***Soap***

**Introduction:**

 According to an ancient Roman legend, soap got its name from Mount Sapo, where animals were sacrificed. Rain washed a mixture of melted animal fat or tallow and wood ashes down into the clay soil along the Tiber River. It was found that this clay mixture cleaned the washed clothes with much less effort.

The term soap is a class name for the sodium and potassium salts of fatty acids. These fatty acids were found in animal fats and in plant oils such as coconut oil, palm oil, olive oil, castor oil, or cottonseed oil.

**History:**

 Records show that ancient Egyptians bathed regularly. The Ebers Papyrus, a medical document, describes the combining of animal and vegetable oils with alkaline salts to form a soap-like material used for treating skin diseases, as well as for washing.

The early Greeks bathed for aesthetic reasons and apparently did not use soap. Instead, they cleaned their bodies with blocks of clay, sand, pumice, and ashes, then anointed themselves with oil, and scraped off the oil and dirt with a metal instrument known as a strigil. They also used oil with ashes. Clothes were washed without soap in streams.

The roman civilization showed a more positive progression in cleanliness than did the early Greeks. As Roman civilization advanced, so did bathing. The first of the famous Roman baths was supplied with water from their aqueducts. The baths were luxurious, and bathing became very popular.

In Europe, by the 7th century, soap making was an established craft.

Soap-maker guilds guarded their trade secrets closely. Vegetable and animal oils were used with ashes of plants along with fragrance. Gradually more varieties of soap became available for shaving and shampooing, as well as bathing and laundering.

Italy, Spain, and France were early centers of soap manufacturing, because of their ready supply of raw materials such as oil from olive trees. The English began making soap during the 12th century. The soap business was so good that in 1622, King James I granted a monopoly to a soap maker for US$100,000 a year. Well into the 19th century, soap was heavily taxed as a luxury item in several countries. When the high tax was removed, soap became available to ordinary people and cleanliness standards improved.

A major step toward large-scale commercial soap making occurred in 1791 when a French chemist, Nicholas Leblanc, patented a process for making soda ash, or sodium carbonate, from common salt. Soda ash in the alkali obtained from ashes combines with fat to form soap. The Leblanc process yielded quantities of good quality, inexpensive soda ash.

Some soap manufacture took place in Venice and Sauona in the 15th century and in Marseilles in the 17th century. By the 18th century, manufacture was widespread throughout Europe and North America and by the 19th century the making of soap had become a major industry.

**Fatty Acid Distribution:**



**Raw materials:**

 Soaps are manufactured from a renewable source. The triglycerides (or triesters of fatty acids) are the raw material for the production of soap.

The triglycerides occur widely in plants and animals. Tallow and coconut oil are the principal fatty materials in soap making in the United States. The palm oils, palm kernel oil, and their derivatives are used in 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. Coconut oil has long been important in soap making. The soap from coconut oil is firm and lathers well. It contains a 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 soap. In particular, tetrasodium pyrophosphate and sodium tripolyphosphate were usually effective soap builders.

**Chemistry of soaps:**

 Soaps are water-soluble sodium or potassium salts of fatty acids containing 8 to 22 carbon atoms. The fatty acids are generally a mixture of saturated and unsaturated moieties.

Saturated soap:  **CH3(CH2)nCOOM**

Mono-unsaturated soap: **CH3(CH2)nCH2CH=CHCH2(CH2)m—COOM**

Poly-unsaturated soap:  **CH3(CH2CH=CH)xCH2(CH2)y—C00M**

*[M=Na, K, R4N+]*

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



 *Sodium Sodium stearate*

*Glyceryl stearate hydroxide Glycerin*

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





Sodium hydroxide, potassium hydroxide, sodium carbonate, and triethanolamine are the most commonly used alkaline moieties in both the

processes.

Recently, soap manufacture by the saponification of fatty methyl esters has been developed in Japan and Italy. The methanolysis of triglycerides takes place in the presence of enzymes (lipase) as catalysts to produce fatty methyl ester and glycerin. The fatty methyl ester undergoes the saponification and forms the final product.



 Fat Methyl stearate Glycerin



 *Methyl stearate Sodium stearate*

**Classification of soaps:**

 The two main classes of soaps are toilet soap and industrial soap. Toilet soap is usually made from mixtures of tallow and coconut in the 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 a mixture of tallow and coconut oil in ratios 50—60:40—50. All soaps practically contain 10 to 30 percent water and also contain perfume that serves to improve the original soap odor. Toilet soaps usually contain only 10 to 15 percent moisture; they have little added material, except for perfume and a fraction of a percent of titanium dioxide used as a whitening agent. 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 generally has an 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:**

 Before the 1950s, soap was manufactured in the saponification process. Soap was prepared in large kettles in which fats, oils, and caustic soda were mixed and heated. After cooling, salt was added to the mixture forming two layers: soap and water. The soap was pumped from the top

layer to a closed mixing tank where builders, perfumes, and other ingredients were added. Finally, the soap was rolled into flakes, cast, or milled into bars, or spray-dried into soap powder.

After the 1940s, an important modern process for producing soap is based on the direct hydrolysis of fats by water at high temperatures. The process involves splitting (or hydrolysis) where fatty acids are neutralized to soap.

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

 The fatty acids are also converted into their corresponding sodium salts that form the soap.

 Neutralization

 Fatty acid + NaOH Soap

 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.

