CHAPTER 5

SOAPS AND DETERGENTS

CHAPTER 5 OBJECTIVES

- Soap
  - Raw Materials
  - Chemistry of soaps
  - Classification of soaps
  - Manufacturing of soaps
  - Environmental aspects
- Detergents
  - Introduction and History
  - Principle groups of synthetic detergents
  - Surfactants
  - Inorganic Builders
  - Sundry Organic Builders
  - Manufacturing of Detergents

SOAP
RAW MATERIALS

- The triglycerides (or triesters of fatty acids) are the raw material for the production of soap.
- Tallow and coconut oil are the principal fatty materials in making soap.
- The palm oils, palm kernel oil, and their derivatives are used in the soap manufacture in many other parts of the world.
- Greases, obtained from hogs and smaller domestic animals, are the second most important source of glycerides of fatty acids.

SOAP
RAW MATERIALS

- Coconut oil has long been important in soap making. The soap from coconut oil is firm and lathers well. It contains large amount of the desired glycerides of lauric and myristic acids.
- The soap maker represents one of the larger consumers of chemicals, especially caustic soda, salt, soda ash, caustic potash, sodium silicate, sodium bicarbonate and trisodium phosphate.
- Builders are inorganic chemicals added to the soap. In particular, tetrasodium pyrophosphate and sodium tripolyphosphate were usually effective soap builders.

SOAP
CHEMISTRY OF SOAPS

- Soaps are water-soluble sodium or potassium salts of fatty acids containing from 8 to 22 carbon atoms.
- The fatty acids are generally a mixture of saturated and unsaturated moieties:
  - Saturated soap: $CH_3(CH_2)_nCOOM$
  - Mono-unsaturated soap:

    $CH_3(CH_2)_nCH_2CH{=}CHCH_2(CH_2)_m{-}COOM$
  - Poly-unsaturated soap: $CH_3(CH_2CH{=}CH)_xCH_2(CH_2)_y{-}COOM$ [M = Na, K, R_4N^+].

SOAP
CHEMISTRY OF SOAPS

- The basic chemical reaction in the making soap is saponification:

$$3\,NaOH + C_{17}H_{35}COO_3C_3H_5 \longrightarrow 3\,C_{17}H_{35}COONa + C_3H_5(OH)_3$$

Sodium hydroxide | **Glyceryl stearate** | **Sodium stearate** | **Glycerin**

- The other method for making soap consists of fat splitting followed by the neutralization process with sodium hydroxide.

$$(C_{17}H_{35}COO)_3C_3H_5 + 3\,H_2O \xrightarrow[\text{Splitting}]{\text{Fat}} 3\,C_{17}H_{35}COOH + C_3H_5(OH)_3$$

Stearic acid | Glycerin

$$C_{17}H_{35}COOH + NaOH \xrightarrow{\text{Neutralization}} C_{17}H_{35}COONa + H_2O$$

Stearic acid | Sodium hydroxide

CLASSIFICATION OF SOAPS

- The two main important classes of soaps are toilet and industrial. Toilet sop is usually made from mixtures of tallow and coconut in ratios 80-90/10-20.
- The bar soap includes regular and super fatted toilet soaps, deodorant and antimicrobial soaps, floating soaps and hard water soaps.
- The super fatted soaps are also made from mixture of tallow and coconut oil in ratios 50-60/40-50.
- All soaps contain practically 10-30% water and also contain perfume that serves to improve the original soap odor. Toilet soaps usually contain only 10 to 15% moisture.

CLASSIFICATION OF SOAPS

- Shaving soaps, in contrast, contain a considerable amount of potassium soap and an excess of stearic acid; the combination gives a slower drying lather.
- Milled toilet soap is another type of bar soap. Because of the milling operation, the soap lathers better and has a generally improved performance, especially in cool water.
- Laundry soap bars are precursors of the chip and the powder forms. They are generally made from tallow or a combination of tallow and coconut oil.
- Borax and builders, such as sodium silicate and sodium carbonate, are included to improve performance and help soften water.

MANUFACTURING OF SOAPS

- The saponification of triglycerides with an alkali is a bimolecular nucleophilic substitution (SN2).
- The rate of the reaction depends on the increase of the reaction temperature and on the high mixing during the processing.
- In the saponification of triglycerides with an ‘alkali’, the two reactants are immiscible.
- The formation of soap as a product affects the emulsification of the two immiscible reactants, which causes an increase in the reaction rate.

Triglyceride + 3 NaOH → 3 RCOONa + Glycerin

MANUFACTURING OF SOAPS

- The fatty acids are sent to a flash tank, where the water is separated or flashed off.

$$\text{Triglyceride} \xrightarrow[\text{Fat splitting}]{+H_2O} \text{Fatty acids + Glycerin}$$

- The fatty acids are sent to a flash tank, where the water is separated or flashed off.

