→ Fats and oils:→

- Fats and oils belong to the group of naturally occuring compounds called Lipids (Greek, lipos = fat)
- Lipids are constituents of animals and plants which are soluble in organic solvents such as ether, chloroform, carbon tetrachloride, hexane etc. but insoluble in water.
- The lipids which give fatty acids and alcohols on base hydrolysis (saponification) are called simple lipids.
- These can be further divided into two classes:-

(i) Fats and oils:→ These give long-chain fatty acids and glycerol upon hydrolysis.

(ii) Waxes:→ These give long-chain fatty acids and long chain alcohols upon hydrolysis.

→ Natural Fats:→

- Natural fats are made up of triesters. These triesters are obtained from long-chain carboxylic acids and also called triglycerides or triacylglycerols because all three -OH groups of glycerol take part in ester formation. So, natural fats are complex mixtures of carboxylic acids of high molecular weight and esters of glycerols. Therefore, natural fats are also called glycerides.

→ Natural sources:→

→ Animal fats:→ These are located in adipose tissue cells.

E.g. → Tallow (animal fat) obtained from cattle, sheep and goats.
Lard (animal fat) from hogs (pigs).

In the human body about 12% of its total weight is fat.

- Butter and ghee are special type of animal fat because they are obtained from milk.

→ Vegetable fats:→

- These are mainly present in seeds and nuts of plants.

Example:- Soya bean, groundnut, coconut, palm kernel, mustared seed, niger seed etc. (edible oil).

Cotten seed, linseed, castor seed and mowrah (mahua) seed (non edible oil).

→ Marine fats:→

- Obtained from water animals – sardines, herrings, salmons, whales, dolphins, seals, porpoises etc.

→ Edible and industrial oils of vegetable origion:→

1. Edible oils of vegetable origion:→

- These edible oils are obtained from vegetables and hence are called edible vegetable oils.
- These are obtained from seeds, roots and fruits of plants.

Ex. Peanut oil, cottonseed oil, Mustard oil, Til oil, Soyabean oil, Linseed oil etc.

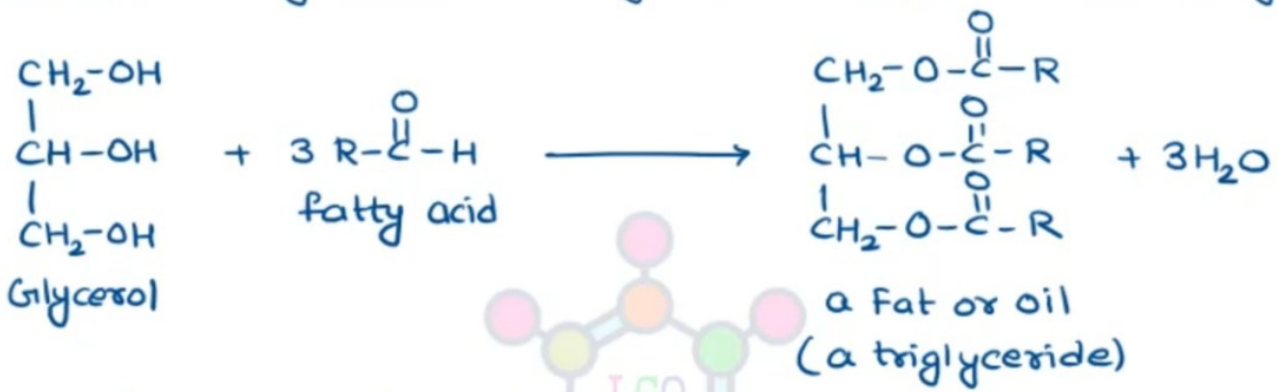
- The fatty acids present in glycerides of edible vegetable oils are oleic acid, linoleic acid, linolenic acid, ricinoleic acid, palmatic acid and stearic acid.

2. Industrial oils of vegetable origion:→

- Industrial oils of vegetable origion are coconut oil, palm oil, mustard oil, Olive oil, soyabean oil etc.
- Uses of industrial oils of vegetable origion are-
  - In soap and detergent industries.
  - Linseed oil is used in paints and varnishes.
  - Groundnut oil is used in vegetable ghee industries.
  - In manufacturing of printing ink.
  - Castor oil is used in pharmaceutical and lubricant industries.
  - Groudnut oil is useful as hair oil and monufacturing of candles and polishes.

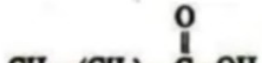
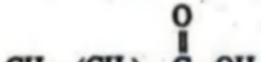
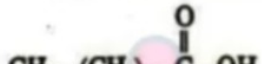
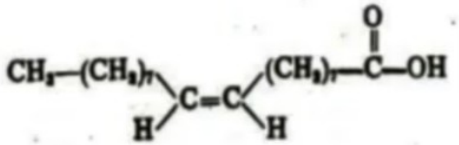
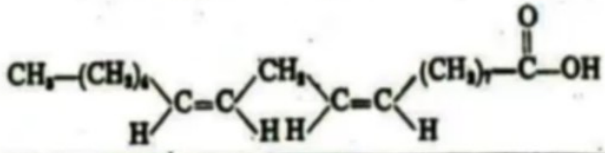
→ Common fatty acids and glycerides (Structure and composition of fats and oils):→

- Animal and vegetable fats and oils have similar chemical structures. These are triesters formed from glycerol and long chain carboxylic acids (often called fatty acids).



