# Soaps and Detergents

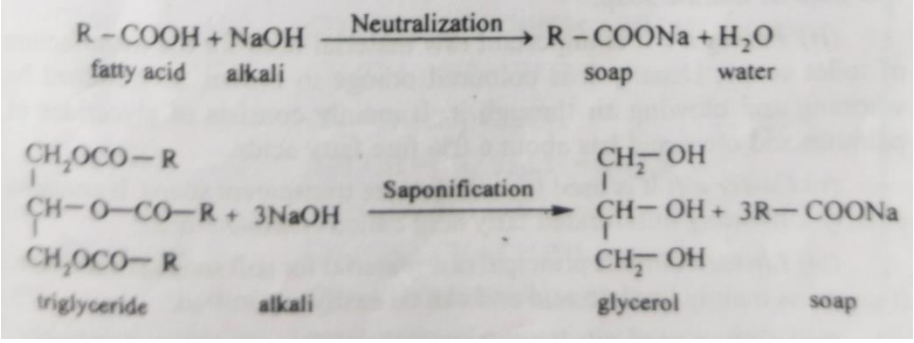
## 1: Introduction

- Earlier alkaline solution of fatty material was used as cleansing agent.After words from this, the soap was invented. In the beginning soap was a luxurious item, meant for only rich people. But the growing awareness about health and hygiene and improving economic conditions created demand for soap.
- With the increased availability of new raw material and the discovery of newer manufacturing processes, soap became not only a popular item but an essential item too in day-to-day life.
- Disadvantages of soap in hard water stressed the need for more efficient substituent for soap. Consequently syndets (synthetic detergents) were discovered. The growth of petrochemical industry provided impetus for the detergent revolution by supplying raw materials. Presently, about 70 percent of detergent demand met by syndets.

## 2: Soaps

Till 18th century soap was believed to be a mechanical mixture of fat and alkali. But understanding of saponification reaction removed the miss-conception.

- Soaps are alkali metal salts of higher fatty acids. They are represented by general formula RCOOM, where $RCOC^-$ is the acetyl ion of higher fatty acid and $M^+$ is alkali metal ion ($Na^+$ or $K^+$). Soap is produced by reacting fatty acid with alkali or hydrolysing the glycerides with alkali.




### i.Raw Materials

**1. Fats, Oils 2. Fatty acids 3.Alkaline Materials 4.Common Salt 5. Other additives**

### ii. Types of Soaps

Depending upon the utility of seep, different soup varieties are

### 1. Washing Soaps:

- These soaps are used for sanitation purposelike washing clothes, cleaning utensils, floors etc.
- They are prepared from oils or fats using sodium hydroxide. They contain alkali, fillers like $Na_2CO_3$, silicate, clays, optical whiteners etc.

- Typical soap contains 20 % soap, 40 %soda ash( $Na_2CO_3$) and 40 % water as water of crystallization. Jelly soaps prepared from coconut oil and caustic potash.

**2. Toilet soaps:**

- They are made from best quality selected materialsand usually contain only l0-15 % moisture and some quantity of glycerol.
- Pure alkali (caustic potash) is added in right proportion avoiding any excessalkali, as it may harm the skin.
- It also contain expensive perfumes and no fillers are used.
- Transparent soaps are prepared from best quality coconut oil, castor oil and caustic potash.
- Shampoos used for hair washing contain lauric acid, oleic acid. propylene glycol, triethanolamine, perfumers and water. The medicated soaps contain phenol, cresol etc. which act as antiseptic and germicidal agents.

**3. Shaving soaps:**

- Shaving soap is a mixed soap of sodium and potassium.
- It contains excess of stearic acid to give lasting lather. Shaving creams contain stearic acid and fats with much less soap.

**4. Industrial soaps :**

- They are used as cleaning agents for cleaning industrial machinery. In textile industry they are used as wetting agents.
- Insoluble calcium and aluminium soaps also called non-alkali metal soaps are used as water repellents in the manufacture of water proof textiles and walls.
- Zinc and magnesium sterate soap is used in face powders. Soapsareused for sizing(act as protective filler or glaze)for paper.Thesesoapsaremade from oils likecoconut, castor, olive and ground nut oils.