MANUFACTURING OF SOAPS

- The resulting crude mixtures of fatty acids may be used, but a separation into more useful components is made.
- The hot fatty acids are cooling down to room temperature into two parallel condensers prior to neutralization with 50% caustic soda in a high-speed mixer neutralizer.
- The fatty acids are converted into sodium salts, which form the soap.

$$\text{Fatty acids} + \text{NaOH} \xrightarrow{\text{Neutralization}} \text{Soap}$$

MANUFACTURING OF SOAPS

- The amount of caustic soda (NaOH) required neutralizing a fatty acid blend can be calculated as follows:

$$NaOH = [Weight_{fatty\ acid} \times 40] / M_{Fatty\ acid}$$

- The average molecular weight of a fatty acid is calculated from the following equations:

$$M_{Fatty\ acid} = 56.1 \times 1000 / AV$$

  Where AV = Acid Value of fatty acid blend = mg of KOH required to neutralize 1 g of fatty acid.
- The neat soap (60-63% total fatty matter) is discharged into a slowly agitated blender to assure a complete neutralization.

MANUFACTURING OF SOAPS

- The neat soap at this stage may be extracted for conventional soap production (bar, flake or powder).
- The heated soap is sent to a flush tank for a partial drying then mixed with air in a heat exchanger, where the soap is cooled from 105°C to 65°C.
- The advantages of soap manufacturing by this process include the color improvement of the soap, the excellent glycerin recovery and the need for less space and labor.

DETERGENT
INTRODUCTION

- ***Detergent:*** Product that after formulation is devised to promote the development of detergency.
- ***Surface Active Agent:*** Chemical compound which, when dissolved or dispersed in a liquid is absorbed at an interface, giving rise to a number of important chemical properties.
- ***Amphiphilic Product:*** Product which contains in its structure one or more hydrophilic groups and one or more hydrophobic groups.

PRINCIPLE GROUPS OF SYNTHETIC DETERGENTS

- Detergents are complex formulations that contain more than 25 different ingredients, which can be categorized into the following main groups:
  1. Surfactants
  2. Builders
  3. Bleaching agents
  4. Additives

PRINCIPLE GROUPS OF SYNTHETIC DETERGENTS *SURFACTANTS*

- Surfactants represent the most important group of detergent components. They are present in all types of detergents.
- Surfactants are water-soluble surface-active agents comprised of a hydrophobic group (a long alkyl chain) attached to hydrophilic group.
- The hydrophilic group is usually added synthetically to a hydrophobic material in order to produce a compound, which is soluble in water.
- This solubilization does not necessarily produce a detergent, since detergency depends on the balance of the molecular weight of hydrophobic portion to that of the hydrophilic portion.

PRINCIPLE GROUPS OF SYNTHETIC DETERGENTS *SURFACTANTS*

- Four main groups of surfactants: anionic, cationic, non-cationic and amphoteric.
  1. **Anionic Surfactants** are compounds in which the detergency is realized in the anion.

     $R\text{-}SO_3^- \, Na^+$

     Alkylsulfonates (anionic surfactants)
  2. ***Cationic Surfactants*** are compounds in which the detergency is in the cation. No neutralization takes place. The material is in effect neutralized by a strong acid.

     $R_2N^+(CH_3)_2Cl^-$

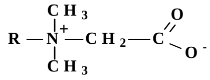
     Dialkyl dimethylammonium chlorides (cationic surfactants)

PRINCIPLE GROUPS OF SYNTHETIC DETERGENTS *SURFACTANTS*

- Non-ionic Surfactants contain non-ionic constituents.

  $RO\text{-}(CH_2\text{-}CH_2\text{-}O)_nH$

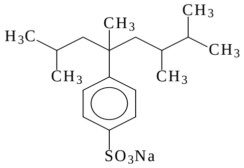
  Alkyl poly(ethylene glycol)ethers (non-ionic surfactants)
- Amphoteric Surfactants includes both acidic and basic groups in the same molecule.



Betain (amphoteric surfactants)

ANIONIC SURFACTANTS
Alkylbenzenesulfonates (LAS and TPS)

- Alkylbenzene sulfonates represent the largest class of synthetic surfactants.
- Tetra propylene benzene sulfonate (TPS) was the most prominent detergent.



TPS

ANIONIC SURFACTANTS
Alkylbenzenesulfonates (LAS and TPS)

- LAS were found interesting foaming characteristics, which are very significant for their application as detergents.
- LAS can be controlled by foam regulators.
- The foam produced is stabilized by form stabilizers.
- The dehydrogenation of paraffins, followed by alkylation of benzene with a mixed olefin/paraffin feedstock represents the most important route for the production of LAS.

ANIONIC SURFACTANTS
Alkylbenzenesulfonates (LAS and TPS)

- This process is catalyzed by hydrogen fluoride (HF).
- Another important route toward LAS: the partial chlorination of paraffins, followed by alkylation of the chloroparaffin/paraffin feedstock using aluminum chloride (AlCl3) as a catalyst.
- The third process implicates the partial chlorination, but includes a dehydrochlorination to olefins prior to alkylation with AlCl3 or HF as a catalyst.
- UOP offers processes, catalysts, adsorbents and equipment for the production of linear alkylbenzenes (LAB) from kerosene or normal paraffins.

ANIONIC SURFACTANTS

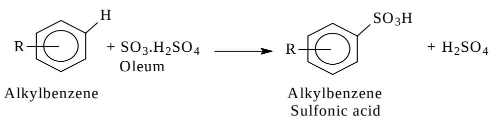
Alkylbenzenesulfonates (LAS and TPS)

- ***Sulfonation of LAB***
  - The sulfonation reaction takes place by using oleum ($SO_3.H_2SO_4$) or sulfur trioxide (SO_3).
  - Although, the oleum sulfonation requires relatively inexpensive equipment, the oleum process has major disadvantages compared to sulfur trioxide.
  - The need for spent acid stream disposal and the potential corrosion due to sulfuric acid generation increased the problems related to oleum process.