**Environmental aspects:**

 The main atmospheric pollution problem in soap manufacturing is odor. The sources of this odor are from the storage and handling of liquid ingredients such as sulfonic acids and salts, and also from sulfates. The raw materials and product storage, the ventilation lines, the vacuum exhausts, and the waste streams are all potential odor sources. The control of these odors may be achieved by scrubbing exhaust fumes, or by incinerating the remaining volatile organic compounds. The odors originating from the spray dryer may also be controlled by scrubbing with an acid solution.

Blending, mixing, drying, packaging, and other operations may involve dust emissions. The dust emission from the finishing operations can be controlled by dry filters such as bag houses. The large sizes of the particulate from the soap powder dryer mean the high-efficiency cyclones installed in a series can achieve a satisfactory control.

**SOAP AND DETERGENT MANUFACTURE**

Soaps and detergents are widely used in our society. Soaps are the product of the reaction

between a fat and sodium hydroxide:

fat + 3NaOH → glycerine + 3 soap

Soap is produced industrially in four basic steps. This article lists different steps because

in the industrial processes described each of these is done over several process steps, but

in principle it could be done in the three steps outlined here.

**Step 1 - Saponification**

A mixture of tallow (animal fat) and coconut oil is mixed with sodium hydroxide and

heated. The soap produced is the salt of a long chain carboxylic acid.

**Step 2 - Glycerine removal**

Glycerine is more valuable than soap, so most of it is removed. Some is left in the soap to

help make it soft and smooth. Soap is not very soluble in salt water, whereas glycerine is,

so salt is added to the wet soap causing it to separate out into soap and glycerine in salt

water.

**Step 3 - Soap purification**

Any remaining sodium hydroxide is neutralised with a weak acid such as citric acid and

two thirds of the remaining water removed.

**Step 4 - Finishing**

Additives such as preservatives, colour and perfume are added and mixed in with the soap

and it is shaped into bars for sale.

Detergents are similar in structure and function to soap, and for most uses they are more

efficient than soap and so are more commonly used. In addition to the actual ’detergent’

molecule, detergents usually incorporate a variety of other ingredients that act as water

softeners, free-flowing agents etc.

***Detergent***

**Introduction and history:**

 It is not easy to determine when the detergent industry came into existence. The problem was to define exactly what is being referred to as a

synthetic detergent. For example, in the United States the term *surfactants*

was used, while in Europe the term *tenside* was applied to point out the detergent industry.

Many general definitions of a detergent have been suggested:

**Detergent.** A product that after formulation is devised to promote the

development of detergency.

**Surface active agent.** A chemical compound, which when dissolved or dispersed in a liquid, is absorbed at an interface giving rise to a number of important chemical properties. The compound includes in its molecule one group that has an affinity for polar surfaces, ensuring solubilization in water, and a group that has little affinity for water.

**Amphiphilic product.** A product that contains in its structure one or more hydrophilic groups and one or more hydrophobic groups.

In the last 1000 years, soap has been used as a general-purpose washing and laundry agent. Soap remained a luxury until the beginning of the 20th century when the first self-acting laundry detergent was introduced in Germany (Persil, 1907). Soap took its place as an ingredient in the multicomponent systems for the routine washing of textiles. Soap was combined with the so-called builders, such as sodium carbonate, sodium silicate, and sodium perborate. The first practical substitutes for soap were fatty alcohol sulfates, discovered in Germany by Bertsch and coworkers in 1928. The availability of synthetic alkyl sulfates based on natural fats and oils made the introduction of the first neutral detergent for delicate fabrics (Fewa) possible in Germany in 1932. Fatty alcohol sulfates and their derivatives (alkyl ether sulfates, obtained by tracking fatty alcohols with ethylene oxide and subsequent sulfation) still retain their importance in many applications: heavy-duty detergents, dishwashing agents, cosmetics, and toiletries. In 1946, Procter and Gamble introduced the synthetic detergent Tide in the United States. By the 1950s, the widespread availability of tetra propylenebenzene sulfonate (TPS), a product of the petrochemical industry, had largely displaced soap as the key surfactant from the detergent.

 In 1977, the German firm Hankel patented the use of synthetic zeolites as a partial replacement for phosphates. The sodium aluminum silicates as zeolites have a particular lattice structure capable of absorbing heavy metal cations through ion exchange process. The role of zeolites that were added to TPS was to soften water by rapid reaction with calcium at normal temperature.

 Nitrilo triacetic acid (NTA) also represents a partial replacement of phosphate. However, the US Surgeon General issued a report stating that NTA caused birth defects in rats. The use of NTA was immediately phased out in the United States.

 An important new criterion, the so-called biodegradability of detergents, appeared for surfactants. The insufficient biodegradability of TPS and nonylphenol ethoxylates caused great masses of stable foam to build up in the vicinity of weirs, locks, and other constructions in waterways.

Subsequently, the first German Detergent Law was adopted in 1961.

 The German precedent was soon followed by the adoption of a similar legislation in France, Italy, and Japan. In the United Kingdom and the United States, voluntary agreement toward the transition to biodegradable surfactants took place between the industry and government.

 The world production figures of different countries showed that the per capita consumption of detergents varies quite largely. For example, it amounted to 2 to 3 kilograms per year (kg/a) in countries such as Brazil, China, and Russia, and to more than 10 kg/a in Mexico and some European countries in 1997.

 The world production of laundry detergents amounted to 21.5 x 1061in 1998. The total produced volume remained constant in the 1990s worldwide.

The use of enzyme additives was the most important and revolutionary trend in the detergent industry in the past decade. The lower-temperature washes of the new high-efficiency machines are expected to give a boost to the demand for enzymes. As catalysts, enzymes are efficient and effective at low doses and at low temperatures where surfactant Figure 5.2 Per capita consumption of detergents in 1996 (kg/a).

activity is challenged. Enzymes continue to be popular additives for stain removal and fabric care.

