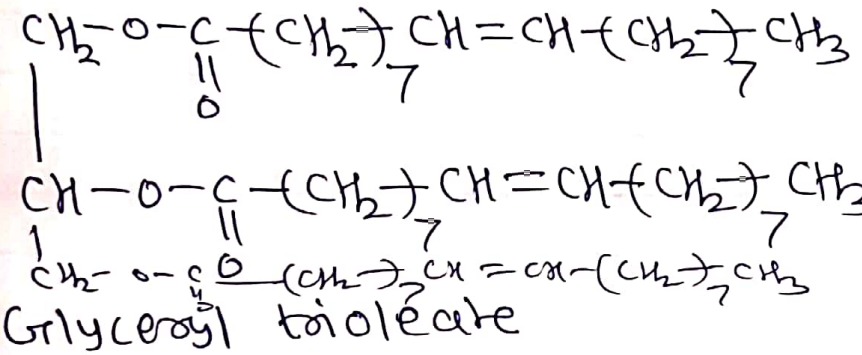
b] Hydrogenation (vanaspati ghee)

(Formation of fats from oils)

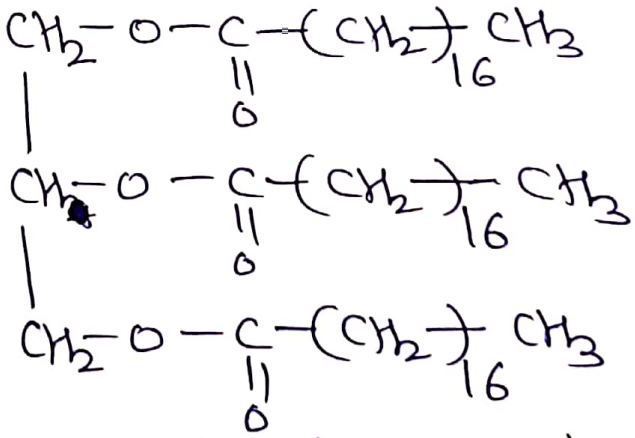
– [Hardening of soap]

– Vegetable oils are triglycerides of unsaturated fatty acids such as oleic acid & linoteic acid.

– on catalytic hydrogenation at low pressure hydrogen adds across the carbon-carbon double bonds of acid of triglycerids. to form saturated glycerides which are solids fats at room temperature, this hydrogenation process is called hardening.



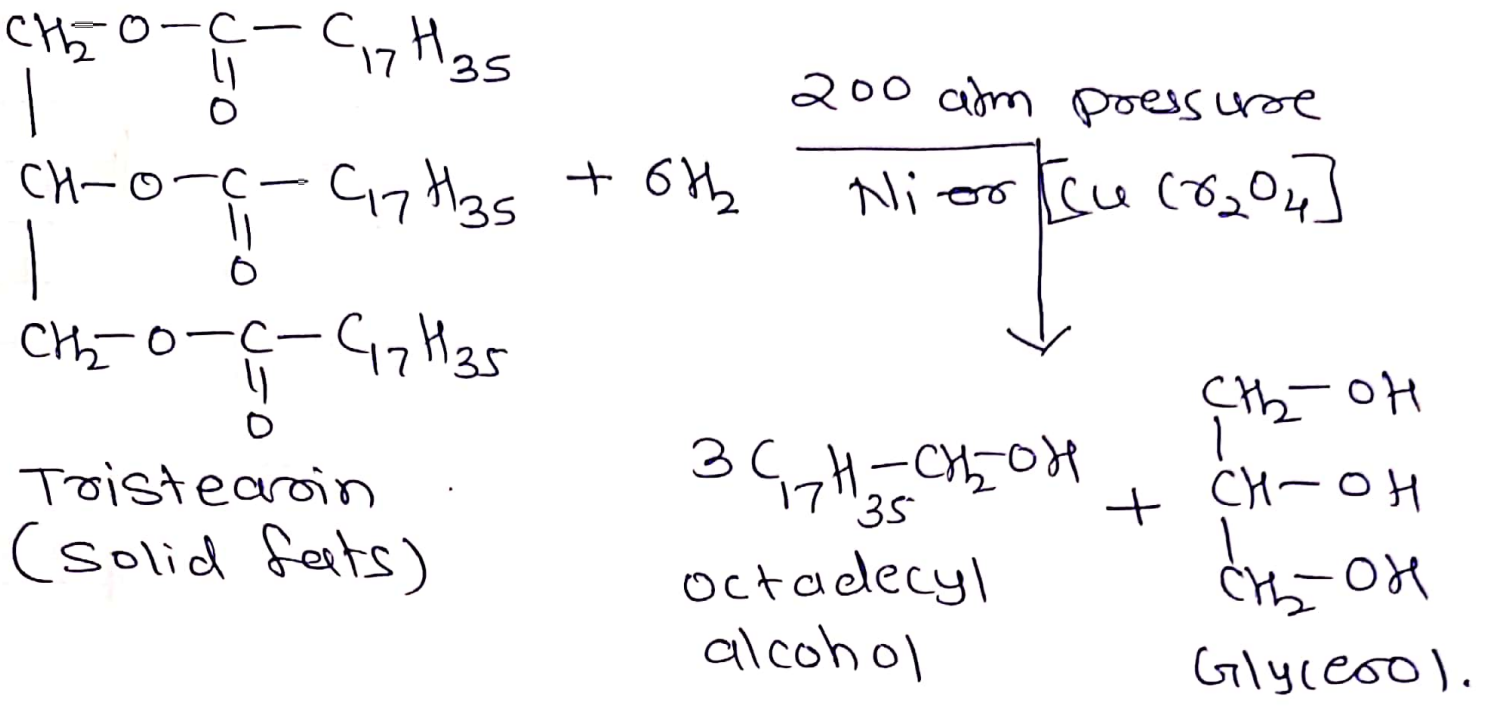
Glyceroyl trioleate
(m.p. $-17^{\circ}C$)
(Liquid)
Oil