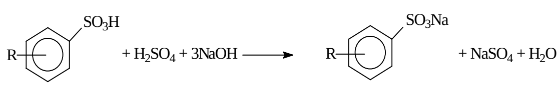
ANIONIC SURFACTANTS

Alkylbenzenesulfonates (LAS and TPS)

- Sulfonation:



- Neutralization:



ANIONIC SURFACTANTS

Secondary Alkanesulfonates (SAS)

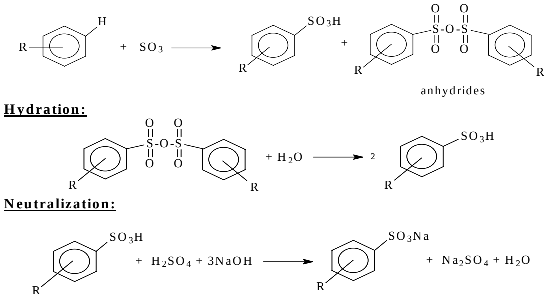
- The gaseous air/SO_3 sulfonation process leads to high yields of sulfonic acid (95-98%).
- This process comprises three major steps.
- The sulfonation of alkylbenzene with air/SO_3 forms the alkylbenzene sulfonic acid and anhydrous.
- Decomposition into the alkylbenzene sulfonic acid by hydration.
- The neutralization of the sulfonic acid into the corresponding sodium salt represents the last chemical step in the process of formation of detergents.

ANIONIC SURFACTANTS
Secondary Alkanesulfonates (SAS)

Sulfonation:

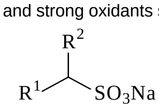
Hydration:

Neutralization:



ANIONIC SURFACTANTS
Secondary Alkanesulfonates (SAS)

- The secondary alkanesulfonates are known to have high solubility, fast wetting properties, chemical stability to alkali, acids, and strong oxidants such as chlorine.



$R^1, R^2 = C_{11-17}$

- Sodium alkanesulfonates are produced by photochemical sulfoxidation or sulfochlorination of suitable C12-C18 paraffin cuts.
- SAS can largely be substituted for LAS in formulations due to the similarity in terms of solubility, solubilizing properties and wetting power.

ANIONIC SURFACTANTS
Sulfonated Olefins

$R\text{-}CH = CHCH_2SO_3Na$ and	$R\text{-}CH(OH)\text{-}(CH_2)nSO_3Na$
$R = C_8\text{-}C_{12}$	$R = C_7\text{-}C_{13}$
Alkenesulfonates	Hydroxyalkanesulfonates

- The reaction between a-olefins and SO_3 is not straightforward due to the formation of mixtures of alkene sulfonic acids, sulfones, alkene disulfonic acids and sulfone sulfonic acids.

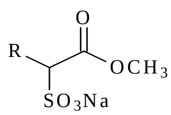
ANIONIC SURFACTANTS

Sulfonated Olefins

- Alkaline hydrolysis of the sulfone intermediate results in Ca. 60-65% alkenesulfonates and Ca. 35-40% hydroxyalkanesulfonates.
- The materials are sold as a-olefinsulfonates (AOS) because of the use of olefinic precursors.
- AOS has not yet made great strides in the heavy-duty laundry field but is being used successfully for light duty detergents, hand dishwashing shampoos, bubble baths and synthetic soap bars.

ANIONIC SURFACTANTS

α-Sulfo Fatty Acid Ester (Methyl Ester Sulfonates -MES)



$R = C_{12\text{-}16}$

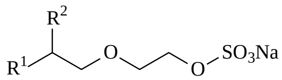
- α-sulfofatty acid esters represent another class of anionic surfactants.
- Methyl ester sulfonates (MES) are surfactants that derived from a variety of methyl ester feedstocks such as coconut, palm kernel, palm stearin, beef tallow, and soy.

ANIONIC SURFACTANTS

α-Sulfo Fatty Acid Ester (Methyl Ester Sulfonates -MES)

- Palmitic and stearic acid derivatives lead to good detergency due to the long hydrophobic residues.
- The sensitivity of MES to water hardness is similar to AOS and small compared to LAS and SAS.
- MES have exceptional dispersion power with respect to lime soap. They have only been used in a few Japanese detergents.

ANIONIC SURFACTANTS
Alkyl Ether Sulfates (AES)



$R^1 = H, R^2 = C_{10-12}$ Fatty alcohol ether sulfates

$R^1 + R^2 = C_{11-13}$ Oxo alcohol ether sulfates

- Alkyl ether sulfates (AES) are anionic surfactants obtained by ethoxylation and subsequent sulfation of alcohols derived from feedstocks or synthetic alcohol.
- AES, also known as alcohol ether sulfates have low sensitivity to water hardness, high solubility, and good storage stability at low temperature.

ANIONIC SURFACTANTS
Alkyl Ether Sulfates (AES)

- The main components of the commercial AES are alkyl ether sulfates and alkyl sulfates.
- Other byproducts such as unsulfated alcohols, alcohol ethoxylates, inorganic salts, and polyethylene oxide sulfates are also present in the commercial product.
- AES are very intensively foaming compounds, which increased their use in high-foam detergents for vertical-axis washing machines.
- AES are suitable components of detergents for delicate or wool washables, as well as foam baths, hair shampoos, and manual dishwashing agents because of their specific properties.
- The optimal carbon chain length has been established to be C12-14 with 2 mol of ethylene oxide.