- A triester of glycerol is called a trigyceride or glyceride. If all the R groups in the above general formula are identical, the triester is called a simple glyceride, and if they are not, a mixed glyceride.
- Most natural fats and oils are mixed triglycerides having two or more different fatty acid groups.
- The carboxylic acids or fatty acids that go to form the fat or oil molecules (glycerides) have carbon chain with only even number of carbon atoms.
- The most common fatty acids have unbranched carbon chains of 14, 16 or 18 carbons. The chaim may be saturated or may include one or more double bonds.
- The glycerides are referred to as saturated or unsaturated depending on whether the fatty acid component chains are saturated or contain double bonds.

Structure and Melting Points of some Common Fatty acids

Name	*Structure*	*mp° C*
A. SATURATED :		
Caproic acid		−2°
Caprylic acid		17°
Capric acid		31°
Lauric acid		44°
Myristic acid		54°
Palmitic acid		63°
Stearic acid		70°
B. UNSATURATED :		
Oleic acid, *cis*-9-octadecanoic acid		16°
Linoleic acid, *cis-cis*-9, 12-octadecadienoic acid		−5°

- The most common saturated fatty acids found in fats and oils are myristic acid ($C_{13}H_{27}COOH$), palmitic acid ($C_{15}H_{31}COOH$) and stearic acid ($C_{17}H_{35}COOH$).
- Amongst the unsaturated fatty acids, oleic acid ($C_{17}H_{33}COOH$) and linoleic acid ($C_{17}H_{31}COOH$) are widely distributed in almost all fats and oils.
- Unsaturated fatty acids shows geometrical isomerism due to presence of double bond. Generally, cis-isomers are found naturally occuring in the unsaturated fatty acid components of fats and oils.

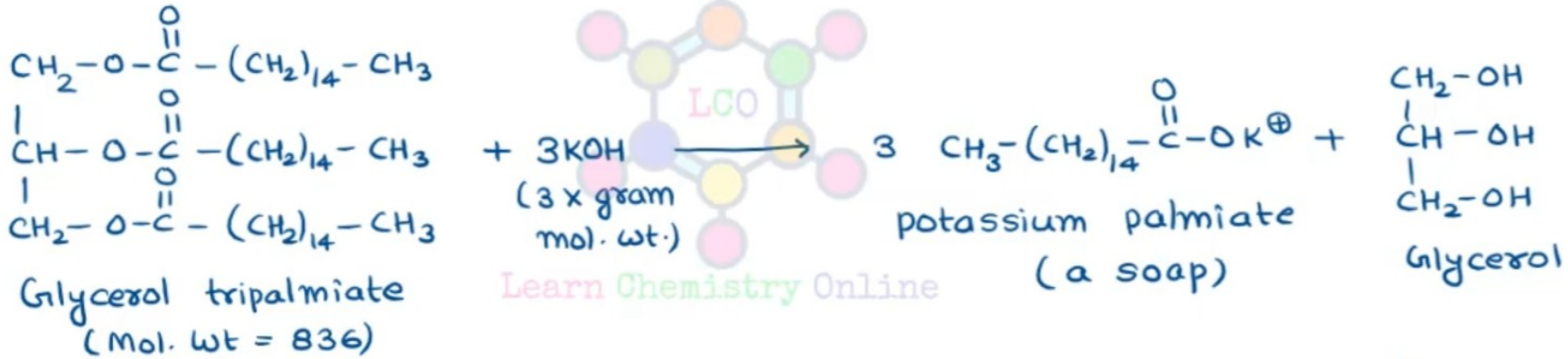
Composition (%) of some Common Fats and Oils

FAT OR OIL	*FATTY ACID*				
	Myristic acid	*Palmitic acid*	*Stearic acid*	*Oleic acid*	*Linoleic acid*
OILS:					
Olive oil	—	6—10	1—4	83—84	4—7
Peanut oil	—	6—9	2—5	50—60	20—30
Groundnut oil	—	6—14	2—7	46—72	13—38
Cottonseed oil	1—2	17—29	1—4	13—44	33—58
Mustard oil	—	1—3	1—3	8—40	10—29
Cocoanut oil	1—2	17—29	1—4	13—44	33—58
Sunflower oil	—	2—10	1—6	7—42	55—80
Soyabean oil	—	7—12	2—6	20—50	36—65
FATS:					
Beef tallow	2—6	24—32	15—25	37—43	2—3
Butter fat	7—12	23—30	8—13	30—40	4—5
Human fat	3—6	24—26	5—8	40—45	8—10
Lard	1—2	25—30	12—18	40—50	5—7
MARINE OILS					
Whale	5—10	10—20	2—5	33—40	—
Fish	6—8	10—25	1—3	—	—

→ Saponification value:→

- Saponification value or saponification number is used for the analysis of fats and oils.
- Saponification is a term specifically applied to the hydrolysis of an ester when the reaction is carried out in alkaline solution.
- The saponification value of a fat or oil is an arbitrary unit that is defined as the number of milligram of potassium hydroxide required to sponify one gram of the fat or oil.
- Since there are three ester bonds in a molecule to hydrolyse, three equivalents of potassium hydroxide are needed to saponify one molecular weight of any fat or oil.