Glyceroyl tristearate
(m.p. $55^{\circ}C$) solid [fats]

- partial hydrogenation of vegetable oil used for manufacture of vegetable ghee (Dalda)

C] Hydrogenolysis :-



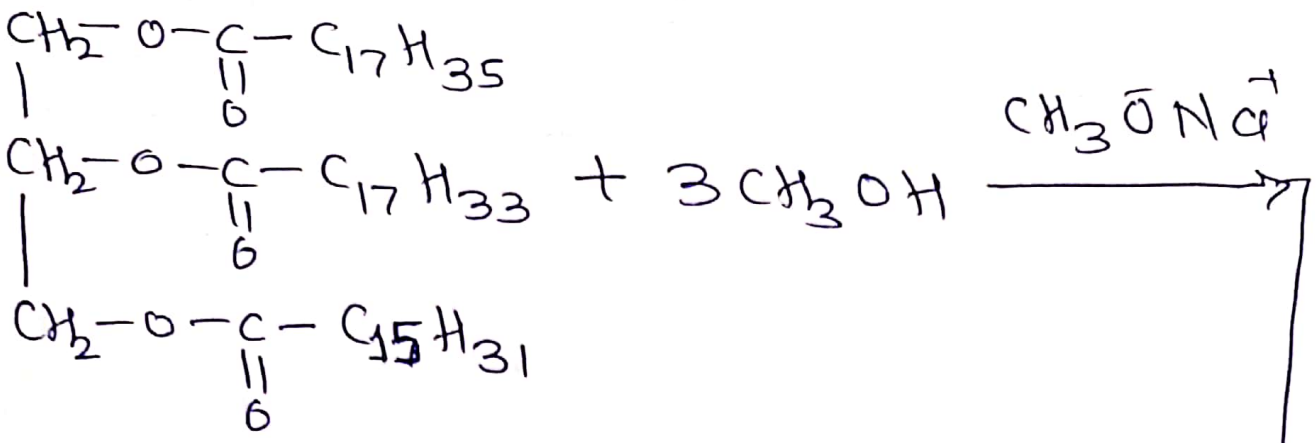
Tristearin (solid fats)

octadecyl alcohol

Glycerol.

- Hydrogenation of oils at high pressure & temperature in presence of Ni or copper chromites catalyst [Cu Cr_2O_4].
- Oil or fats undergo cleavage to glycerol & aliphatic alcohol. This process is called hydrogenolysis.

d] Trans-esterification :-



2-oleo-3-palmito-1-stearate

$CH_3(CH_2)_{17}COOCH_3$
methyl stearoate +

$C_{17}H_{33}COOCH_3$ +
methyl oleate
+

$C_{15}H_{31}COOCH_3$
Methyl palmitate.

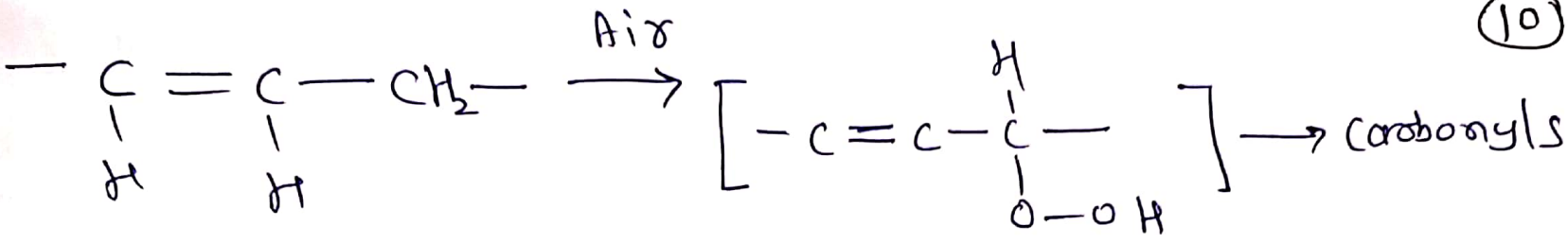
+ $CH_2(OH)CH(OH)CH_2(OH)$
Glycerol.

e] Rancidity & Autoxidation :-

- The term rancidity is applied to oil & fats develop disagreeable odour due to its slow decomposition (by air) into lower acids.
- The reactions responsible for rancidity is "hydrolysis & oxidation".