NONIONIC SURFACTANTS

- The majority of nonionic surfactants are condensation products of ethylene oxide with a hydrophobe.
- This hydrophobe is invariably a high molecular weight material with an active hydrogen atom.
- The nonionic material can be one of the reaction products.
  1. Fatty alcohol and alkylphenol condensates.
  2. Fatty acid condensates.
  3. Condensates of ethylene oxide with an amine.
  4. Condensates of ethylene oxide with an amide.

NONIONIC SURFACTANTS

Fatty Alcohol and Alkylphenol Condensates

$R\text{-}O\text{-}CH_2\text{-}CH_2\text{-}(OCH_2CH_2)_{n-1}\ OCH_2CH_2OH$

R = alkyl or phenyl

- The alcohol ethoxylates and alkylphenol ethoxylates are produced by the reaction of alcohol with an excess of ethylene oxide.

$R\text{-}O\text{-}CH_2CH_2OH + n\ CH_2\text{—}CH_2\ (O) \longrightarrow R\text{-}O\ CH_2CH_2\text{-}(OCH_2CH_2)_{n-1}\text{-}OCH_2\text{-}CH_2OH$

R = alkyl or phenyl; n=16-50

NONIONIC SURFACTANTS

Fatty Alcohol and Alkylphenol Condensates

- The ether linkage is a strong bond, therefore, the material cannot be hydrolyzed and ionized.
- The optimum detergency is found in the range of 10-15 molecules of ethylene oxide per molecule of fatty alcohol.
- The ethoxylation of these alcohols is done in two stages.
  i. The product containing 1 mol of ethylene oxide is produced first with an acid catalyst.
  ii. After this stage the catalyst and the unreacted alcohol are removed and ethoxylation is produced usual.

NONIONIC SURFACTANTS

Fatty Alcohol and Alkylphenol Condensates

- The alkylphenols behave in the same manner as fatty alcohols. The nonyl (or octyl) phenol is widely used with 8-12 molecules of ethylene oxide.
- Nonylphenol is completely soluble in water at room temperature and exhibits excellent detergency.
- The alkylphenol ethylene oxide condensates have been the most widely produced nonionic detergent.
- These condensates are solubilized by the ethylene oxide units forming hydrates with water.

NONIONIC SURFACTANTS

Fatty Acid Condensates

- Fatty acid condensates are another type of nonionic surfactants, which are prepared by the reaction of fatty acids with ethylene oxide.

$$RCOOH + n\,(CH_2OCH_2) \longrightarrow RC(=O)OCH_2CH_2\text{-}(OCH_2CH_2)_{n-2}\text{-}OCH_2\text{-}CH_2OH$$

NONIONIC SURFACTANTS

Fatty Acid Condensates

- These condensates can be also produced by the esterification of a fatty acid with a polyethylene glycol, $HOCH_2(CH_2CH_2)_nCH_2OH$.
- Nonionic detergents are not affected by metallic ions, acids or alkalis.
- The fatty acid condensates of ethylene oxide are readily hydrolyzed by acids or alkaline solutions into corresponding fatty acid and polyethylene glycol.
- They do perform well as components of the household detergent powders.

NONIONIC SURFACTANTS

Condensates of Ethylene Oxide with an Amine

- The condensation of alkylamines with ethylene oxide leads to sec. or tert. substituted amines depending on the concentration of ethylene oxide.
- This class has not been used largely in cleaning detergents.
- These materials in acidic solution can exhibit cationic characteristics, whereas, in neutral or alkaline solution they are nonionic.

$$R\text{-}NH\text{-}CH_2\text{-}CH_2(OCH_2CH_2)_{n-2}\text{—}OCH_2\text{-}CH_2OH$$

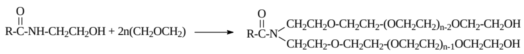
$$R\text{-}N\begin{cases} CH_2CH_2(OCH_2CH_2)_{n-2}\text{—}OCH_2CH_2OH \\ CH_2CH_2(OCH_2CH_2)_{n-2}\text{—}OCH_2CH_2OH \end{cases}$$

R = 11-17

NONIONIC SURFACTANTS

Condensates of Ethylene Oxides with an Amide

- Fatty acid alkanolamides are amides of alkylolamines and fatty acids.
- Certain members of this class exhibit detergency and others do not.
- The non-detergent materials are converted into detergents by the condensation with ethylene oxide:



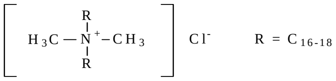
$R = C_{11-17}$
n= 1,2

CATIONIC SURFACTANTS

- These surfactants are very strongly absorbed to the surface of natural fibers, such as cotton, wool and linen.
- Cationic surfactants are mainly employed in certain applications such as in rinse-cycle fabric softeners and antistatic agents.
- Nonionic surfactants are more tolerant of the presence of cationic surfactants than anionic surfactants. Production of specialty detergents, which are powerful anti-static products.

CATIONIC SURFACTANTS

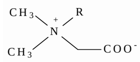
- The cationic detergents invariably contain amino compounds.
- Quaternary ammonium salts, such as cetyltrimethylammonium chloride, a well known ***germicide*** and distearyldimethylammonium chloride (DSDMAC); are used as ***fabric softener*** for cotton diapers and as a laundry rinse-cycle fabric softener.