Example:-



Glyceral tripalmiate (Mol. wt = 836)

potassium palmiate (a soap)

Glycerol

Here 836 grams of fat requires 168,000 milligrams KOH for saponification. Therefore, one gram of fat require 168,000/836 mg of KOH. Hence,

$$\text{saponification Number of glycerol tripalmiate} = \frac{168{,}000 \text{ mg of KOH}}{836 \text{ g fat}} = 208$$

- If M be the molecular weight of the fat, the saponification value = 168,000/M.
- Since the saponification value of a given fat can be determined experimentally, the average molecular weight of the fat can be found.
- The higher the saponification value of a fat, the greator the percentage of low-molecular weight glycerides it contains.
- As the average molecular weight of the fat depends on the average length of the carbon chain of the fatty acid components, the saponification number also gives an indication of the average length of the carbon chain in the glycerides under examination.

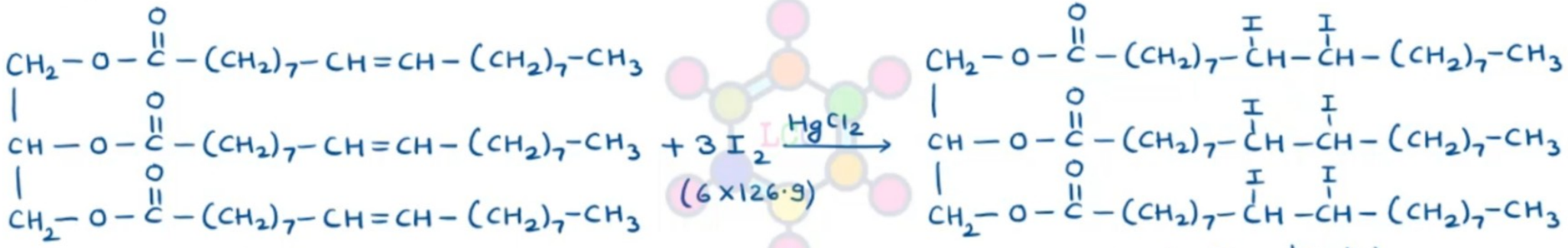
→ Experimental method:-

- The weighed quantity of fat is refluxed with excess of standard ethanolic KOH solution, and then titrating the unused alkali against a standard acid solution.

Fat or Oil	Saponification number
Rapeseed oil	170–179
Menhaden oil	190.6
Corn oil	188–193
Olive oil	185–196
Soy bean oil	193
Cacao butter	193.55
Linseed oil	192–195
Cottonseed oil	193–195
Lard	195.4
Mutton tallow	192–195.5
Peanut oil (arachis)	190–196
Horse oil	195–197
Beef tallow	193.2–200
Palm oil	196–205
Butter	220–233
Palm kernel oil	242–250
Coconut oil	246–260

→ Iodine value or Iodine number:→

- Iodine value or Iodine number is used for the analysis of the fats or oils.
- The extent of unsaturation in a fat or oil is expressed in terms of its iodine value or iodine number.
- The iodine number is defined as the number of grams of iodine which will add to 100gm of fat or oil.
- Example:-



Glycerol trioleate (triolein)
(M.wt. = 884)

A treble diiodide

The above equation tells that $6 \times 126.9 = 761.4$ g of iodine will add to 884 g of triolein. The number of grams of iodine will add to 100 g of triolein will be $761.4 \times 100/884$. Therefore

$$\text{Iodine number of triolein} = \frac{761.4 \times 100}{884} = 86$$

- The value of iodine number depends on the number of double bonds present in the acid component of the glycerides.
- A high iodine number indicates that the glycerides contains large number of double bonds, while a low iodine number implies the presence of few double bonds. The iodine number of tripalmitin with no double bonds would be zero.

→ Experimental determination of Iodine value :→

1. Hubl's method :→

- A weight amount of the fat or oil dissolved in CCl_4 is allowed to react with a solution of iodine and mercuric chloride (catalyst) in ethanol. The unreacted iodine is titrated against standard sodium thiosulphate solution.

2. Wij's method :→

- In this method, the molecular iodine has been replaced by the more reactive iodine monochloride (ICl), the rest of the procedure remaining the same.

Fat or Oil	*Iodine Number*
FATS :	
Butter	30—40
Lard	46—70
Tallow	30—48
EDIBLE OILS :	
Soyabean oil	127—138
Cottonseed oil	105—114
Sunflower oil	140—156
NONEDIBLE OILS :	
Linseed oil	170—185
Tung oil	163—171

→ Acid value and Reichert-Meissl value: →

- Acid value and Reichert-Meissl value are used for the analysis of the fat or oil.

1. Acid value or Acid number: →

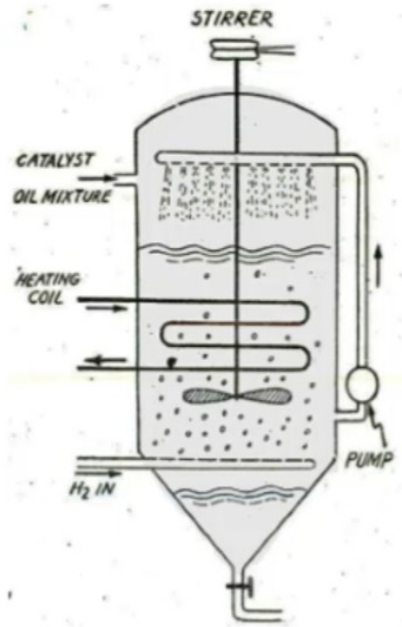
- The acid value of a fat or oil tells the amount of free fatty acid present in it.
- The acid value is defined as number of milligrams of potassium hydroxide required to neutralise one gram of fat.
- It is determined by dissolving a weight quantity of the fat in ethanol and titrating the solution against standard alkali.
- The acid number of a fat can give the extent of rencidity in a stored sample.