Example :→ (1) Butter is susceptible to hydrolytic rancidity as it contains lower acid (butyric & caproic acid) which have offensive odour, liberated during hydrolysis of ester linkages.

- Further Microorganism present in air contain enzyme lipase that catalyses hydrolytic process.
- This type of rancidity can be prevented by storing butter in a refrigerator.
- Triglycerides containing unsaturated acids are more susceptible to oxidative rancidity on storing for a long period.
- This reaction take place via. formation of free radical, followed by production of hydroperoxide, which cleaved into carbonyl



peroxides.

- common antioxidant added (0.01%.) to fats/oils to prevent rancidity are ascorbic acid (Vit. C) & Vit. E.

* Analysis of oils & fats.

The analysis of oils & fats give an idea about the composition & quality of given oils & fats.

- Analysis is important when adulterations of expansive fats with cheaper fats are suspected.

1. Acid value :-

condition.

1] Saponification value :→

- Alkaline hydrolysis of fat / oil is called saponification.
- Def^{n} :- The number of milligram of potassium hydroxide required to completely saponify 1 gm of fat / oil, i.e. to neutralize the fatty acids resulting from the complete hydrolysis of 1 gm of oil/fat.

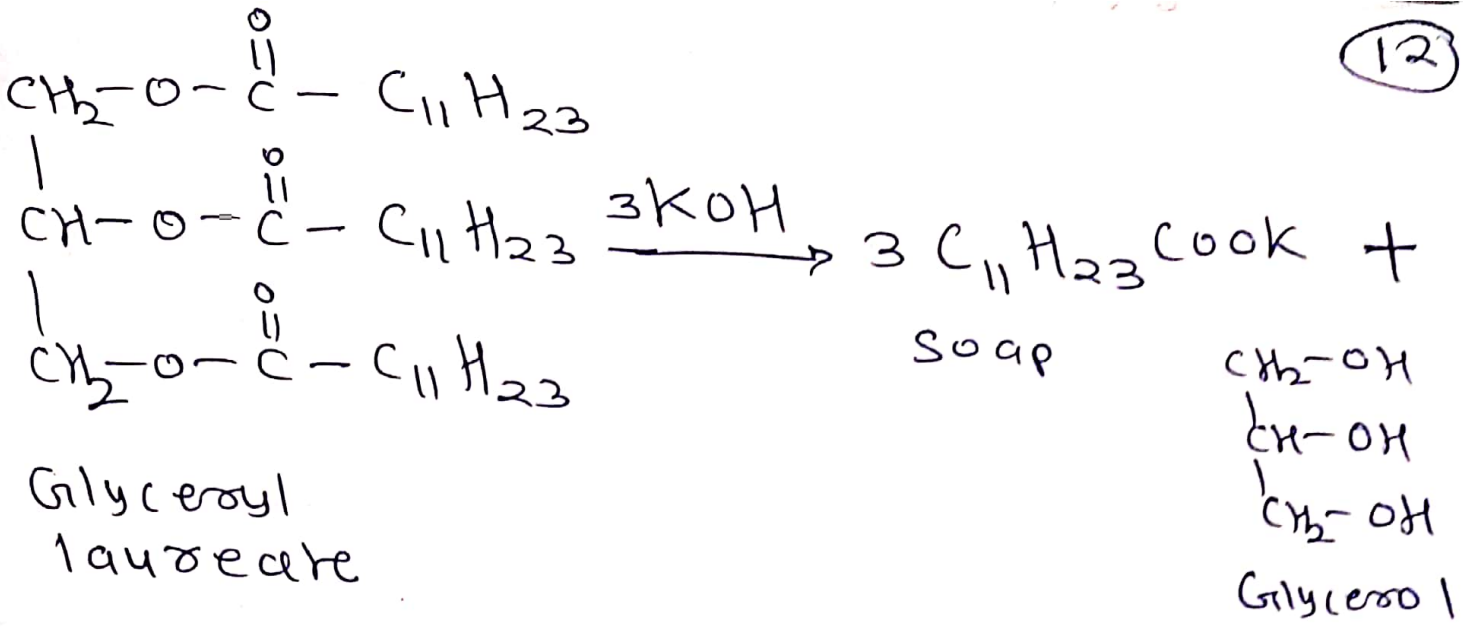
Examples :→

Saponification value of trilaureate & tristerin can be calculated as,

$$\text{Saponification value} = \frac{3 \text{ mole of KOH} \times 1000}{1 \text{ mole of fat / oil}}$$

$$= \frac{3 \times 56 \times 1000}{638}$$

$$= 263.3 \text{ mgm KOH / gm fat}$$



- In saponification reaction,
- one mole oil/fat react with 3 moles of KOH ∴
- Saponification value of fat give an idea about its average molecular weight.
- Higher the molecular weight of fat, smaller its saponification value.
- It also indicate length of carbon chain of acid of oil/fat.