**(iii) Cleaning Action of Soap**

- A Soapmolecule can be represented as head and tail structure [Fig. ].(- $COONa^+$) group represents the *polar head* and the [$(CH_2)$n,] chain represents the *non-polar tail*.
- Thehead is*hydrophilic (Waterloving)*in nature, while the tail is *hydrophobic (water hating)* in nature. Such a molecule containing bothhydrophilic and hydrophobic regions is called *amphipathic molecule*.
- So, we can say it is molecular weight amphipathic molecules do not dissolvein water to form true solutions.
- But when vigorously shaken they *disperse* inwater to form *aggregates* called *micelles*.[Fig.].
- They are ball likestructures in which the *polar hydrophobic heads are exposed and interact with water* molecules at the surface.
- The *non polar hydrophobic tails are drawn inside to remain away from water*.
- It forms stablestructure having strong hydrophobic interactions between the tails and polarinteractions between head and water molecules.

- The dirt or soil particles are held to the skin, cloth and other surfaces by somegreesy materials like oil, cooking fats, sweat etc.
- Since oils are not miscible with water, washing with Wateralone will not help it removing dirt, but a soap or detergent can remove it.

The cleaning process of a soap or detergentinvolves:

(i) Thoroughly wetting the dirtand its surface in contactwiththe detergent solution for cleaning action,

(ii) Removing the dirt from surface,

(iii) Maintaining the dirt in a stable solution or suspension.

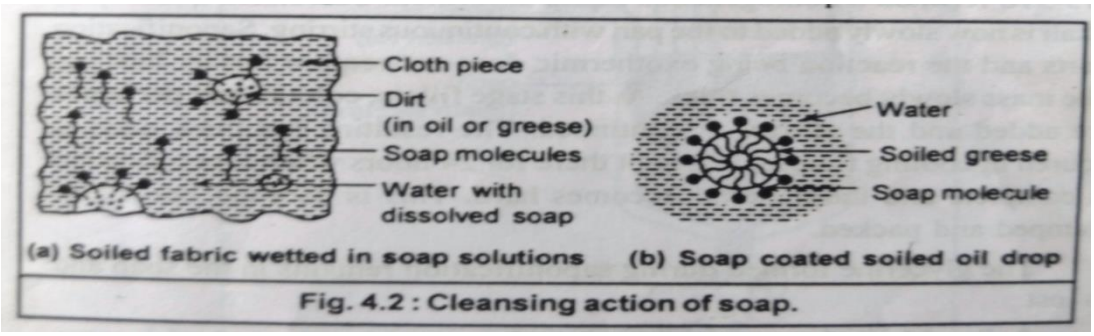


Fig. 4.2 : Cleansing action of soap.

- Other than micelle of soap used to remove dirt, it also reduces the surface tension of wateras works and surface active agent. As a result the wetting ability of water increases.
- So water penetrates the fabric more easily and reaches the soil (dirt).
- The detergent molecules emulsifying the water insoluble oily or greasy droplets, while the hydrophilic polar heads face to water form fine dispersion or emulsion of oily or greasy dirt.
- The hydrophilic coat around the greasy droplet makes it water soluble, loosens the grip and is removed when rinsed with water.

**3: Manufacture of Soap**

- Two different ways are used to obtain soap. One is to hydrolyse the oil or fat by alkali, this is called as **saponifrcation**and other is**neutralization**to neutralize the directly the fatty acid by alkali.
- **Hard Soap**- The common soaps are usually obtained from saturated fatty like acids like stearic, palmitic and caustic soda.
- **Soft soap-** The soap obtained from unsaturated fatty acids like linolenic and caustic potash. **i.e.**The sodium soap comparatively harder than potassium soap which is soft.

**Soap Manufacture**

1. **Cold Process :-**

- This process is carried atcomparatively low temperature 3l3-318 K (40-45°C), coconut oil and tallow are used
- The process is carried out in a cylindrical flat bottomed **crutcher.**
- The oil or oil mixture or fat is taken in the crutcher and heated to 313-3l8 K when a homogeneous liquid is formed.

- Calculated alkali is now slowly added to the pan with continuous stirring.
- Saponification starts and the reaction being exothermic does not require further heating.
- At this stage thick mass form and into that fillers, colours and perfumes are added with continuous stirring.
- This thick mass is now poured in cooling frames which is kept for 24 hrs to become hard material.
- Now it is ready for cutting into slabs and for packing.
- In this method also glycerine remains in soap and is lost

2. **Semi boiled process** :
   - The principle used in this method as that used in cold process. The difference in the two methods is the temperature at which the process is carried out.
   - Semi boiled carried out at about 353 K i.e. at 80°C.
   - The oil or fat is taken in a big size pan which is kept in a furnace. The material is heated to about 353K when it becomes a homogeneous liquid to this calculated quantity of alkali is added with continuous stirring.
   - Boiling is continued for few hours and fillers, colours, perfume are added at the end.The hot mass poured into frames and allowed to cool. This is then cut into bars, and packed.
   - In this method also glycerine remains in soap and is lost
   - Good quality laundry and toilet soaps are manufactured by this or by fee next hot or full boiled process.