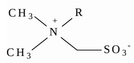
DSDMAC

AMPHOTERIC SURFACTANTS

- These compounds have the characteristics of both anionic detergents and cationic fabric softeners.
- They work best at neutral pH, and are found in shampoos, skin cleaners and carpet shampoo.
- They are very stable in strong acidic conditions and have found favor for use with hydrofluoric acid.
- These surfactants are rarely employed in laundry detergents due to their high costs.



$R = C_{12-18}$ Alkylbetaines



$R = C_{12-18}$ Alkylsulfobetaines

INORGANIC BUILDERS

- Builders enhance the detergency action so that less can be used of the more expensive detergents of high activity.
- The combination of builders and surfactants exhibits a synergistic effect to boost total detergency and cleaning efficacy.
- Detergent builders should have the ability to control water hardness and other metal ions, i.e. by eliminating calcium and magnesium ions, which arise from the water and from soil.
- Builders should be also compatible with other formulation ingredients and detergent additives.

INORGANIC BUILDERS

- The inorganic constituents fall into five following groups:
  1. Phosphates
  2. Silicates
  3. Carbonates
  4. Zeolites
  5. Bleach-active compounds

INORGANIC BUILDERS
Phosphates

- There are two classes of phosphate - orthophosphates and complex phosphates.
- The orthophosphates used in detergent industry:
  - Trisodium phosphate in hydrated and anhydrous forms (Na_3PO_4 and $Na_3PO_4.12H_2O$).
  - Disodium phosphate, another form of orthophosphates, is also available in anhydrous form (Na_2HPO4) and the crystalline $Na_2HPO_4.12H_2O$.
  - The "condensed phosphates" have a higher proportion of P_2O_5 and a lower proportion of Na_2O in the molecule. These phosphates have a lower alkalinity than trisodium phosphate.

INORGANIC BUILDERS
Phosphates

- The commonly used complex phosphates are:
  - Tetrasodium pyrophosphate $Na_4P_2O_7$ (TSPP)
  - Sodium tripolyphosphate $Na_5P_3O_{10}$ (STP)
  - Sodium tetraphosphate $Na_6P_4O_{13}$
  - Sodium hexametaphosphate $(NaPO_3)_6$
    - Both sodium tetraphosphate and sodium hexametaphosphate are hygroscopic and are unsuitable for formulation into dry powders.
    - Tetrasodium pyrophosphate (TSPP) is used for specialized purposes only but its potassium analogue is used in liquids.

INORGANIC BUILDERS
Silicates

- The Sodium silicate is prepared by the fusion of sand with soda ash:

  $$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$
- The ratio of silica sand and soda ash is important in providing a variety of alkalinity.
- The molecular formula of silicates has been adopted according to the method of Berzlins and is written: ***Na_2O: SiO_2*** .
- The sodium metasilicate ***(Na_2O/SiO_2=1/1)*** is used in dry blending.
- The liquid-silicates having ***Na_2O/SiO_2*** ratio of ***1/2*** or higher are used in laundry and automatic-dishwashing applications.

INORGANIC BUILDERS
Silicates

- Soluble glass and soluble powders are two forms of detergents which are prepared in the ratios of ***Na_2O:SiO_2*** of ***1:2*** and ***1:33***, respectively.
- A ratio of **1:2.4** is commonly used in making detergent powders.
- A "wet method" for the production of soluble detergents of up to 40% disilicate by the reaction of fine sand and caustic soda (3-50%).

$$2\ SiO_2 + 2\ NaOH \longrightarrow Na_2O.2SiO_2 + H_2O$$

- Potassium silicate, available commercially in colloidal ratios, is used nowadays, for specialized liquid detergents. It is available in weight ratios of 1:1.5-1:2.5.

INORGANIC BUILDERS
Carbonates

- Soluble Carbonates are being used due to restriction in the use of phosphates in certain areas of the United States.
- Sodium carbonate (Na_2CO_3) or a combination of Na_2CO_3 and zeolite has replaced sodium tripolyphosphate (STP) as a builder in granular laundry products.
- Sodium carbonate provides high alkalinity. Na_2CO_3 softens water by precipitation of calcium and magnesium carbonates, provided the pH of the solution is grate than 9.
- There are two important grades of carbonates: light soda ash and dense soda ash. Light soda ash can absorb large amounts of liquid material onto its surface and remains dry.
- Sodium carbonate is commonly used in powdered laundry detergent, automatic-dishwashing compounds and hand surface cleaners.

INORGANIC BUILDERS
Carbonates

- Sodium carbonate is produced by the Solvay process, which uses sodium dichloride, carbon dioxide and ammonia.
  - Carbon dioxide obtained from burning limestone to lime is introduced in counter-current to the solution of sodium chloride (known as brine) saturated with ammonia. The sodium bicarbonate, which is almost insoluble in solution and precipitates is separated and roasted to sodium carbonate .