2] Iodine value / Number :-

- The degree of unsaturation of a fat or oil is measured by its iodine number.

Defn :- "The number of gram of iodine that add to carbon-carbon double bond (-C=C-) present in 100 gm of ~~iodine~~ fat or oil."

- Greater the number of double bonds in the acid of triglycerides, greater will be amount of iodine that add to 100 grams.

Ex:→

① oleic acid has one C=C bond has iodine number of 90.

② Linoleic acid has two C=C bond has iodine number of 181.

③ Linoleonic acid with three C=C bond has iodine no. 274.

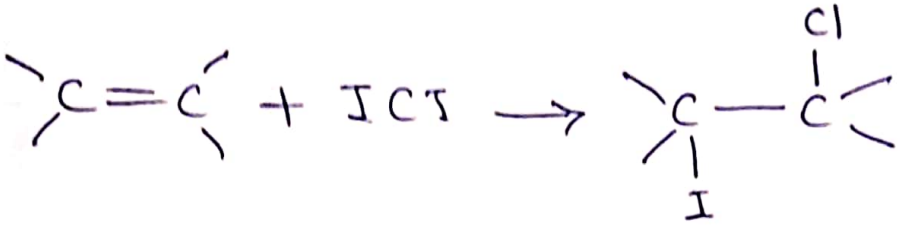
④ Animal fats having large proportion of saturated acid have low iodine number.

⑤ Vegetable oil have greater proportion of unsaturated acid have high iodine value.

procedure :→

- A known weight of oil/fat is dissolved in chloroform.
- Wij's solution (Iodine chloride dissolved in acetic acid) is then added.
- Iodine chloride (ICl) adds across carbon carbon double bond (-C=C).
- Excess Iodine chloride ~~added~~ is treated with KI sol^n to libreate equivalent

- amount of I_2 & is back titrated against stand. $Na_2S_2O_3$ soln using starch as indicators.
- ICl add across $-C=C-$ double bond & determined.
- Iodine value of fat/oil can be calculated.



$$ICl + KI \longrightarrow KCl + I_2$$

$$2\,Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2\,NaI$$

$$\text{Iodine value / Number} = \frac{(V_2 - V_1)\,N \times 127}{W}$$

where

V_1 = volume of hypo used for blank

V_2 = volume of hypo used by unreacted iodine in back titration.

N = Normality of hypo solution.

W = wt. of sample (oil / Fat)

Ex:→ ① Linseed oil (highly unsaturated) = 170–185.

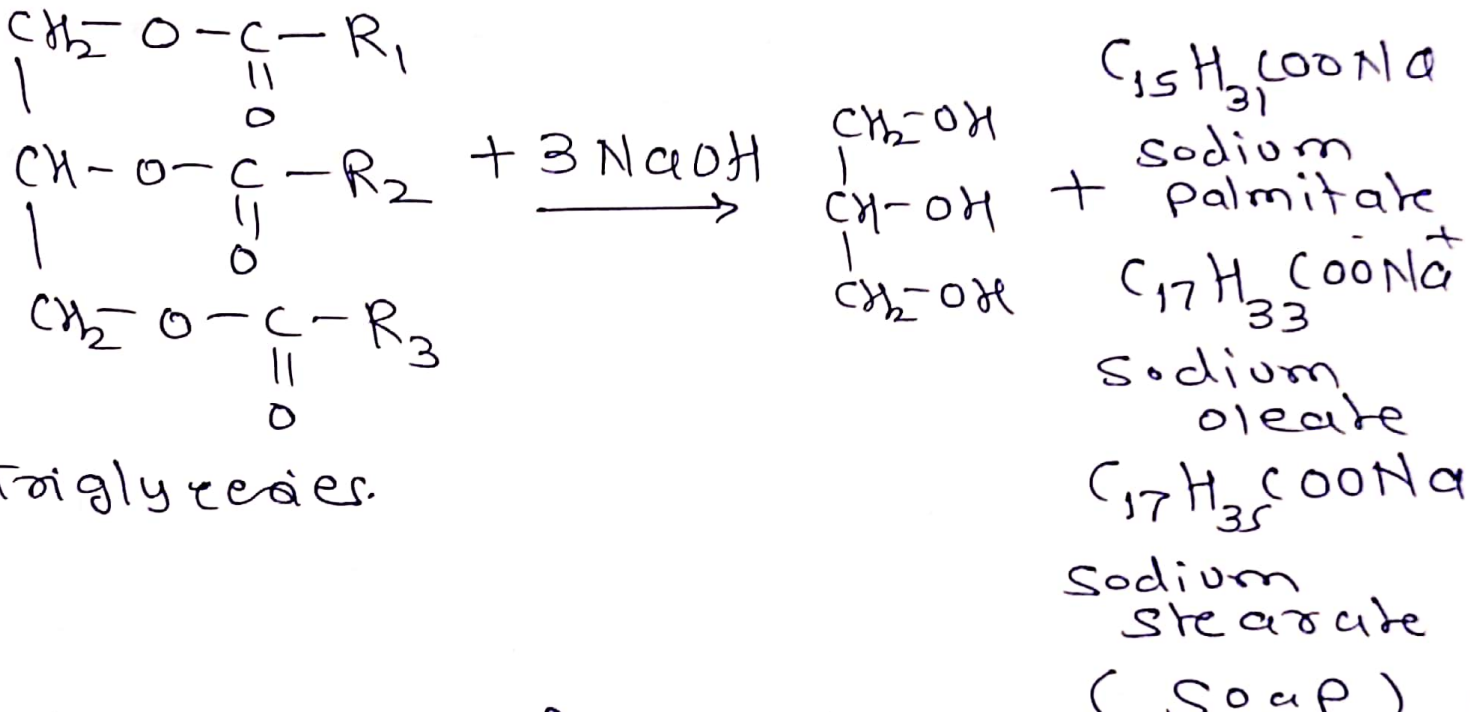
② Beef tallow (Saturated oil) = 30–48.