3. **Hot or Boiled Process:-**

   **1. Boilling or saponification:**
   - Here big kettle pan is used which is about 9.0 m in diameter and 10 m in height with a slightly conical bottom (Fig.).
   - Oil or fat is taken into that kettle and melted by steam. To this calculated amount of aqueous caustic soda solution (12 to 15%) called *lye* added slowly.
   - The reacting mixture is heated by passing steam through the perforated coils at the bottom of kettle and it is kept boiling until the reaction is complete.
   - Agitation is done by a direct steam jet provided at the centre and 80-85% of saponification is effected in 4 hours.

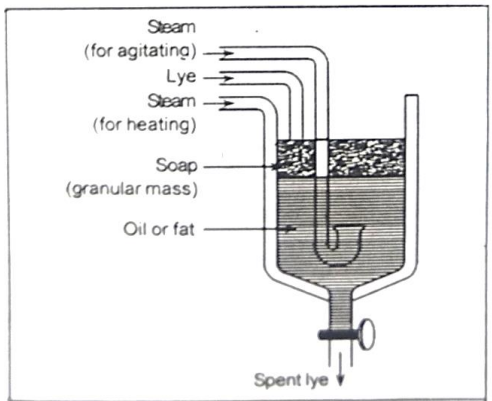


Fig. 4.3 : Vertical kettle

**2. Graining or salting out:**

- Mixture of soap and glycerine is obtained in first step to which rock salt (or brine, NaCl) is added and allowed to dissolve with boiling.
- Soap being insoluble in brinesolutionand separates from the mixture to form a floating granular mass hence the step name is **graining.**
- The lower aqueous layer called *spent lye* contains dissolved glycerine (about 4 per cent) and salt. So, it is drawn off from the kettle, to recover glycerine and salt solution.
- The soap left in the kettle is boiled again with some lye and spentlye is collected.
- The whole operation is repeated once again. This treatment completes saponification.

**3. Finishing:**

- The soap now contains excess alkali and salt adhered to it. So, to remove them, soap is boiled with water for some time and allowed to settle.
- Three layers will be formed. The upper layer consists of melted soap, middle layer is a mechanical mixture of soap in soap solution; it contains some impurities, so dark in colour and is called *nigre* and. It is reused for next batch operation. The lower layer contains some alkali, it is wasted.
- The melted soap is smooth with grossy appearance and is called *neat soap.*
- It is taken in to a crusher and fillers, colouring agents, perfumes etc. are added and thoroughly mixed.
- It is then, spray dried and allowed to stand tor 2-3 days, until it becomes hard. Then cut into cakes, stamped, packed and marketed.

Hot process has several advantages over other processes.

(i) Glycerine is obtained as most valuable byproduct. This considerably reduces the cost of operation.

(ii) Fats and oils are completely saponified. This greatly increases quality and yield of soap.

(iii) The unused alkali in the spent lye can be recycled in next batch.

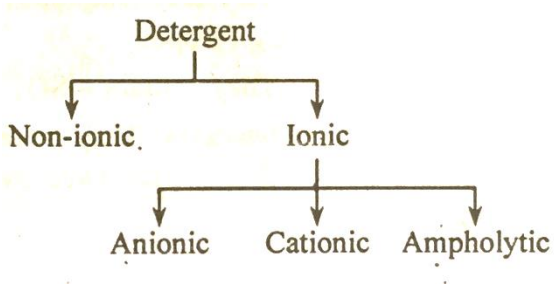
**4. Detergents (Synthetic Detergents) or Syndets**

- Truely speaking detergent is a general term used for any surface active (chemical) agent capable of removing dirt from the surface. Soap was the first known detergent.
- In order to differentiate synthetic detergent from soap new term syndet is introduced.
- But in practice term detergent itself is more popular than syndet.
- Syndet is also soap or soapless detergent.

- **Detergent: -** Surface active agent nicknamed as surfactant clean the surface by reducing surface tension at the boundary between two phases. So, soap, detergents, emulsifiers, wetting and penetrants are all surfactants, because they modify the properties.