***Principle groups of synthetic detergents:***

 Detergents are complex formulations that contain more than 25 different ingredients that can be categorized into the following main groups:

1. Surfactants

2. Builders

3. Bleaching agents

4. Additives

***Surfactants:***

 Surfactants represent the most important group of detergent components.

They are present in all types of detergents. In general, surfactants are water-soluble surface-active agents comprising a hydrophobic group (a long alkyl chain) attached to a hydrophilic group.

The hydrophilic group is usually added synthetically to a hydrophobic material to produce a compound that is soluble in water. However, this solubilization does not necessarily produce a detergent, because detergency depends on the balance of the molecular weight of the hydrophobic portion to that of the hydrophilic portion.

In a two-phase system, for example, liquid-liquid or liquid-gas, a surfactant tends to locate at the interface of the two phases, where it introduces a degree of continuity between the two different materials. These substances consist of a [hydrophobic](http://www.answers.com/topic/hydrophobic) tail portion, usually a long-chain [hydrocarbon](http://www.answers.com/topic/hydrocarbon), and a hydrophilic polar head group, which is often ionic or strongly polar groups. A material possessing these characteristics is known as an amphiphile. It tends to dissolve in both [aqueous](http://www.answers.com/topic/aqueous) and oil phase and to locate at the oil-water interface. Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface.

Therefore, there are four main groups of surfactants: anionic, cationic, nonionic, and amphoteric.

**Anionic surfactants.** Anionic surfactants are surface active substances dissociated in water to give a linear or branched chain with hydrophilic negatively charged head group such as carboxylate, sulfate, sulfonate and phosphate in addition to a metallic cation.

These are compounds in which the detergency is realized in the anion that has to be neutralized with a basic material before the full detergency is developed.



anionic surfactant sodium dodecyl sulphate (SDS)

**Cationic surfactants.** This type of surfactants ionizes in solution giving an oil soluble cation (active part of the molecule) and an anion.

These are compounds in which the detergency is in the cation, and although in the manufacturing process no neutralization

takes place, the material is in effect neutralized by a strong acid.



cationic surfactant dodecyl trimethyl ammonium bromide (DTAB)

**Nonionic surfactants.** These contain nonionic constituents. They don't ionize in aqueous solution, because their hydrophilic group is of non dissociable type, such as alcohol, phenol, ether, ester, or amide. A large part of these nonionic surfactants are made hydrophilic by the polycondensation of ethylene oxide or propylene oxide.



nonionic surfactant hexaethylene glycol monododecyl ether (C12E6).

**Amphoteric surfactants.** They include both acidic and basic groups in the same molecule.



**Betain (amphoteric surfactants)**

 ***Anionic surfactants:***

 Alkylbenzene sulphonates (LAS and TPS). Alkylbenzene suofonates represent the largest class of synthetic surfactants and until the mid-1960s tetra propylene benzene sulfonate (TPS) was the most prominent detergent.



TPS

TPS has largely replaced soap as an active ingredient in laundry detergents in Europe, the United States, and Japan. However, the branched side present in TPS prevents the compounds from undergoing sufficient biodegradation. The replacement of TPS by more degradable straight-chain homologues was an urgent task for scientists in the 1950s. Economic circumstances have permitted the straight-chain or linear alkylbenzenesulfonates (LASs) to take the lead in the detergent industry in Europe, the Americas, and Asia.



LAS

LASs were found to possess interesting foaming characteristics, which are very significant for their application as detergents. However, LAS can be controlled by foam regulators. Also, the foam produced is stabilized by form stabilizers. The basic processes have been applied for the manufacture of LAS. The dehydrogenation of paraffins, followed by alkylation of benzene with a mixed olefin or paraffin feedstock, represents the most important route for the production of LAS. This process is catalyzed by hydrogen fluoride (HF).

 The partial chlorination of paraffins, followed by alkylation of the chloroparaffin or paraffin feedstock using aluminum chloride (AlCl3) as a catalyst, represents another important route toward LAS.

The third process implicates partial chlorination, but includes a dehydrochlorination to olefins prior to alkylation, with AlCl3 or HF as a catalyst.

 Universal Oil Products Company (UOP) offers processes, catalysts, adsorbents, and equipment for the production of linear alkylbenzenes (LAB) from kerosene or normal paraffins. The UOP LAB processes consist of a combination of several UOP processes, including the kerosene prefractionation and detergent alkylate. The LAB technology is the most economical technology available today, and over 70 percent of the world's LAB is produced using UOP technologies. Until 1995, alkylation used hydrofluoric (HF) acid as the catalyst. In 1995, the first commercial Detal process unit using a solid best catalyst alkylation process was commissioned. This revolutionary technology abolished the use of liquid acid in the plant, reducing capital investments, maintenance costs, and waste treatment.

 The continued worldwide demand for LAB creates new growth and development of new technologies to improve the process. LAS made from sulfonation of LAB is the most cost-effective surfactant available for use in detergent formulation. Environmentally proven LAS has the largest volume of existing surfactants.

**Sulfonation of LAB.** The sulfonation of alkylbenzenes leads to sulfonic acid tyre product, which is then neutralized with a base such as sodium hydroxide to produce sodium alkylbenzene sulfonate. The sulfonation reaction is highly exothermic and instantaneous. An efficient reactor heat removal system is used to prevent the decomposition of the resultant sulfonic acid. The sulfonation reaction takes place by using oleum (SO3H2SO4) or sulfur trioxide (SO3). 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 owing to sulfuric acid generation increased the problems related to oleum process.