* Soap *

- Soap are sodium & potassium salts of fatty acids such as stearic palmitic & oleic acids.

- Oil / fats $\xrightarrow[KOH/NaOH]{\text{hydrolysis}}$ Soap. (surfactants)

- Soap is a mixture of saturated & unsaturated long chain carboxylic acids containing 12 to 18 carbon atoms.



Triglycerides.

- Higher proportion of salts of saturated acids gives hard soap.
- Higher proportion of salts of unsaturated acids yield soft soap.

Ex:→ Potassium soap (soft) shaving creams, Liquid shampoo.

* Manufacture of soap :-

soap is manufacture by two methods

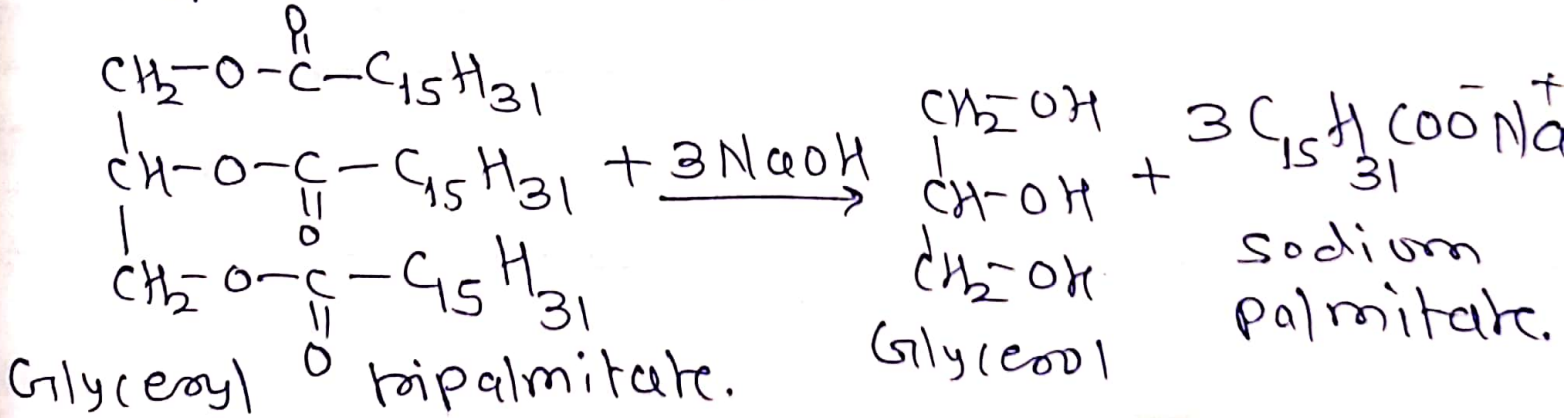
[A] kettle Method [B] Hydroolytic methods

[A] kettle Methods :→

It is oldest process used in small factories & production on limited scale. This method involves following steps

[1] Boiling :→

- The oil / Fats is taken in a steel tank called kettle & excess NaOH solution added to it.
- The mixture is boiled with steam from perforated coil at bottom of kettle.
- Boiling is continued till all soap stock get saponified into 80% soap.



Glyceryl tripalmitate. Glycerol Sodium palmitate.

② Salting out :→

- NaCl salt is added & boiling resumed till soap has separated (common ion effect).
- Soap ligher floats to surface as curdy mass.
- Lower layer contain glycerol & salt is drawn off, leaving soap & unreacted fat.

③ Soap + NaOH $\xrightarrow{\Delta}$ complete saponification.

④ Finishing :→

- Soap is boiled with water to remove alkali & curdy mass rising to top is transfer to finishing with help of pump.
- ~~Mix~~ Then it is mixed with **dye** & **perfume**
- & also with **filling agent** such as starch talc, **borax** & stirred with help of mechonical stirrer.
- Soap is drawn out & allow to solidified It is dried by hot air, milled & stamped into cakes.