**(i) Raw Materials -** Detergent is not a single chemical compound, but a mixture of different Chemicals. Principally it contains the surfactants along with other supplementary chemicals called additives. The growing demand for detergents and the superiority of syndets over soaps has made syndets as of choice.

**(ii)Types of Detergents**



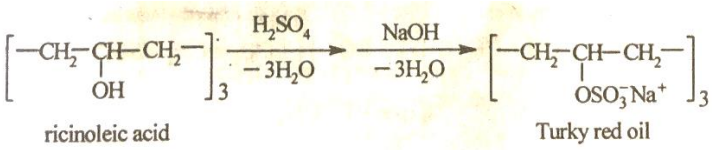

Detergents can be represented by the general structure, R - X, where, R is linear or slightly branched, hydrophobic, hydrocarbon chain containing 8 to 18 carbon atoms. X is a hydrophilic group it may be ionic or non-ionic. Depending on the nature of (X), surfactants are classified into different types as shown aside.

**Ionic (or ionogenic) surfactants:** They ionise in solution and form Slits with metallic ions or hard water. Depending on the nature of ions ionic surfactants are of following three types.

**[I] Anionic detergents:** The surface active property is due to the lively charged anion groups. They are most used surfactants and most suitable for water absorbing fibres like cotton, wool and silk. Widely used anionic detergents are discussed below.

**(a) Sulphate:** They contain $-SO_3^-$ anionic group. They can be.

**(i) Aliphatic sulphates :** The first synthesised aliphatic sulphate is Turky red oil (sulphonated castor oil). The main chemical reaction is sulphonation of ricinoleic acid (an hydroxy acid).




Turky red oil is used as textile finishing agent, in cutting oils as emulsifying agent, in cresoate disinfectants and agricultural sprays etc.

**(ii) Sodium alkyl sulphates :** They are fatty alcohol sulphates. Sodium alkyl sulphates are salts of strong acid, therefore most effective in acid solution. In hard water, they form soluble calcium and magnesium salts. So they can act effectively in hard water too. e. g. Sodium lauryl sulphate, sodium cetyl sulphate, sodium oleyl sulphate etc.

$$CH_3 \cdot (CH_2)_{10} \cdot CH_2 \cdot OSO_3^- Na^+$$

Na-lauryl sulphate

Sodium lauryl sulphate has excellent foaming characteristics and its effect on skin is mild. So it is used in shampoos, cosmetics, tooth pastes and as a component of household detergents. Sodium cetyl and sodium oleyl sulphates are used as general detergents.

(iii) Sodium secondary alkyl sulphates (teepol):- They are sodium salts of alkyl sulphates e.g. teepol.

**(b) Sulphonates :** They contain $SO_3$ anion group. They can be,

(1) Sodium alkyl sulphonates : They are obtained by sulphochlorination of C14 - C16 alkanes ($C_nH_{2n+2}$) followed by neutralization with sodium hydroxide.

$$C_{14}H_{30} + SO_2 + Cl_2 \xrightarrow[-HCl]{} C_{14}H_{29}SO_2Cl$$

$$C_{14}H_{29}SO_2Cl + SO_2 + Cl_2 \xrightarrow[-HCl]{} C_{14}H_{28}(SO_2Cl)_2$$

$$C_{14}H_{29}SO_2Cl + NaOH \xrightarrow[-NaCl]{} C_{14}H_{29}SO_3^-Na^+$$

- Although, sodium alkyl sulphonates are good detergents, they are inefficient in hard water. Because, they form less soluble calcium and magnesium salts.

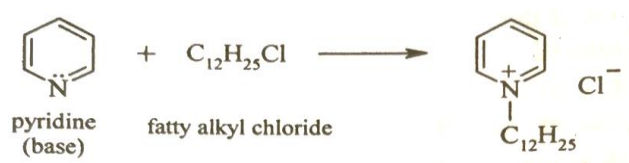
(ii) Amide sulphonates : They are the taurine derivatives. An important member of this group namely Igepon-T (oleyl methyl taurate).

$$\underset{\text{Oleyl chloride}}{CH_3(CH_2)_7CH=CH(CH_2)_7COCl} + \underset{\text{Na-salt of methyl taurine}}{HN(CH_3)-CH_2-CH_2SO_3Na} \xrightarrow[-HCl]{}$$

$$\underset{\text{Igepon - T}}{CH_3(CH_2)_7CH=CH(CH_2)_7-CO-N(CH_3)-CH_2-CH_2-SO_3Na}$$