**Sulfonation**

*******Alkylbenzene Alkylbenzene*

 *sulfonic acid*

**Neutralization**

****

 The gaseous air or SO3 sulfonation process leads to high yields of sulfonic acid (95 to 98 percent). This process comprises three major steps.

The sulfonation of alkylbenzene with air or SO3 forms the alkylbenzene sulfonic acid and anhydride. The latter is decomposed 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.

**Sulfonation**

****

 *anydrides*

**Hydration**

****

**Neutralization**



**Secondary alkanesulfonates (SAS).** The large-scale production of sodium

alkanesulfonates (SAS) began in the late 1960s.

 These sulfonates are still valued as anionic surfactants for consumer products. The secondary alkanesulfonates are known to have high solubility, fast wetting properties, chemical stability to alkali, acids, and strong oxidants such as chlorine.



R1, R2 = C11-17

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

**Sulfonated olefins**

*****Alkenesulfonates Hydroxyalkanesulfonates*

 The first commercial sulfonation of olefins with SO3 involved the use of an SO3-organo compound complex. Nowadays best results are obtained by sulfonating with uncomplexed diluted SO3 in a film reactor.

 The reaction between a-olefins and SO3 is not straightforward because of the formation of mixtures of alkene sulfonic acids, sultones, alkene disulfonic acids, and sultone sulfonic acids. Alkaline hydrolysis of sultone intermediates results in Ca 60 to 65 percent alkenesulfonates and Ca 35 to 40 percent hydroxyalkanesulfonates. The materials are sold as α-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.

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*(α-Sulfo fatty acid ester (MES)*

 The α-sulfo fatty acid esters represent another class of anionic surfactants. Methyl ester sulfonates (MES) are surfactants that are derived from a variety of methyl ester feed stocks such as coconut, palm kernel, palm stearin, beef tallow, and soy. Palmitic and stearic acid derivatives lead to good detergency because of 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.

**Alkyl ether sulfates (AES)**



R1 = H, R2 = C10-1 2  Fatty alcohol ether sulfates

 R1 + R2 = C11-13 Oxo alcohol ether sulfates

 Alkyl ether sulfates (AES) are anionic surfactants obtained by ethoxylation and subsequent salfation of alcohols derived from feedstock 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.

 The main components of the commercial AES are alkyl ether sulfates and alkyl sulfates. Other by-products such as unsulfated alcohols, alcohol ethoxylates, inorganic salts, and polyethylene oxide sulfates are also present in the commercial product.

Sodium *C12-14* n-alkyl diethylene glycol ether sulfates demonstrate increased detergency performance as the hardness increases. This is a result of the positive electrolyte effects attributable to calcium or magnesium ions.

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.

**AES** have been used in the United States and Japan because of their

critical micelle concentration, which is lower than LAS, resulting in

very satisfactory washing power. In Europe, the use of alcohol ether sulfates

has been largely restricted to specialty detergents.

***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, and the nonionic material can be one of the following 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

**Fatty alcohol and alkylphenol condensates**

R-O-CH2-CH2(OCH2CH2)n-1OCH2CH2OH

 *R = alkyl or phenyl*

 The alcohol ethoxylates and alkylphenol ethoxylates are produced by the reaction of alcohol with an excess of ethylene oxide. The reaction of one molecule of ethylene oxide is not sufficient to produce a water soluble detergent product.



*R = alkyl or phenyl; n = 16-50*

 The ether linkage is a strong bond, therefore, the material cannot be hydrolyzed and there is no possibility of ionization and subsequently it is not affected by metal ions. In practice, the optimum detergency is found in the range of 10 to 15 molecules of ethylene oxide per molecule of fatty alcohol. The source of the alcohol varies greatly, but natural, Ziegler and OXO alcohols of various molecular weights are being used.

 Another source of alcohols is the one used by Union Carbide. These alcohols are obtained from n-paraffins that are oxidized to secondary alcohols. The ethoxylation of these alcohols is done in two stages. The product containing 1 mol of ethylene oxide is produced first with an acid catalyst. After this stage the catalyst and the unreacted alcohol are removed and ethoxylation takes place as usual. The alkylphenols behave in the same manner as fatty alcohols. The nonyl (or octyl) phenol is widely used with 8 to 12 molecules of ethylene oxide. Nonylphenol is completely soluble in water at room temperature and exhibits excellent detergency. Dodecylphenol ethoxylate is used in certain agriculture emulsifiers and dinonylphenol as low or nonfoaming ingredients of household washing machine powders.

 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. Compared with all other materials that dissolve in water, these products show an apparent anomaly: their solutions are completely clear in the cold, but when heated they become turbid and, if the temperature is raised sufficiently, separation into two phases can take place. This is explained by the fact that at an elevated temperature the hydrates are destroyed.

The important use of polyester fibers in clothing and bedding increased the nonionic constituent in laundering as it was found that nonionics remove soil from these fibers better than the anionics.

**Fatty acid condensates.** Fatty acid condensates are another type of nonionic

surfactants that are prepared by the reaction of fatty acids with

ethylene oxide.



 These condensates can also be produced by the esterification of a fatty acid with a polyethylene glycol, HOCH2(CH2CH2)nCH2OH. Esters are materials that have some disadvantages compared to other nonionic detergents. In general, nonionic detergents are not affected by metallic ions, acids, or alkalis. However, the fatty acid condensates of ethylene oxide are readily hydrolyzed by acids or alkaline solutions to the corresponding fatty acid and polyethylene glycol. In strong alkaline solutions the esters are no better than the soap of the corresponding fatty acid, and in strong acid solution they are much affected. However, they do perform well as components of household detergent powders.