B Hydrolytic methods :-

- It is modern continues process for soap manufacture.
- It is economical than kettle process.
- It gives better quality soap.
- It contain following procedure & steps.

① Hydrolysis of fats with water in presence of zinc oxide at high temperature & pressure.

② Distillation of fatty acids under vacuum

③ Neutralisation of fatty acids with alkali.

$$C_3H_5(COOR)_3 + 3H_2O \xrightarrow[\text{pressure}]{ZnO,\ \Delta} 3RCOOH + C_3H_5(OH)_3$$

Fat — fatty acid — glycerol

$$RCOOH + NaOH \text{ or } Na_2CO_3 \longrightarrow RCOO^-Na^+ + H_2O + CO_2$$

soap

Fat $+ ZnO \xrightarrow[40-45^\circ,\ \text{Atm P.}]{\Delta,\ \text{Hydrolysis}}$ fatty acid

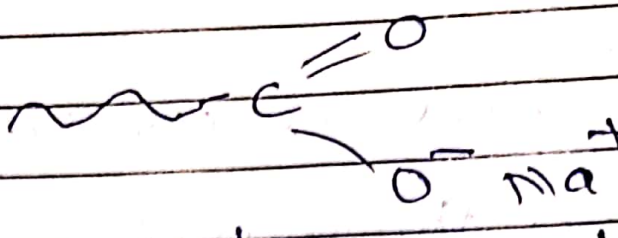
- Fatty acids mixed with waters are discharged at top into steam flash tank.
- H_2O vaporize & cooling fatty acids are passed through water condenser.
- The condensed fatty acids are neutralized in the mixer & product is soap.

* Cleaning Action of Soap :-

- The soap molecule is composed of a large non-polar (hydrophobic water repellent) hydrocarbon tail & polar ($-COO^-Na^+$) head hydrophilic (water soluble).
- polar head is water soluble & non-polar head is oil soluble.
- dirt in cloth contain oil / fats or grease.
- When soap & dirt come in contact with each other in presence of water, non-polar tail of soap molecule dissolved the fat / grease contained in the dirt.
- The polar head ($-COO^-Na^+$) being water soluble remains in aq. layer surrounding fat / grease.

fatty acid chain

Soap molecule

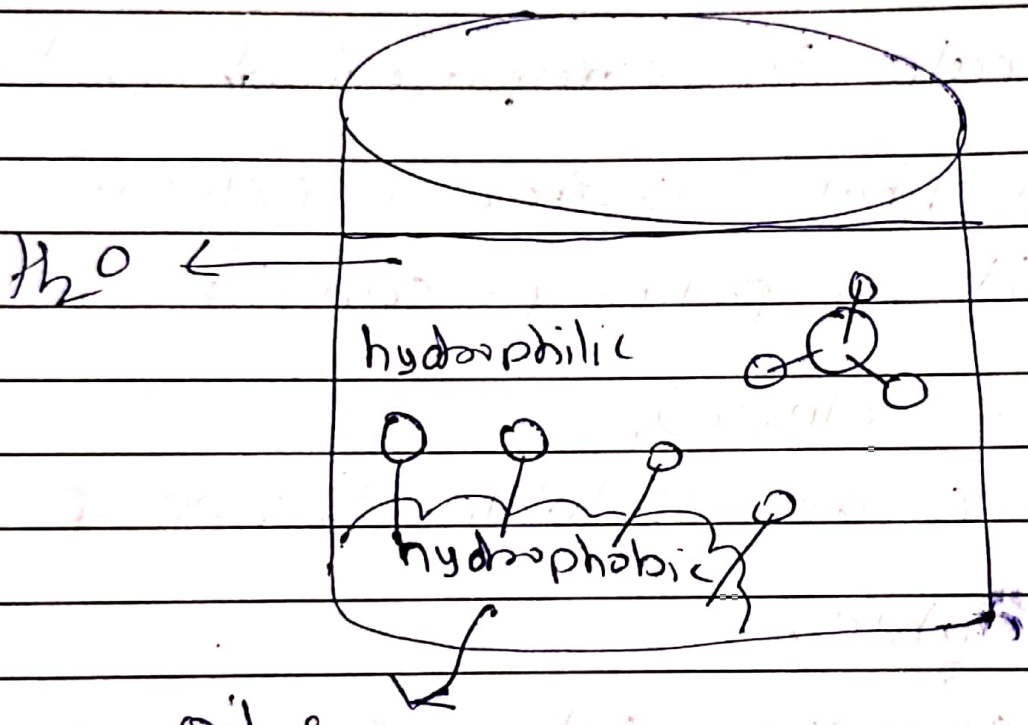


non polar

polar

hydrophobic

hydrophilic



- Due to mechanical & physical action such as scrubbing causes oil/grease disperse into tiny droplets & soap molecule arrange around surface of globules called micelles.
- The carboxylate (COO^-) of soap molecule project outwards.
- The surface of micelles carrying negative charge.