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CO_2 + NaCl + NH_4OH \longrightarrow NaHCO_3 + NH_4Cl$$

$$2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$$

INORGANIC BUILDERS

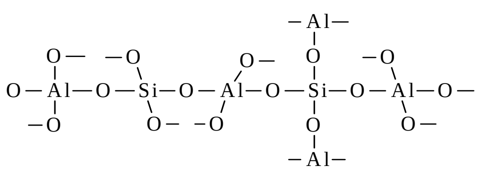
Zeolites

- Zeolites, also known as molecular sieves, are important alternative builders for powdered laundry detergents and replaced phosphate salts, which were banned in USA for legislative reasons.
- Zeolites exist in calcium, sodium, magnesium, potassium and barium salts forms.
- The most widely used form of zeolites is the **type A**, which are hydrated sodium aluminum silicates of empirical formula $Na_2O.Al_2O_3.xSiO_2.yH_2O$.

INORGANIC BUILDERS

Zeolites

- The crystalline material of type A zeolites has three-dimensional lattice structure of a simplified formula:



INORGANIC BUILDERS

Zeolites

- Type A zeolites are the most widely used form for laundry detergents.
- The main advantage of the zeolites compared to phosphates is non-solubility in water and subsequently they remove readily and rapidly from the solution heavy metal ions such as manganese and iron.
- Magnesium ions are not totally removed by zeolites due to the size of magnesium; therefore, zeolites are then used in association with other builders such as sodium carbonate.

INORGANIC BUILDERS

Bleach-Active Compounds

- Oxygen-releasing compounds are added to detergent powders as bleach-active materials.
- Peroxide active compounds are the most used bleaches in Europe and many other regions of the world.
- Among these peroxides, hydrogen peroxide (H_2O_2) is converted by alkaline medium into hydrogen peroxide anion as active intermediate.

$$H_2O_2 + OH^- \rightleftharpoons H_2O + HOO^-$$

INORGANIC BUILDERS

Bleach-Active Compounds

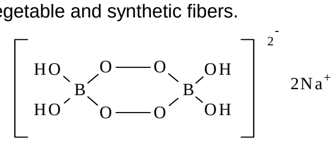
- HOO^- oxidizes bleachable soils and stains. The most used source of hydrogen peroxide is **sodium perborate** known as ***sodium peroxoborate tetrahydrate, $NaBO_3.4H_2O$***:
- Peroxodiborate is hydrolyzed in water to form hydrogen peroxide.

$$(NaBO_2H_2O_2)_2 \cdot XH_2O \longrightarrow 2NaBO_2 + 2H_2O_2 + XH_2O$$

INORGANIC BUILDERS

Bleach-Active Compounds

- In solution, sodium perborate monohydrate is similar in action that of hydrogen peroxide.
  - At elevated temperatures active oxygen is released and has a bleaching effect but does not affect animal, vegetable and synthetic fibers.



Sodium Perborate

INORGANIC BUILDERS
Bleach-Active Compounds

- Sodium perborate is a stable material when mixed with other dry ingredient.
- However, the presence of traces of water and certain heavy metal will catalyze the decomposition of the perborate.
- Therefore, a magnesium sulphate or silicate, or tetrasodium pyrophosphate is added to adsorb traces of water and metal to prolong the storage life of the powders.
- Hypochlorite is another effective bleaching compound at normal temperature. Hypochlorite reacts with an alkaline to produce hypochlorite anion.

INORGANIC BUILDERS
Bleach-Active Compounds

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- Hypochlorite is another effective bleaching compound at normal temperature. Hypochlorite reacts with an alkaline to produce hypochlorite anion.
- The aqueous solution of sodium hypochlorite (NaOCl) is used as a source of active chlorine, which can be used in either the wash or the rinse cycle.

$$HOCl + OH^- \rightleftharpoons ClO^- + H_2O$$

INORGANIC BUILDERS
Bleach-Active Compounds

- Powdered sodium perborate has some advantages over liquid sodium hypochlorite (NaOCl).
  - NaOCl must be added separately in either the wash or the rinse cycle whereas perborate can be included directly in the powder laundry product.
  - A high dosage of NaOCl may cause a significant damage to laundry and colors.
  - Sodium hypochlorite solutions have limited storage stability especially in the presence of some impurities such as heavy metal ions.
  - Sodium hypochlorite has a high reactivity and oxidation potential and may cause problems with textile dyes and most fluorescent whitening agents.

SUNDRY ORGANIC BUILDERS

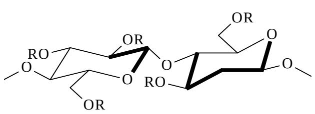
ANTI-REDEPOSITION AGENTS

- The redeposition displaced soil can be prevented by the addition of special anti-redeposition agents.
- The role of these agents is to be adsorbed on the surface of the textile creating a protective layer that satirically inhibits redeposition of the removed soil.
- The carboxymethyl cellulose (CMC) derivatives and carboxymethyl starch (CMS) are effective anti-redeposition agents
- They are formed from cellulose-containing fibers such as cotton and blends of cotton and synthetic fibers.
- CMC has virtually no effect on pure synthetic fibers.

SUNDRY ORGANIC BUILDERS

ANTI-REDEPOSITION AGENTS

- CMC has virtually no effect on pure synthetic fibers.
- The nonionic cellulose ethers have been found suitable for the use with synthetic fibers.