**Condensates of ethylene oxide with an amine.** The condensation of alkylamines with ethylene oxide leads to secondary or tertiary substituted

amines depending on the concentration of ethylene oxide.



R = C11-17

 This class of nonionic surfactants has not been used largely in cleaning detergents. However, it is noteworthy that these materials in acidic solution can exhibit cationic characteristics, whereas, in neutral or alkaline solution, they are nonionic.

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 nondetergent materials are converted into detergents by condensation with ethylene oxide.



Fatty acids alkanolamides find only a little application in laundry detergents. They are used as foam booting, that is, adding desired stability to the foam produced by detergents. Small amounts of these materials as cosurfactants are capable of enhancing the soil removal properties of the classical detergent components at low washing temperatures.

***Cationic surfactants.*** Long chain cationic surfactants such as disteral

diamethyl ammonium chloride (DSDMAC) exhibit extraordinarily high sorption power with respect to a wide variety of surfaces. These surfactants are very strongly absorbed by the surface of natural fibers, such as cotton, wool, and linen.

 Cationic surfactants are mainly employed for the purpose of achieving certain special effects, which include applications in rinse-cycle fabric softeners, antistatic agents, and microbicides, Nonionic surfactants are more tolerant of the presence of cationic surfactants than anionic surfactants.

Mixtures of the two are sometimes used in the production of specialty detergents that are powerful antistatic products.

 The cationic detergents invariably contain amino compounds. The most widely used would be the quaternary ammonium salts, such as cetyltrimethylammonium chloride, a well-known germicide and distearyldimethylammonium chloride (DSDMAC), known as fabric softener

for cotton diapers and as a laundry rinse-cycle fabric softener.



*DSDMAC*

Imidazolinium salts, such as l-alkylamidoethyl-2-alkyl-3- ethylimidazolinium methylsulfate have been used as rinse-cycle softening

agents, but in less significance compared to DSDMAC.



 *DSDMAC*

 The compounds based on alkyldimethylbenzylammonium chloride type have been used as laundry disinfecting agents. They show limited fabric softening character.



 Esterquats represent a new generation of fabric softeners that have been developed in the 1980s or 1990s and have replaced DSDMAC.

****

*N-Methyl-N,N-bis[2-(C16.18-acyloxy)ethyl]-N-(2-hydroethyl) ammonium methosulfate.*

*(Esterquat) EQ*

***Amphoteric surfactants.*** These compounds have the characteristics of both anionic detergents and cationic fabric softeners. They tend to work

best at neutral pH, and are found in shampoos, skin cleaners, and carpet

shampoos. They are very stable in strong acidic conditions and are favorably used with hydrofluoric acid. For example, compounds of alkylbetain or alkylsulfobetaine type possess both anionic and cationic groups in the same molecule even in aqueous solution. These surfactants are rarely employed in laundry detergents because of their high costs.



 *Alkylbetaines*

 *Alkylsulfobetaines*

***Gemini surfactants:***

In recent years novel forms of surfactants consisting of two conventional surfactants joined chemically at the head group have generated much interest. This new class of amphiphilic molecules called gemini or dimeric surfactant. Gemini surfactants are new family of surfactant molecules possessing more than one hydrophobic tail and hydrophilic head group. These surfactants usually have better surface-active properties and lower critical micelle concentrations than corresponding conventional surfactants of equal chain length (114). Gemini surfactants are also classified according to the hydrophilic head groups according to anionic, cationic, nonionic and amphoteric gemini surfactants. They are used as promising surfactants in industrial detergency and have shown efficiency in skin care, antibacterial property.

In general, the hydrophobic part of the surface active agents is usually a long chain hydrocarbon, whatever its one or more hydrophobic tail and the water soluble grouping can be sulphate, sulphonate, carboxylate, and quaternary ammonium salt and hydroxyl groups. In this work will present the necessary knowledge on the concerned subject which is the nonionic, anionic and gemini (nonionic, anionic) surfactant.

The gemini surfactant consists of two conventional surfactant molecules chemically bonded together by a spacer. The two terminal hydrocarbon tails can be short or long; the two polar head groups can be ionic, zwitterionic or nonionic as with conventional surfactants. The spacer can be short or long, flexible or rigid. Geminis are considerably more surface-active than conventional surfactants. A schematic representation of gemini is shown below.



All gemini surfactants possess at least two hydrophobic chains and two ionic or polar groups, and a great deal of variation exists in the nature of spacers.

***Inorganic builders:***

 The use of the detergents mentioned so far as end products, would be costly, and so water is used to dilute these ingredients into the more consumer useable form. Sodium sulphate that is used as a diluting agent in powder detergents is cheap and user friendly.

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 by eliminating calcium and magnesium ions that arise from the water and soil. Builders should also be compatible with other formulation ingredients and detergent additives.

Consumer safety and environmental acceptability are important characteristics of builders.

The inorganic constituents fall into the five following groups:

1. Phosphates
2. Silicates
3. Carbonates
4. Zeolites
5. Bleach-active compounds

**Phosphates.** There are two classes of phosphates—orthophosphates and complex phosphates. The orthophosphates used in the detergent industry are trisodium phosphate in hydrated and anhydrous forms (Na3PO4 and Na3PO4 • 12H2O), disodium phosphate, another form of orthophosphates in anhydrous form (Na2HPO4), and crystalline Na2HPO4 • 12H2O In the past, trisodium phosphate was used as a soap builder, but it is seldom used in detergent formulations nowadays because phosphates cause eutrophication of water. It has the property of softening water by precipitating metallic ions, as a gelatinous precipitate.