∴ Two micelles do not coalesce with each other due to similar charges.

- The entire micelle become water soluble & able to washed away together with dirt by stream of water the overall process involves lowering the surface tension of water & emulsification.

$$2\ C_{17}H_{35}COO^-Na^+ + CaCl_2 \rightarrow \underset{\text{Cal. Stearate (Insoluble)}}{(C_{17}H_{35}COO)_2Ca} + CaCl_2 + 2NaCl$$

* Synthetic * Detergents *

- Synthetic Detergents is called 'Syndets' are superior to soap.
- They can be used in hard water without precipitated.
- Synthetic detergents like soaps are cleaning agents having a large non-polar end (tail) which is oil soluble & polar water soluble end (head.).
- They are purely synthetic chemicals.
- It is classified into 3 classes

  i] Anionic detergents..

  ii] Cationic detergents.

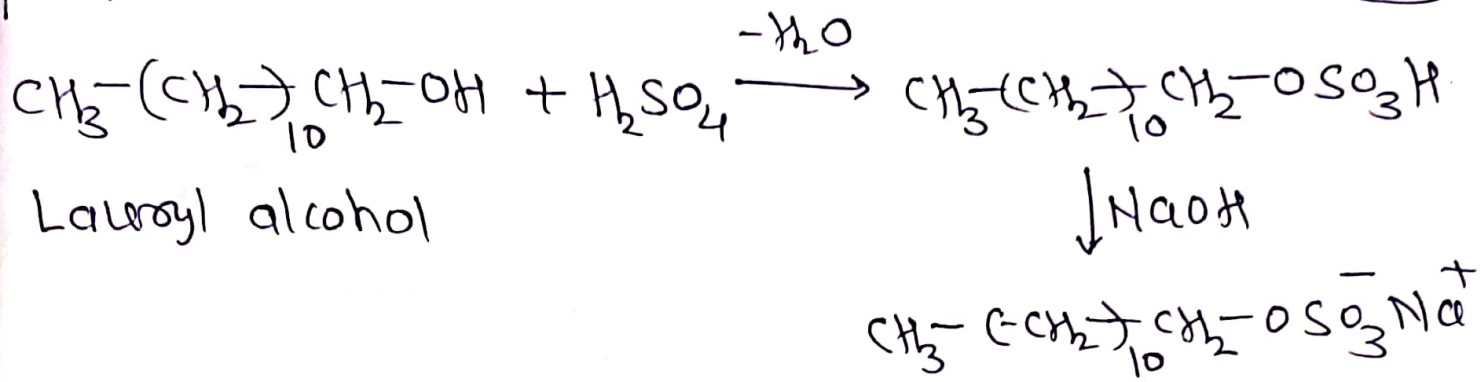
  iii] Non-Ionic —11— .

i] Anionic detergents :-

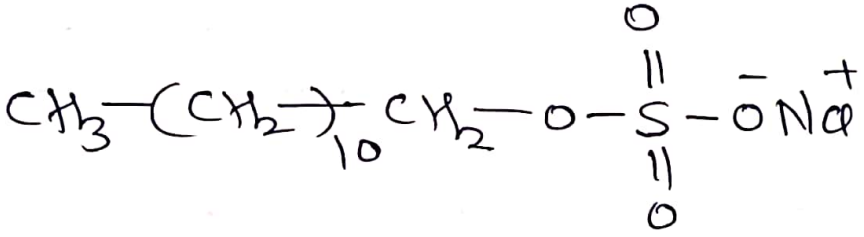
These are sulphates of long chain primary alcohols (C_{12} - C_{18} alcohols) or salts sulphates of hydrocarbons.

Ex:-

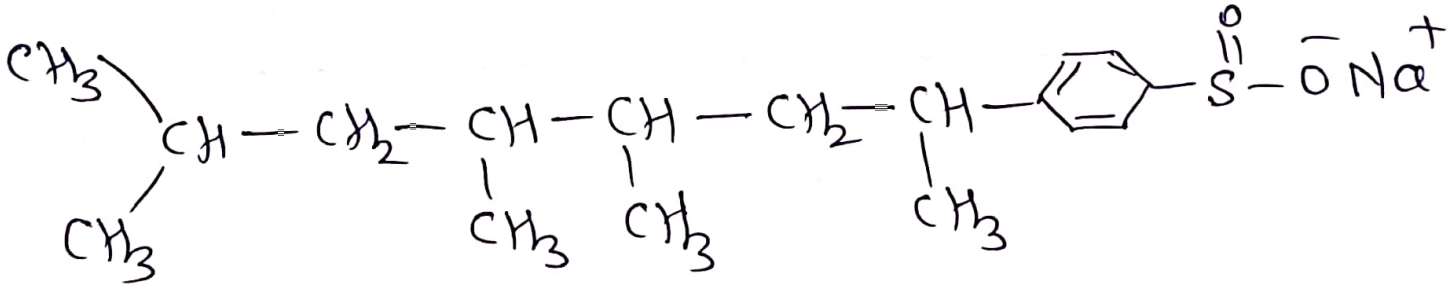
preparation



Detergents.