2. Reichert-Meissl value or Reichert-Meissl number: →

- The amount of free water soluble, volatile fatty acids (Butyric - C_4 to capric - C_{10}) present in a fat or oil is expressed in terms of Reichert-Meissl value.
- It is defined as the number of millilitres of 0.1M potassium hydroxide solution required to neutralise 5 grams of fat.
- It is determined by treating known weight of fat with ethanolic alkali and distilling the volatile acids. These are titrated against 0.1M potassium hydroxide and Reichert-Meissl value

→ Hydrogenation of unsaturated oils:→

- In india 'vanaspati' or 'Vegetable ghee' was first introduced after the first world war (1919) and it has found immense popularity because it resembles natural ghee in appearance.
- It is made industrially by hydrogenation of vegetable oils such as groundnut oil, sesame oil, cottonseed oil, soyabean oil and sunflower oil.
- The hydrogenation is carried out by passing hydrogen gas through the heated oil in the presence of metallic nickel as catalyst.
- The nickel catalyst required for the process is obtained by mixing a nickel salt (such as nickel formate or nickel carbonate) with unsaturated oil and then heating the mixture and passing hydrogen into it. Thus the salt is reduced to finely divided nickel dispersed in the oil and is ready for use.
- The hydrogenation of an oil is actually carried in a 'hydrogenation tower' or 'converter'. It is a tall cylindrical steel vessel with cone-shaped base, fitted with a stirring device and also heating and cooling coils.
- The mixture of oil and nickel catalyst is pumped into the converter. Here it is partially mixed by stirring and partially by the flow of hydrogen entering at the base through a perforated pipe.



- Steam is passed through the heating coils, while the oil mix is continuously pumped to the top of the converter where it is sprayed back down the tower.
- Since the reaction is exothermic, the steam-heating is stopped as the reaction gets going and the temperature is maintained at about 200°C by passing cooling water through the coils if necessary.
- The hardening of oil takes place most readily with a high catalyst concentration and low pressure (30-35 psi).
- When hardening has taken place to required degree, the reaction is stopped by lowering the temperature to about 70°C.
- The catalyst is filtered and the product is rebleached and deodorised under vacuum.
- The vanaspati so prepared has melting point 31-37°C and has the texture of ghee which would melt like ghee when placed on tongue.

→ Composition of vanaspati or vegetable ghee:→

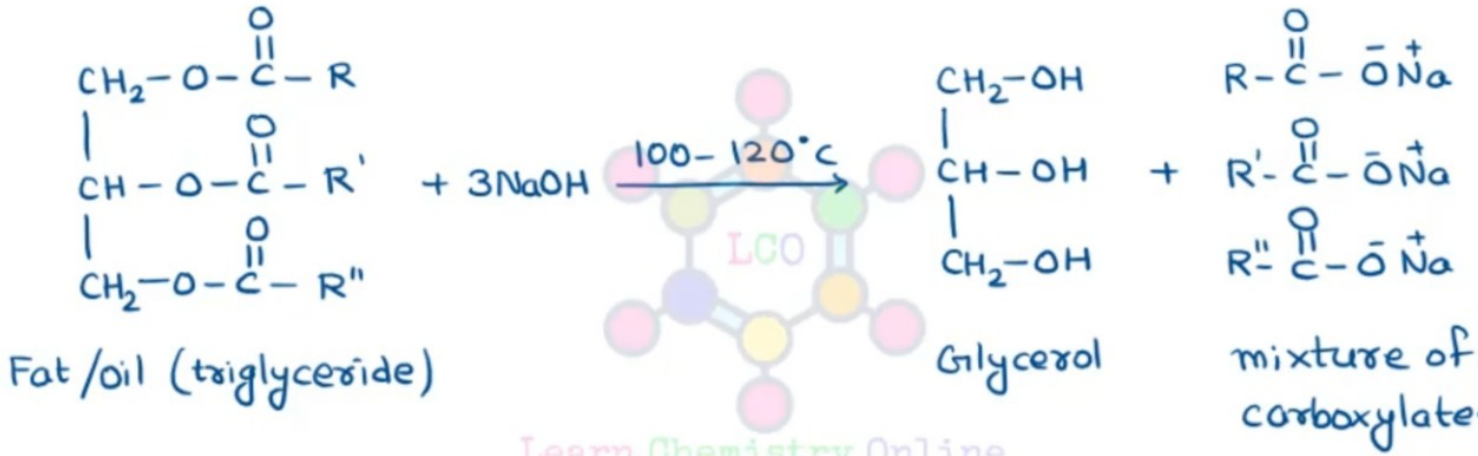
- Hydrogenation of an oil involves the saturation of double bonds present in the acid components of glycerides. Thus the fatty acids with both single and two or more double bonds are saturated.
- The composition of fatty acids and iodine value of vanaspati and original groundnut oil is given below:-

	Groundnut oil	Vanaspati
Iodine value	92	67-70
Total saturated	20%.	25%.
Oleic (cis-nonene)	55%.	35%.
Linoleic acid	25%.	5%.
trans- nonene	Nil	35%.