 Trisodium phosphate can cocrystallize with sodium hypochlorite to produce the material called commercially *chlorinated trisodium phosphate* that has a formula approximating to (Na3PO4 • 12H2O) NaOCl. This material is added to the cleaning detergents that require the bleaching and sterilizing effect of NaOCl together with the high alkalinity and water-softening of trisodium phosphate.

 The detergent industry has introduced another form of phosphate

the so-called *condensed phosphates.* These materials have a higher proportion of P2O5 and a lower proportion of Na2O in the molecule. These phosphates have a lower alkalinity than trisodium phosphate. The commonly used complex phosphates are:

* Tetrasodium pyrophosphate, Na4P2O7 (TSPP)
* Sodium tripolyphosphate, Na5P3O10 (STP)
* Sodium tetraphosphate, Na6P4O13
* Sodium hexametaphosphate, (NaPO3)6

Both sodium tetraphosphate and sodium hexametaphosphate are hygroscopic and are unsuitable for formulation into dry powders.

 Tetrasodium pyrophosphate (TSPP) is now used for specialized purposes only, but its potassium analogue is used in liquids. The combination of TSPP and sodium carbonate was more effective than either ingredient used separately.

 Sodium tripolyphosphate (STP) was commercially available in the mid-1940s and had replaced TSPP because of its superior detergent processing, solubility, and hardness ion-sequestering characteristics.

 Sequestration is defined as the reaction of a cation with an anion to form a soluble complex. The sequestration of Ca2+ and Mg2+ ions leads to softened water and is the most important function of any detergent builder.

STP is the major builder ingredient in heavy duty laundry detergents, automatic dishwashing compounds, and industrial and institutional cleaners.

**Silicates.** The addition of sodium and potassium silicates to synthetic detergent has proved very beneficial. They have in solid or solution form important characteristics such as emulsification, buffering, deflocculation, and antiredeposition ability.

Sodium silicate is prepared by the fusion of sand that contains a high amount of silica with soda ash according to the following equation:

 Na2CO3 + SiO2 Na2SiO3 + CO2

 The proportion 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 as Na2Or SiO2.

Silicates are produced in liquid, crystalline, or powdered form. The ratio of Na2O: SiO2 is usually selected to meet the product requirement and its application. The sodium metasilicate (Na2O/SiO2 = 1/1) is used in dry blending. The liquid silicates having Na2O : SiO2 ratio of 1:2 or higher are used in laundry and automatic dishwashing applications.

 Soluble glass and soluble powders are the two forms of detergents that are prepared in the ratios of Na2O: SiO2 of 1:2 and 1:33, respectively. A ratio of 1:2.4 is commonly used in making detergent powders and is produced by blending the neutral soluble powder and the alkaline soluble glasses or by adding caustic soda to neutral glass.

A *wet method* for the production of soluble detergents of up to 40 percent disilicate by the reaction of fine sand and caustic soda (3 to 50 percent) is as follows:

 2 SiO2 + 2NaOH Na2O.2SiO2 + H2O

Potassium silicate, available commercially in colloidal ratios, is used nowadays for specialized liquid detergents. It is available in weight ratios of 1:1.5 to 1:2.5. Silicates soften water by the formation of precipitates that can be easily rinsed away. Silicates are corrosion inhibitors of stainless steel and aluminum that can be caused by synthetic detergents and complex phosphates.

**Carbonates.** Carbonates are being used because of the restriction in the use of phosphates in certain areas of the United States. Sodium carbonate (Na2CO3) or a combination Of Na2CO3 and zeolite has replaced sodium tripolyphosphate (STP) as a builder in granular laundry products.

Sodium carbonate provides high alkalinity because only sodium hydroxide is high on a weight per volume basis. Na2CO3 softens water by the precipitation of calcium and magnesium carbonates, provided the pH of the solution is greater than 9.

 Synthetic soda is of superior quality compared to mined natural soda ash. 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. 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 countercurrent to the solution of sodium chloride (known as brine) saturated with ammonia. Sodium bicarbonate, which is almost insoluble in solution and precipitates, is separated and roasted to sodium carbonate.



 The carbon dioxide released from the conversion of the bicarbonate to carbonate is reused in the absorption tower in addition to CO2 obtained from the burning of the lime.

**Zeolites.** Silicon is the second most abundant element in the earth's crust after oxygen. Silicon, which is never found free, is invariably associated with oxygen (silica, quartz) and with metallic oxides.

Zeolites, also known as molecular sieves, are important alternative builders for powdered laundry detergents and replaced phosphate salts that were banned for legislative reasons. Zeolites exist in the form of calcium, sodium, magnesium, potassium, and barium salts.

 The most widely used form of zeolites is type A—which are hydrated sodium aluminum silicates of empirical formula Na2OAl2O3X SiO2yH2O.

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



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

**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 (H2O2) is converted by alkaline medium into hydrogen peroxide anion as active intermediate .



HOO oxidizes bleachable soils and stains. The most used source of hydrogen peroxide is sodium perborate, known as sodium peroxoborate tetrahydrate, NaBO3-4H2O, that in crystalline form contains the peroxodiborate anion.



*Peroxodiborate anion*

Peroxodiborate is hydrolyzed in water to form hydrogen peroxide.



In solution, sodium perborate monohydrate is similar in action to 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*

 Sodium perborate can be used as the universal laundry bleach and has been used in Europe for the past 50 years.

Sodium perborate is a stable material when mixed with other dry ingredients.

 However, the presence of traces of water and certain heavy metals will catalyze the decomposition of the perborate. Therefore, 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. The use of liquid hypochlorite has gained importance in many

countries where laundry habits, such as cold water washing, made the sodium perborate less effective. Hypochlorite reacts with an alkaline to produce hypochlorite anions.