**[II] Cationic detergents:** The surface activity of these compounds is due to positively charged cationic group. Therefore, they are also known as invert soaps. They include nitriles, amines, amide linked amines or quaternary nitrogen bases. They are manufactured by reacting alkyl chlorides with fatty amines or tertiary amines.

$$N(CH_3)_3 + C_{12}H_{25}Cl \longrightarrow [C_{12}H_{25}N^+(CH_3)_3]Cl^-$$




They are the first used textile softners. Because of their bactericidal character, they are also used as antibacterial and algicidal agents and detergent sanitizers.

**[III] Ampholytic detergents:-** They are also called amphoteric or zwitterionic surfactants, Because, they have both positively and negatively charged groups. So, they can behave as cationic and anionic surfactants depending on the pH environment. A typical ampholyte of this class of surfactants is N-lauryl - B - amino sodium propionate.

$$\underset{\text{deriphat}}{CH_3 \cdot (CH_2)_{11} \cdot NH \cdot CH_2 \cdot CH_2 \cdot COO^- Na^+}$$

Deriphat is an enzyme inhibitor, so used in tooth-paste to reduce dental caries. Such compounds are also used in shampoos, cosmetics, water emulsion paints etc.

**4.5: Comparison between Soaps and Detergents**

Soap is the first known and used detergent. But some serious disadvantages have limited it's all round applications and they are listed below.

1. In **hard water** it forms insoluble **curd** (i.e. $Ca^{2+}$ and $Mg^{+2}$ precipitate). The curd being sticky cause greying of fabrics. This not only hinders the detergent action of soap but soap is wasted.
2. It is **not suitable for textile** processing in hard water and acid solution. Because in hard water the curd is formed and in acid solution soap decomposes to form insoluble precipitate of free fatty acid.
3. Aqueous solution of soap is **alkaline** due to hydrolysis. So, it cannot be used for washing fabrics dyed with **alkali sensitive dyes**. Also, soap solutions cause irritation to the sensitive skin.
4. Soap is **not a suitable detergent in dry cleaning** as it is not soluble in organic solvents.
5. The raw materials (**oil and fat**) used for the manufacture of soap have high **nutritional value** so they are valuable as food.

<u>In spite of these limitations soap is still widely used because of following reasons:</u>

1. It is **least toxic** of all detergents and easily biodegradable. So, it **does not cause stream pollution**.
2. It does **not require any added soil suspending agents** as required by syndets.
3. It can be **recovered from the waste** water by acidifying it. This can prove valuable if common washing centers are used by population.

**Syndets:** A detergent is superiour to soap in following respects:

1. They can be efficiently **used even in hard water**. Because non-polar detergents do not react with $Ca^{+2}$ or $Mg^{2+}$ions, while, the polar detergents react to form soluble salts. Therefore, they are most suited in textile processing and as cleansing agents in hard water.
2. Because of their higher solubility in organic solvents they are **most suited for dry cleaning** of wool, silk fabrics.
3. The **raw materials** needed for the manufacture of detergents are **cheap** and available in plenty from petrochemical industry.
4. Compared to soap, detergents are **more potent surfactants** even at much lower concentration.
5. Detergents are excellent foaming agents. They have **bactericidal and germicidal properties.**

<u>This does not mean that, syndets are the ideal detergents, but they suffer from following disadvantages.</u>

(i) Use of **phosphorus** compounds in detergents has **eutrophication** effect on ponds and lakes. The phosphorus substituents developed so far are either are costly or suffer from other disadvantages.

(ii) The foam produced by some detergents is so extensive and stable, that, it forms a foam bed over river, ponds and lakes receiving the sewage water. This is mainly due to the branched chain hydrocarbon surfactants which are **not easily biodegradable.**

In spite of all these realities both soap and detergents have come to stay because of their wide spread applications in, <u>(l) Textile manufacture, (2) Sanitation, (3) Food processing, (4) Paints (water emulsion formulation), (5) Synthetic rubber and plastics (emulsion polymerization), (6) Paper (application of sizing), (7) Oil production (drilling fluid oil), (8) Inks (water oil emulsions), (9) Agriculture (emulsifying agents for sprays), (l0) Construction (water proofing cement), (l 1) Cosmetics, (12) Metallurgy (froth flotation) etc.</u>