R = CH_3, C_2H_5, CH_2CH_2OH, $CH_2CH(OH)CH_3$, $CH_2CH_2CH(OH)CH_3$

Nonionic Cellulose Ethers

SUNDRY ORGANIC BUILDERS

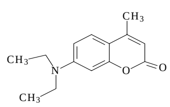
THICKENING AGENTS

- Carboxymethyl cellulose (CMC) is also used as a thickening agent in addition to its characteristic as a soil anti-redeposition agent.
- Modified non-ionic celluloses, methyl cellulose, hydroxyethyl cellulose methylhydroxy propyl cellulose are being used as thickening agents.
- These modified celluloses are soluble in cold water and insoluble in hot water and most organic solvents.

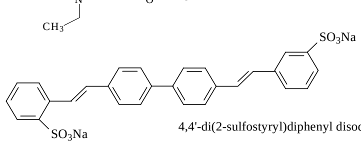
SUNDRY ORGANIC BUILDERS
OPTICAL BRIGHTENERS

- Optical brighteners are organic compounds capable of converting a portion of the invisible ultraviolet light into longer wavelength visible blue light.
- They are a dyestuff, which is absorbed by textile fibers, but are not easily rinsed off. The reflection of blue light makes the clothes look brighter than they actually are.
- Optical brighteners are usually derivatives of coumarin, stilbene, distyrylbipheny and bis(benzoxazole).
- The optical brighteners binding occur, in the case of cotton and chlorine-resistant materials, through the formation of hydrogen bond to the fibers.

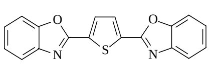
SUNDRY ORGANIC BUILDERS
OPTICAL BRIGHTENERS



7-Dimethylamino-4-Methyl Coumarin



4,4'-di(2-sulfostyryl)diphenyl disodium salt



2,5-bis(benzoxazol-2-yl)thiophene

SUNDRY ORGANIC BUILDERS
CHELATING AGENTS

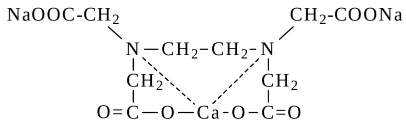
- The role of the chelating agents is to block the polyvalent ions and to make them undetectable and ineffective.
- Sodium salts of ethylene diamine tetraacetic acid (EDTA) and of nitrilo triacetic acid (NTA) are members of the group of chelating agents.

$$\begin{matrix} NaOOC\text{-}CH_2 & & & & CH_2\text{-}COONa \\ & N - CH_2 - CH_2 - & & & \\ NaOOC\text{-}CH_2 & & & & CH_2\text{-}COONa \end{matrix}$$

Sodium Salt of EDTA

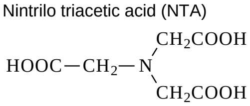
SUNDRY ORGANIC BUILDERS
CHELATING AGENTS

- The sodium salt of EDTA reacts with calcium ions to give a complex in which Ca is bidentated to nitrogen atoms of EDTA.

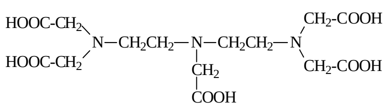


SUNDRY ORGANIC BUILDERS
CHELATING AGENTS

- There are three main groups of the chelating agents.
- Aminocarboxylic acids
  - Nintrilo triacetic acid (NTA)



  - Diethylene triamine pentacetic acid (DTPA)



SUNDRY ORGANIC BUILDERS
CHELATING AGENTS

- NTA sequestrates more calcium ions per unit weight than EDTA due to its lowest molecular weight.
  - Both will sequester more calcium ions than magnesium because the molecular weight of magnesium is smaller than that of calcium.
  - EDTA and NTA are used in laundering formulations to chelate trivalent ions, thus preventing iron stains in laundering.

SUNDRY ORGANIC BUILDERS

ENZYMES

- There are four types of enzymes of interest to the detergent industry:
  1. Proteases – act on protein to form amino acids.
  2. Amyloses – convert starches into dextrins.
  3. Lipases – attack fats and oils.
  4. Celluloses – hydrolyze cellulose of broken surface fibers and remove micro-pills from cotton and restore color.

MANUFACTURING OF DETERGENTS

PRODUCTION OF ALKYLBENZENE SULFONATES

- The alkylbenzene sulfonates are produced by the sulfonation of linear alkylates followed by the neutralization step with a caustic solution containing sodium hydroxide (NaOH).
- The process of sulfonation of alkylbenzenes with oleum takes place in a batch system where five basic processing operations are utilized:
  1. Sulfonation
  2. Digestion
  3. Dilution
  4. Phase separation
  5. Neutralization

MANUFACTURING OF DETERGENTS

PRODUCTION OF ALKYLBENZENE SULFONATES

1. The sulfonation stage includes mixing of alkylate with oleum which leads to an exothermic reaction. The key parameters that control the reaction of sulfonation are the temperature, acid strength, reaction time and oleum-to-alkylate ratio.
2. The reaction was completed at the digestion stage where the product from the sulfonation zone is age for 15 to 30 minutes.
3. The mixture of sulfonic acid and sulfuric acid is diluted with water to quench the reaction.

MANUFACTURING OF DETERGENTS
PRODUCTION OF ALKYLBENZENE SULFONATES

4. The reaction mixture is sent to a separator to allow gravity settling of the spent sulfuric acid from the lighter sulfonic acid. The lower spent acid layer contains approximately ***75 to 80 percent sulfuric acid***. The upper layer contains approximately ***88 to 91% sulfonic acid and 6 to 10% of sulfuric acid***.
5. The linear alkyl sulfonates can be neutralized with aqueous solutions of base such as ***NaOH, KOH, NH4OH, or alkanolamines***. The ***sodium salts*** are used in the formulation process to produce spray-dried detergents for household laundry. However, ***ammonium and alkanolamine*** neutralized salts are usually employed in light duty liquid detergents.