 The aqueous solution of sodium hypochlorite (NaOCl) is used as a source of active chlorine that can be used in either the wash or the rinse cycle.

 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. Also, a high dosage of NaOCl may cause significant damage to laundry and colors. In addition, sodium hypochlorite solutions have limited storage stability especially in the presence of 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.

 Studies showed that chlorine bleach is used predominantly in the Mediterranean countries whereas peroxide bleach use dominates in Europe.

However, hypochlorite bleach in either the wash or the rinse cycle is still

a preferred bleaching agent in a large part of the world.

***Sundry organic builders:***

**Antiredeposition agents.** The detergent has an important characteristic that allows the removal of the soil from textile fibers during the washing process. Furthermore, the redeposition of displaced soil can be prevented by the addition of special antiredeposition agents. The role of these agents is to be adsorbed on the surface of the textile, there by creating a protective layer that strictly inhibits redeposition of the removed soil.

 The carboxymethyl cellulose (CMC) derivatives and carboxymethyl starch (CMS) are effective antiredeposition agents that are cellulose-containing fibers such as cotton and blends of cotton and synthetic fibers. However, CMC has virtually no effect on pure synthetic fibers.

The nonionic cellulose ethers have been found suitable for use with synthetic fibers.



Nonionic cellulose ethers

 The modern detergents are provided with mixtures of anionic and nonionic polymers (e.g., carboxymethylcellulose-methylcellulose) and also with polymers from polyethylene glycol and terephthalic acid.

**Thickening agents.** Carboxymethyl cellulose (CMC) is also used as a thickening agent in addition to its characteristic as a soil antiredeposition agent. Modified nonionic celluloses, methyl cellulose, hydroxyethyl cellulose methylhydroxy propyl cellulose are being used as thickening agents. All these modified celluloses are soluble in cold water and insoluble

in hot water and most organic solvents.

**Optical brighteners.** Optical brighteners are an integral part of laundry products, whether laundry powders or laundry liquids. They are organic compounds capable of converting a portion of the invisible ultraviolet light into longer wavelength visible blue light. They are dyestuffs, which are absorbed by textile fibers, but are not easily rinsed off. The reflection of the blue light makes the clothes look brighter than they actually are.

Optical brighteners are usually derivatives of coumarin, stilbene, distyrylbipheny, and bis(benzoxazole). Examples of chemical structures of

some important optical brighteners are given:

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 The optical brighteners binding occur, in the case of cotton and chlorineresistant materials, through the formation of hydrogen bond to the

fibers. Whitening effects achieved with polyamide brighteners are largely because of the diffusing power of whitening agent molecules present at the fiber surfaces.

**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 and their use has increased in the last few years.



*Sodium salt of EDTA*

The sodium salt of EDTA reacts with calcium ions to give a complex in which Ca is bidentated to nitrogen atoms of EDTA. Two sodium ions are released from the reaction

.

There are three main groups of the chelating agents.

Aminocarboxylic acids:

a. Ethylene diamine tetraacetic acid

b. Nintrilo triacetic acid



c. Diethylene triamine pentacetic acid (DTPA)



 NTA sequestrates more calcium ions per unit weight than EDTA because of its lowest molecular weight. However, 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.

**Enzymes.** Enzymes are defined as organic catalysts that promote specific

chemical reactions in the body upon which all life depends.

Naturally occurring enzymes are related to proteins and are largely composed of amino acids. The most significant development in the detergent industry in recent years is the introduction of enzyme additives.

Enzymes catalyze destruction and removal of stubborn proteinaceous stains and specific types of soils by detergent. Chocolate and starch-based food stains as well as greasy stains that are difficult to remove in low-temperature washing, are eliminated by detergentenzymes.

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.

 The mechanism of the enzymes is to cleave the protein into smaller peptide fraction that is soluble in water. Even if the conversion is not complete, the protein is degraded into a product that can be easily removed by the detergent. The activity of enzymes depends on temperature and pH value. At a certain temperature of the wash bath (mostly above 55°C) the activity of enzymes decreases. The proper choice of the type of enzyme and the appropriate formulation has led to detergentgrade enzymes that are not significantly damaged during the storage or in the wash liquor.

***Manufacturing of detergents:***

**Production of alkylbenzene sulfonates.** The alkylbenzene sulfonates, used as liquid surfactants in making the detergent slurry, 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 used:

1. Sulfonation
2. Digestion
3. Dilution
4. Phase separation
5. Neutralization

The sulfonation stage includes mixing of alkylate with oleum that leads to an exothermic reaction. The removal of heat is done by reactor jacketing. The key parameters that control the reaction of sulfonation are temperature, acid strength, reaction time, and oleum-to-alkylate ratio. The reaction was completed at the digestion stage where the product from the sulfonation zone is aged for 15 to 30 min. The mixture of sulfonic acid and sulfuric acid is diluted with water to quench the reaction.

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 percent sulfonic acid and 6 to 10 percent sulfuric acid.

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.