- Large amounts of saturated fats in the diet may lead to increase in the level of cholesterol in the blood, while the high oil content of the diet tends to diminish cholesterol level in boold. As a result of these findings, sunflower oil and other polyunsaturated oils are now increasingly used as cooking medium in preference to solid fat.

→ Soaps:→

- Soaps are sodium or potassium salts of higher fatty acids containing 12 to 18 carbon atoms.
- They are generally obtained by hydrolysis of fats and oils with sodium hydroxide. The mixture of sodium salts of higher fatty acids so produced are called sodium soaps.



- Sodium carboxylates are common toilet soaps. Potassium carboxylates or Potassium soaps are obtained when the saponification of fat or oil is carried with potassium hydroxide.
- Potassium soaps are softer than sodium soaps are used for special purposes like in making shaving creams or liquid soaps (shampoo).

- The composition of sodium or potassium carboxylates constituting soap depends on the percentage of fatty acids bonded to glycerol in the original triglycerides.

Soft soaps:- Vegetable oil containing unsaturated fatty acids (oleic acid and linoleic acid)

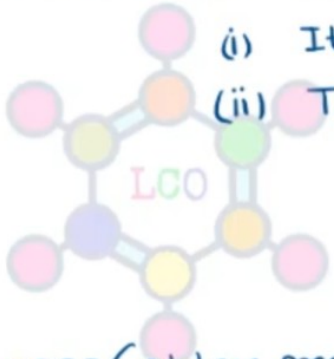
Hard soaps:- Solid fat containing higher fatty acids (palmitic acid and stearic acid)

→ Soap manfacture :→

- In india the main source of soap is coconut oil.
- Palm oil, groundnut oil and cottonseed oil are also used. Therefore, in actual practice, mixtures of solid fats and oils are blended to produce a soap having properties best suited for a particular use.
- Soap can be made from fat blends in two ways:-

(1) Saponification of fats with alkali solutions
(i) Boiling process (hot process)
(ii) Cold process
(iii) Modern continous process

(2) Direct neutrilisation of fatty acids.
(i) Ittner process
(ii) Twitchell process



→ Boiling process (hot process):→

- The manufacture of soap by this process (older process) is carried by the following steps:-

(a) Boiling:→

- The saponification of fat is done by boiling the fat with sodium hydroxide solution (soda lye) in a large cylindrical steel vessel known as soap pan or kettle.
- The soap pan is usually open at the top. The lower part of the pan is funnel shaped and contain a system of steam heating coils.

- Molten fat and appropriate quantity of soda lye are simultaneously run into the pan. steam is then admitted through the steam coils to boil the mixture. Boiling is continued unless the greasy nature of the mixture has almost disappeared and the fat is thus saponified to the extent of about 80 percent.

$$\text{FAT} + \text{SODA LYE} \xrightarrow{\Delta} \text{GLYCEROL} + \text{SOAP}$$

(b) Salting out:→

- This process involves separation of soap and glycerol and called as salting out.
- In this process solid salt or brine is added to mixture of soap, glycerol and excess lye, which is then boiled and allowed to settle. The soap is thrown out of solution as curdy mass which being of lower density than glycerol/brine mixture floats to the surface. The aqueous layer which also contains spent lye (Glycerol containing liquiod that is formed after saponification of fat or oi), salt and dirt is drawn off from the bottom of the pan and pumped to the glycerol recovery plant.
- The soap left in pan is dissolved in water and after boiling for a short time is salted out, the lye being removed after settling.
- The washing operation is repeated to remove glycerol and impurities.
- The soap is again boiled with fresh soda lye to complete the saponification.
- After settling out as before, the spent lye is run off and reused.
- Finally the soap is boiled with water and left to settle in the pan for 2-10 days.

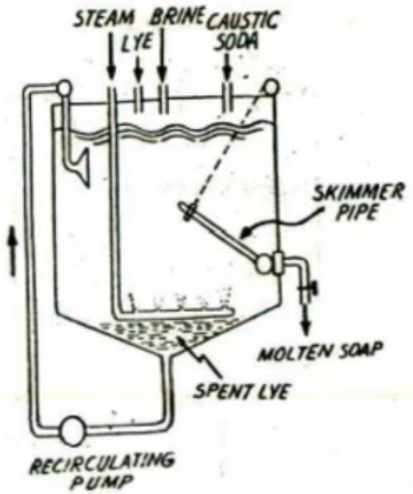
(c) Finishing :→

- The upper layer of soap obtained from step (b) is called 'neat soap' which is in the liquid state.
- This liquid soap is mixed with glycerol, colour, perfumes, germicides etc. till it becomes a homogeneous mass.
- This soap is then poured into moulds or frames, and after solidification cut into small bars using steel wire cutters.
- For making toilet soaps, neat soap is made into thin shreds, dried by hot air and mixed with perfumes, colour etc to thin shavings. These are then stamped into cakes.

→ Soap manufacture:→

→ Cold process:→

- The manufacture of soft coconut oil or soft potassium soaps cannot be carried out by the boiling process. This is because of their greater solubility in water which prevents them from being salt out. In this case, the 'cold process' is used.
- The fat or oil is mixed with the required amount of soda lye in a steam heated vessel called crutcher.
- The saponification is allowed to take place in cold. The process is continued till the soap, begins to set.
- The by product glycerol is not recovered and remains in the soap.
- The cold process is also employed in India to prepare washing soap on a small scale for household use.