Sodium n-dodecyl benzene sulphonate.



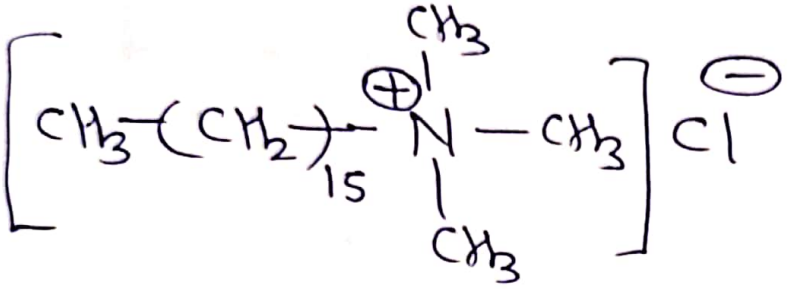
Sodium alkyl benzene sulphonate.

- polar end (hydrophilic) – SO_3Na^+
- non-polar (hydrophobic) – alkyl / aroyl part

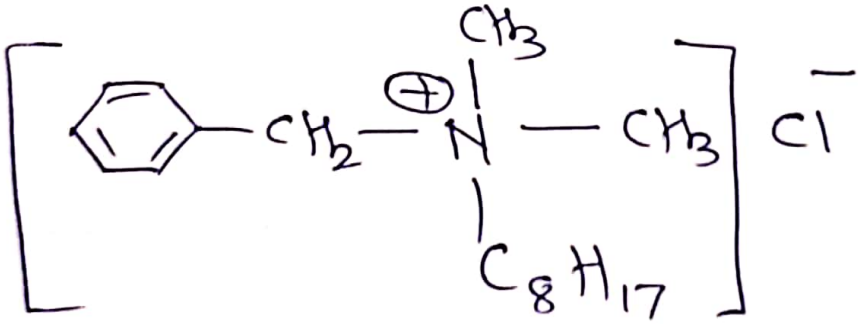
ii] Cationic Detergents :-

- It is also called invert soap/detergents
- It is water soluble carries positive (cation) than negative (anion) charge.
- It is good cleaning agents.
- It posseses germicidal properties used in hospitals.

Ex:→



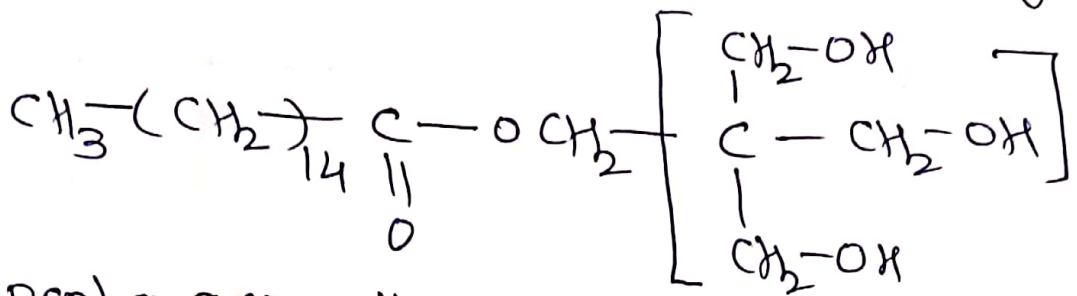
Trimethyl hexadecyl ammonium chloride



Benzyl dimethyl octyl ammonium chloride.

[c] Non-Ionic detergents.

- The polar covalent structure in non-ionic detergents provide the required water solublity.
- It is used in dishwashing liquids.



Penta acry thritryl Palmitate.

Hydrophilic part.

(Non-Ionic detergent)

lauryl alcohol

ethylene oxide

Ethoxylate

- cleaning powes of synthetic detergent increased by adding certain additives.

Ex: Sodium tripolyphosphate ($Na_3P_3O_{11}$) or STPP. is added as builder has ability to coordinate with metal ion & other ions.

- Thus builder breaks up & suspend certain clays & pigments by forming complex with metal & facilitating their removal.

* Synthetic detergents V/s Soap :-

a] Soap :- Soap has certain disadvantage.

- Its cleaning action is reduced in hard waters.
- It can not used in acidic solutions.
- In hard water & acidic solution sticky precipitate get adhered to textile fibres during processing which prevent dye stuff & leaves light spot on fabric.

b] Detergents :- It has many advantage as

- It can be used in hard water
- It cannot used for washing fibres like knitted wool & silk.

- It is more active than soap in low concentration.
- It is excellent foaming agents.
- It is germicidal & bactericidl.

* Soap vls Hard Detergents

a] Hard Detergents :-

- The alkyl benzene sulphonates in which alkyl chain is highly branched are detergents which resists biological degradation in sewage discharge & septic tanks.

b] Soft Detergents :-

The alkyl sulphonate & ethoxylates undergo biological degradation easy & easy to dispose off.

- The soft detergents are preferred for obvious advantages of their easy disposal.