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



A posthydrolysis step includes bleaching to remove color before neutralization. The 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:



**Spray-drying process.** The first step in the spray-drying process includes

the preparation of slurry of thermally stable and chemically compatible ingredients of the detergent. The slurry, the builder, and other additives are mixed in a crutcher. The blended slurry is transferred and held in a stirred storage vessel for continuous pumping to a spray dryer. The slurry is sprayed through nozzles into the tower at pressures of 4.1 to 6.9 kilopascals (kPa) in single-fluid nozzles and at Caustic pressures of 340 to 690 kPa in 2-fluid nozzles. Steam or air is used as the atomizing fluid in the 2-fluid nozzles. The slurry is sprayed at high pressure into a vertical drying tower having a steam of hot air at 315 to 4000C. The dried powder flows off the tower at a temperature of 90 to 1000C. An airlift is used for cooling to prevent lumping. The most common towers designed for detergent production are countercurrent. The slurry is introduced at the top of the tower and heated air is introduced at the bottom. The detergent granules are conveyed mechanically or by air from the tower to a mixer to incorporate additional ingredients, such as a perfume, and finally to packaging and storage.

***Environmental Aspects:***

**Emissions and controls:**

The exhaust air from detergent towers contains two types of contaminants:

1. Fine detergent particles
2. Organics vaporized in the higher zone of the tower

Dust emissions are generated at scale hoppers, mixers, and crutchers during the batching and mixing of fine dry ingredients to form slurry. Conveying, mixing, and packaging of detergent granules can also cause dust emissions. For this process, fabric filters are used, not only to reduce or eliminate dust emission, but also to recover raw materials.

 Dry cyclones are the primary collection equipment used to capture the detergent dust in the spray dryer exhaust and recycle it back to the crutcher. The dry cyclones can remove up to 90 percent by weight of the detergent product fines from the exhaust air. Fabric filters have been used after cyclones but have limited applicability, especially on efficient spray dryers, because of condensing water and organic aerosols binding the fabric filters.

 In addition to particulate emissions, volatile organic compounds (VOCs)

may also be emitted when the slurry contains organic materials with low

vapor pressures. The surfactants included in the slurry represent the origin of the VOCs. The vaporized organic materials condense in the tower exhaust air stream into droplets or particles. Paraffin alcohols and amides in the exhaust stream can result in highly visible plume that persists after the condensed water vapor plume has dissipated. Some of the VOCs identified in the organic emissions are: hexane, methyl alcohol, 1,1,1-trichloroethane, perchloroethylene, benzene, and toluene.

A method for controlling visible emissions would be to remove by substitution the offending organic compounds from the slurry.

**Wastewater and the environment:**

Wastewater is the by-product that has the potential for causing a number of undesirable effects in sewage treatment plants in the environment.

In fact, the clean water, which was brought into the process, is later released to the sewage system in the form of contaminated wastewater containing additional energy, 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 variations in laundry soil levels affect the concentration and the composition of laundry wastewater considerably. Laundry wastewater is generally a heavy source of contamination; therefore, it should not be returned to receiving waters in untreated form.

 Fortunately, the laundry wastewater is mixed with general water in the public sewage and in the sewage treatment plants. As a result of dilution,

both temperature and the high pH value of wastewater are considerably decreased. In addition, if laundry wastewater was treated separately, major problems would be encountered in dealing with the load of organic pollutants introduced by household and commercial laundry operations.

**Biodegradation:**

 The removal of organic compounds from sewages, surface waters, and soils can be done by the biodegradation process. This is a stepwise

process that is mainly affected by aerobic microorganisms.

The first step involves the transformation of the sodium sulfonate to a first degradation product (primary degradation). The subsequent degradation to the second, third, and so on, intermediate steps takes place with the decreasing of molecular mass and structural complexity. The ultimate biodegradation represents the total decomposition of the total organic structure into carbon dioxide, water, inorganic salts, and at the same time, partly into bacterial biomass.

Since 1973, the regulation in Europe requires a minimum of 80 percent biodegradability for the anionic and nonionic surfactants in a package detergent. Anionic surfactants are determined as *methylene blue active substance* (MBAS), that is, materials forming a chloroform soluble complex with cationic dye methylene blue. Nonionic surfactants are defined as *bismuth active substance* (BiAS), that is, 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. 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).



*Biodegradation pathway of fatty alcohol sulfates.*

Primary and ultimate biodegradability of test substances is normally evaluated by applying standardized and internationally used (OECD, ISO, EU) test procedures.

***Economic Aspects:***

 The role of detergents represents an important factor in the worldwide economy. The increase of the standards of living in the last 40 years was accompanied with a tremendous growth in the world consumption of the detergents. The absolute quantity has increased from approximately

10 x 106 t in the late 1950s to 21.5 x 106 t worldwide in 1988. For example, the total consumption of laundry, dishwashing, and cleaning detergents in Europe was 6.4 x 1061 in 1991. The quantity has increased to 6.8 x 106 t in 1999.

The two largest end uses, which are household products and industrial processing aids, together account for 86 percent of the total production of surfactants. Household products include heavy-duty powder and liquid detergents, light-duty liquids, and fabric softeners.

Industrial processing materials are covered by the following major end uses: plastics and elastomers, textiles, agricultural chemicals, leather and paper chemicals, and other miscellaneous uses.

The anionic surfactants, such as linear alkyl-benzene surfactants, represent the largest consumed type of surfactants worldwide followed by alcohol ethoxylate, and alkylphenol ethoxylates .

For legal restrictions, the use of sodium triphosphate as a builder has sharply decreased mainly in the United States, Europe, and Japan. The application of sodium triphosphate in detergents dropped by more than 50 percent within 10 years in these countries.

Zeolite A, the most important phosphate substitute, became the highly demanded builder worldwide. The worldwide production of zeolite A increased in western Europe in the 1990s. Detergent builder zeolites represent the largest application field for zeolite. Almost 90 percent of zeolites produced worldwide (or ~ 215,000 tons/year) in 2003 were used for

detergents. Meanwhile, production capacities for detergent-grade zeolites

have largely surpassed the demand.

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