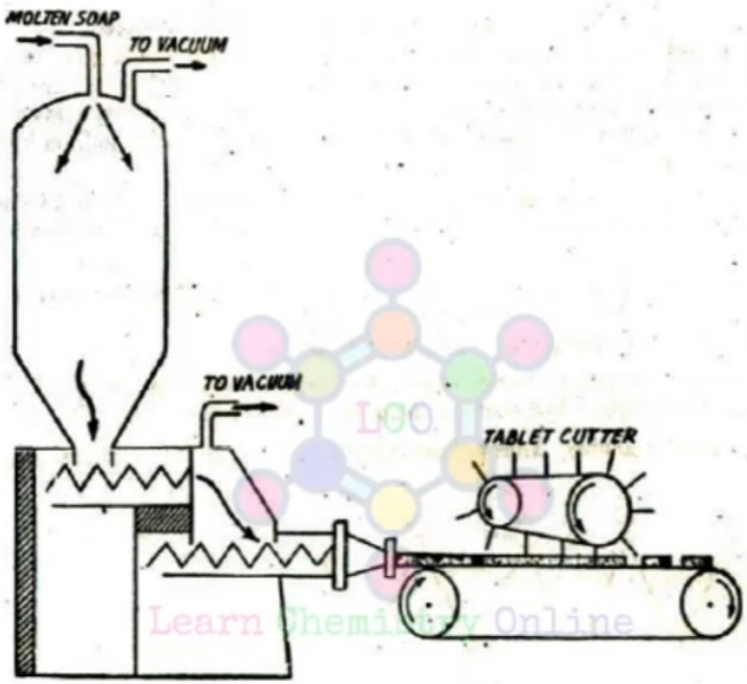


STEAM HEATED CRUTCHER

→ Modern continuous process:→

- In this process saponification can be carried out in about 15 minutes as compared to hours required for the open-pan method. This is achieved by reacting the fat/alkali mixture at high temperature and pressure in closed vessel.
- After cooling, the soap is washed and salted out. Separation of soap and spent lye layers carried out by centrifugation.
- After filtring and centrifugation, the molten soap is partially dried and cooled by spraying from the top of a vacuum.

– After this, perfume is added in soap and converted into tablets using tablet cutter.

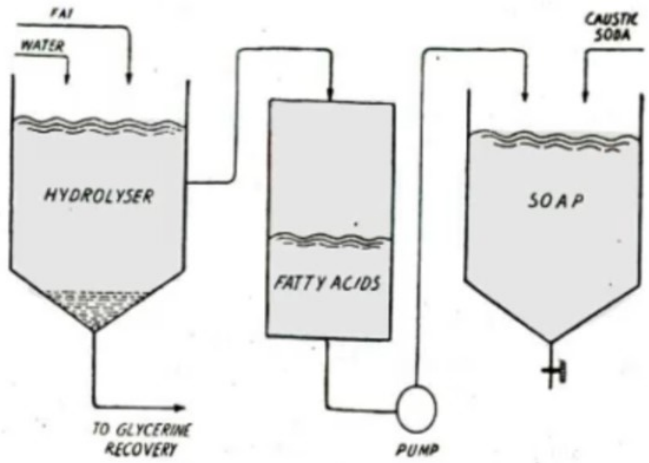


MODERN CONTINUOUS PROCESS

→ Soap manufacture:→

→ Ittner process:→

- In this process the hydrolysis of fat is carried out with water under pressure and at elevated temperature in the presence of lime or zinc oxide as catalyst.
- Hot water is fed into the hydrolyser near the top and fat near the bottom. The hydrolysis is rapid and complete. The fatty acids thus produced rise to the surface and are drawn out at the top, while glycerol is removed in water leaving at the bottom. The fatty acids are then pumped to another vessel, called neutraliser. Here they are neutralised with sodium hydroxide, or the cheaper sodium carbonate to form soap.

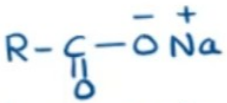


→ Twitchell process:→

- In this process, the hydrolysis of fat is done using a catalyst consisting of dilute H_2SO_4 and aromatic sulphonic acid. All the details are the same as for Ittner process.
- The drying and finishing of soaps for Ittner process and Twitchell process is same as modern continuous process.

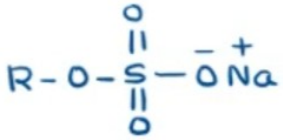
→ Synthetic detergents:→

- Detergents are also called syndets.
- Detergents are either sodium salts of alkyl hydrogen sulphates or sodium salts of long-chain alkyl benzene sulphonic acids.