MANUFACTURING OF DETERGENTS
PRODUCTION OF ALKYLBENZENE SULFONATES

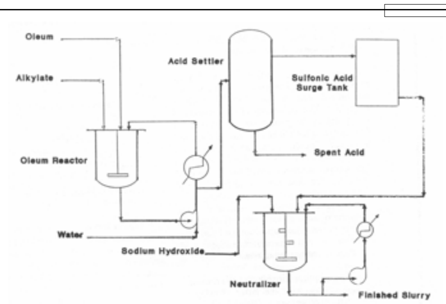


Figure 5.5. Oleum Sulfonation Process

MANUFACTURING OF DETERGENTS
FATTY ALCOHOLS SULFATION

- The sulfation of fatty alcohols takes place in falling film reactors.
- Cooling water and sulfation temperatures are adjusted to lower values.
- The sulfonic acids obtained are neutralized immediately in order to minimize degradation and side reactions in storage.

$$R\text{-}OH + SO_3 \longrightarrow R\text{-}O\text{-}SO_3H$$

MANUFACTURING OF DETERGENTS
FATTY ALCOHOLS SULFATION

- Typical process for the sulfation of fatty alcohols has a post-hydrolysis step that includes bleaching in order to remove color before neutralization.
- Neutralization step of the sulfonic acid is similar to the case of oleum sulfonation process.
- The surfactant slurry, builders and other miscellaneous additives are introduced in the crutcher.
- A considerable amount of water is removed, and the paste is thickened by the tripolyphosphate (used as a builder) hydration reaction:

$$Na_5P_3O_{10} + 6H_2O \longrightarrow Na_5P_3O_{10}.6H_2O$$

MANUFACTURING OF DETERGENTS
FATTY ALCOHOLS SULFATION

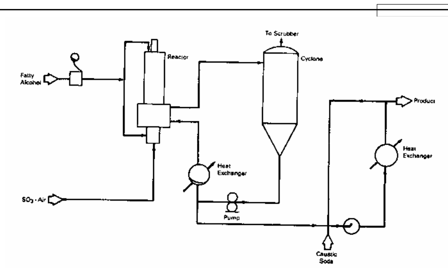


Figure 5.6. Fatty Alcohol Sulfation Process

ENVIRONMENTAL ASPECTS
EMISSIONS AND CONTROLS

- The exhaust air from detergent towers contains two types of contaminants:
  - Fine detergent particles
  - Organics vaporized in the higher zone of the tower.
  - Some of the VOCs identified in the organic emissions are: hexane, methyl alcohol, 1,1,1-trichloroethane, perchloroethylene, benzene and toluene.

ENVIRONMENTAL ASPECTS
WASTEWATER AND THE ENVIRONMENT

- The clean water, which was brought into the process, is later released to the sewage system in the form of contaminated wastewater soil from the laundry, lint, dyes, finishing agents and detergents.
- Detergents are released as the products of reaction with other material during the washing cycle or in unchanged form.
- The Laundry wastewater is a heavy source of contamination; therefore, it should not be returned to receiving waters in untreated form.

ENVIRONMENTAL ASPECTS
BIODEGRADATION

- The removal of organic compounds from sewages, surface waters and soils can be done by the biodegradation process.
- The first step involves the transformation of the sodium sulfonate to a first degradation product (primary degradation).
- The subsequent degradation to the second, third, etc.,.
- The ultimate biodegradation represents the total decomposition of the total organic structure into carbon dioxide, water, and inorganic salts, and in parallel, partly into bacterial biomass.

ENVIRONMENTAL ASPECTS
BIODEGRADATION

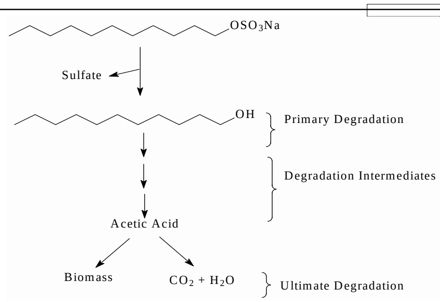


Figure 5.8. Biodegradation Pathway of Fatty Alcohol Sulfates

ENVIRONMENTAL ASPECTS
BIODEGRADATION

- The Anionic surfactants are determined as “methylene blue active substance” (MBAS), i.e., materials forming a chloroform soluble complex with cationic dye methylene blue.
- Nonionic surfactants are defined as “bismuth active substance” (BiAS), i.e., materials forming an insoluble complex with the bismuth-containing Drangendorff reagent.
- The primary biodegradation of anionic and nonionic surfactants is determined in standardized tests by measuring the removal of MBAS and BiAS, respectively.

ENVIRONMENTAL ASPECTS
BIODEGRADATION

- The ultimate biodegradation of chemicals can be followed in the tests by means of nonspecific analytical parameters such as carbon dioxide evolution (BOD) or the removal of dissolved organic carbon (DOC).
- Primary and ultimate biodegradability of test substances is normally evaluated by applying standardized and internationally used (OECD, ISO, EU) test procedures.