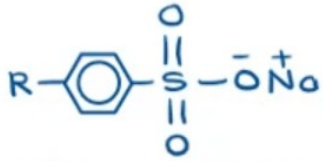
a sodium carboxylate

SOAP



a sodium alkyl sulphate

DETERGENT



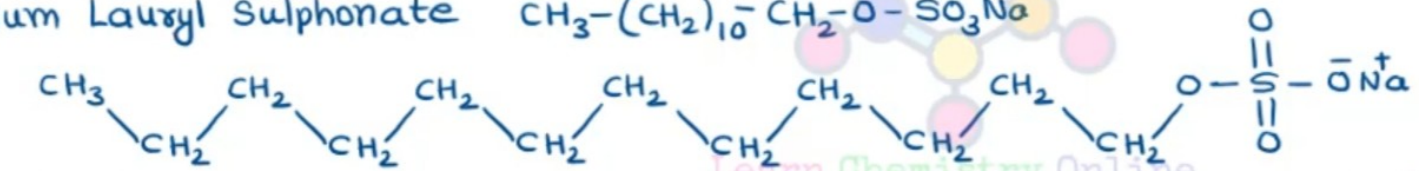
a sodium alkylbenzene sulphonate

DETERGENT

R = a chain of 12 to 18 carbon atoms.

- Example:→

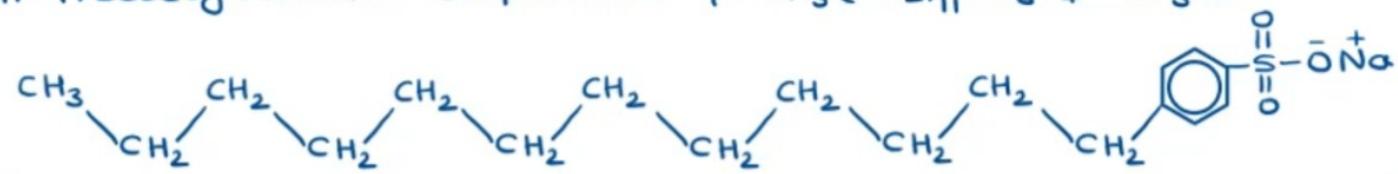
(a) Sodium Lauryl Sulphonate $CH_3-(CH_2)_{10}-CH_2-O-SO_3^-Na^+$



oil soluble part

water soluble part

(b) sodium-n dodecylbenzene sulphonate $p\text{-}CH_3(CH_2)_{11}-C_6H_4-SO_3^-Na^+$

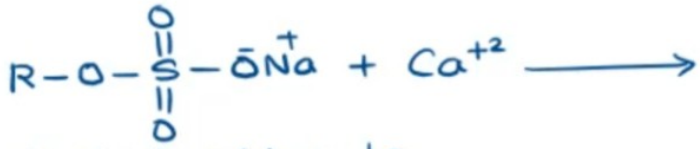


oil soluble part

water soluble part

→ Superiority of detergents to soaps:→

– Synthetic detergents are superior to soaps because of their solubility in water. Ca, Mg and other metal ions present in hard water form insoluble carboxylate (scum) with ordinary soap, decreasing the efficiency of soaps. On other hand, detergents form calcium and magnesium salts which are soluble in water.



Sod. alkyl sulphonate
(Detergent)

– Thus detergents are effective cleasing agents even in hard water.

→ Manufacture of detergents:→

(1) Sodium alkyl sulphates:→

– These are produced commercially from aliphatic long-chain alcohols (C_{10}-C_{14}) available from the hydrogenolysis of appropriate fats or oils. The alcohol is first sulphated with sulphuric acid. The resulting alkyl hydrogen sulphate when neutralised gives the sodium salt.

Example:- Synthesis of sodium lauryl sulphate

Lauryl alcohol (obtained from hydrogenolysis of coconut or palm oil)

sulphuric acid

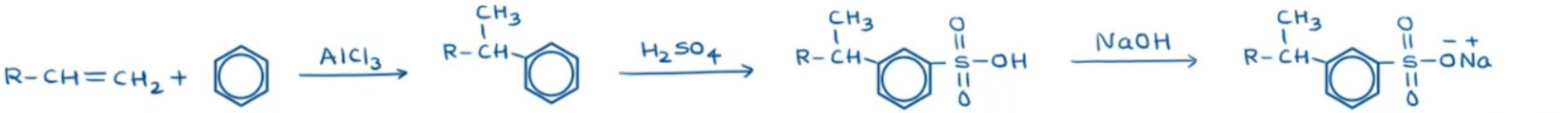
Lauryl hydrogen sulphate

Lauryl hydrogen sulphate

Sodium lauryl sulphate (a detergent)

(2) Sodium alkylbenzenesulphonates (ABS detergents) :→

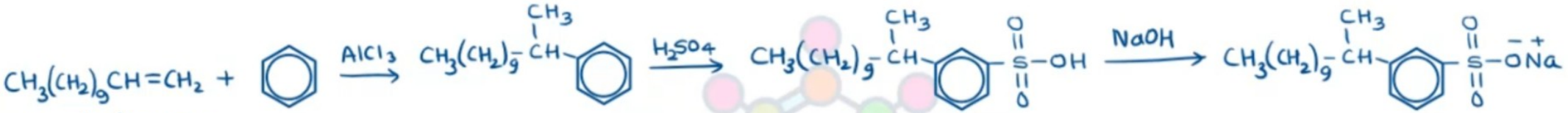
— These are manufactured by a Friedel Carft's alkylation of benzene with long-chain alkenes (C_{10}-C_{11}). The resulting alkylbenzene then suphonated to give alkylbenzenesulphonic acid which is converted to its sodium salt.



Alkylbenzenesulphonic acid

Sodium alkylbenzenesulphonate (A detergent)

Example:→ Synthesis of sodium p-dodecylbenzene sulphonate



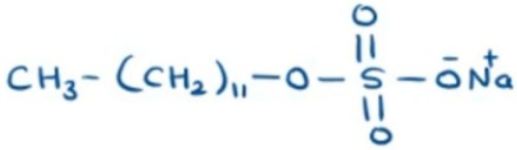
1-dodecene

→ Types of detergents:→

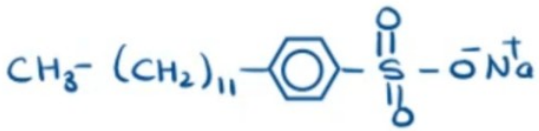
– Detergents are classified into three types on the basis of ionic charge present at the soluble end of their chain.

(1) Anionic detergents:→

– These bear an anion at the soluble end of the chain.



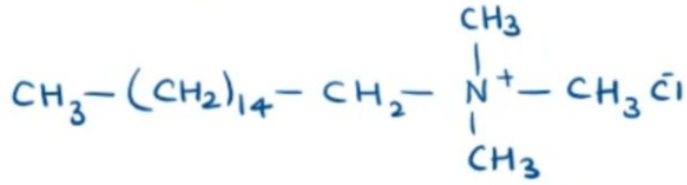
Sodium Lauryl sulphate



Sodium p-n-dodecylbenzenesulphonate

(2) Cationic detergents:→

- These bear a cation at the soluble end of the chain.

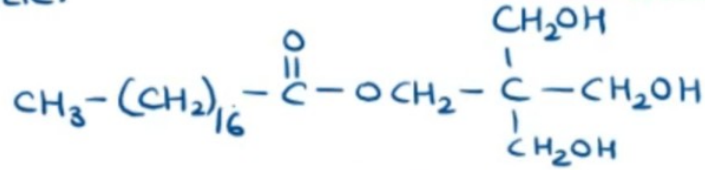


n-hexadecyl-trimethyl ammonium chloride

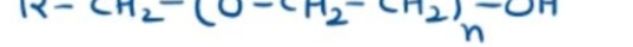
- These are also called Invert detergents and have a strong germicidal action.

(3) Nonionic detergents:→

- This type of detergents posses effective hydrogen bonding groups at one end of the alkyl chain. Due to hydrogen bonding, these detergents show water solubility.
- These include monoesters of polyhydric alcohols or polyethers derived from ethylene oxide.



pentaerythrityl stearate



$n = 8$ to 12 $R = 11$ to 17

Polyether

- They are particularly useful for dishwashing.

→ Difference between soap and detergents:→

SOAP	DETERGENTS
1. Soaps are sodium or potassium salts of higher fatty acids.	1. Detergents are sodium salts of alkyl hydrogen sulphates or sodium salts of alkyl benzenesulphonic acids.
2. Soaps are prepared from vegetable oils and animal fats.	2. Detergents are obtained from the petroleum hydrocarbons.
3. Soaps have relatively weak cleansing action.	3. Detergents have strong cleansing action.
4. Soaps form curdy white precipitate of calcium and magnesium salts with hard water and hence, are not used in hard water.	4. Detergents form soluble calcium and magnesium salts with hard water and hence detergents can be used even in hard water.
5. Soaps cannot be used in acidic medium as they are decomposed into carboxylic acids in acidic medium.	5. They can be used in acidic medium as they are the salts of strong acids and are not decomposed in acidic medium.
6. Soaps do not cause water pollution.	6. Detergents cause water pollution.
7. Soaps are biodegradable	7. Detergents are non-biodegradable.
8. Soaps take time to dissolve in water.	8. They dissolve faster in water.

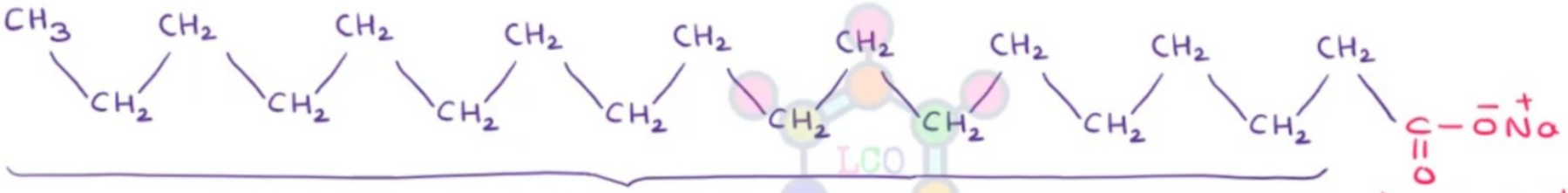
→ Cleansing action of soap :→

- The cleansing action of soap depends on the fact that a soap molecule is made of two parts-

(i) A long non-polar hydrocarbon chain which is oil soluble.

(ii) The salt like polar head which is water soluble.

Example:- sodium stearate, $C_{17}H_{35}COONa$ (a soap) can be represented as-



Non-polar hydrocarbon tail
(oil soluble part)

Polar head
(water soluble part)

- When soap solution is poured onto a solid clothing or a greasy dish, the hydrocarbon tail of soap molecules dissolves in the oily or greasy layer. The greasy layer with soap tails plugged into it is then dislodged by the mechanical action of rubbing, tubling or boiling. Once loosened the greasy layer breaks into tiny globules by soap molecules with heads being attracted to polar water molecules. such tiny droplets of oil carry negative charge due to carboxylate ions. These greasy/oil impurities form oil in water type emulsion which can be easily washed away by stream of water.