REVIEW

Laundry Detergents: An Overview

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Abstract: Nowadays laundry detergents are becoming increasingly popular as they can be metered automatically into the washing machine, impart softness, antistaticness, resiliency to fabrics, mild to eyes and skins and shows good dispersibility in water. Because it is consumed when it is used, the sale of laundry detergent is a rather large business. There are many different kinds or brands of laundry detergent sold, many of them claiming some special qualities as selling points. A Laundry detergent composition is a formulated mixture of raw materials that can be classified into different types based on their properties and function in the final product. The different classes of raw materials are surfactants, builders, bleaching agents, enzymes, and minors which remove dirt, stain, and soil from surfaces or textiles gave them pleasant feel and odour. The physico-chemical properties of surfactants make them suitable for laundry purposes. Laundry detergent has traditionally been a powdered or granular solid, but the use of liquid laundry detergents has gradually increased over the years, and these days use of liquid detergent equals or even exceeds use of solid detergent. This review paper describes the history, composition, types, mechanism, consumption, environmental effects and consumption of laundry detergents.

Key words: laundry detergents, surfactants, builders, anionic, cationic, amphoteric, biodegradation

1 INTRODUCTION

Laundry detergent is the product that contains a surfactant and other ingredients to clean fabrics in the wash. Laundry detergent is a substance which is a type of surfactant¹⁾ that is added, when one is washing laundry to help get the laundry cleaner. Laundry detergent has traditionally been a powdered or granular solid, but the use of liquid laundry detergents has gradually increased over the years, and nowadays uses of liquid detergent equals or even exceeds the use of solid detergent. Some brands also manufacture laundry soap in tablets and dissolvable packets, so as to eliminate the need to measure soap for each load of laundry.

There are two kinds of laundry detergents with different characteristics:

1 Phosphate detergents: These types of detergent contain phosphates and are highly caustic.

2 Surfactant detergents: These types of detergents contain surfactants are very toxic in nature.

The differences are that surfactant detergents used to enhance the wetting, foaming, dispersing and emulsifying

properties of detergents. Phosphate detergents are used in laundry detergent to soften hard water and help to suspend dirt.

A detergent contains one or more surfactants formulated with other components to enhance detergency, where removal of soils is difficult due to the strong attraction of soil to the fabric, poor penetration and adsorption of surfactant molecules onto the soil and fabric interface.

The term 'detergency' is used to describe the process of cleaning by surface active agent. Detergency can be defined as removal of unwanted substance (soil) from a solid surface brought into contact with a liquid²⁾. The word 'soil' in connection with textile surfaces most frequently denotes the unwanted accumulation of oily and/or particulate materials on the surfaces or interior of fibrous structure.

2 HISTORY OF LAUNDRY DETERGENTS

The oldest literary reference to soap is a Sumerian tablet

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from 2200 BC giving a soap formula consisting of water, alkali and cassia oil, but it is not known exactly when it was discovered. The industrial production of soap (boiling fats and oils with an alkali) remained basically the same until 1916, when the first synthetic detergent was developed in Germany in response to a World War I due to the shortage of fats for making soap³. Soaps have an advantage over inbuilt synthetic surfactant systems regarding soil redeposition and whiteness maintenance, it acts as its own water softener and therefore when there is enough soap to form suds and wash, the water has already been softened⁴. The need of anti-redeposition agents began with the introduction of multi-component laundry detergents based on synthetic surfactants⁵ although synthetic surfactants help to prevent the soil redeposition to some extent, this effect is not very pronounced, making a whiteness retention aid a necessity.

Sixty years ago⁶, it was discovered that chemical technology could change the molecular structure of water with the introduction of the very first laundry detergent. It was understood that lowering of surface tension is needed for better cleaning and this was achieved by using chemical surfactants.

Prior to world war first, laundry products consisted principally of sodium and potassium neutralized fatty acid soaps. The first synthetic detergents were produced in Germany during World War II as replacement for the then-scarce animal fats traditionally used in the production of soaps, during the shortages. These were called branched-chain alkyl benzene sulfonates and short chain alkyl naphthalene sulfonates. Like soap, they could take hard minerals out of water, leaving it soft.

Introduction of long chain alkyl aryl sulfonates as detergents in the 1930s and by 1945 had become the main surfactant component of synthetic laundry detergents. The first built synthetic detergent, using sodium diphosphate as a builder was introduced in the United States in 1947.

Straight-chain detergents didn't work in hard water and phosphates were added to detergents to soften the water, but as phosphates were excellent fertilizer for algae in rivers and oceans, resulted in algae blooms that deplete the oxygen in the water, killing fish and then phosphates were replaced with other water softeners such as sodium carbonate and EDTA.

In the mid 1960s concern arose over the environmental fate of complex phosphates due to their implication in eutrophication of waterways. Since then, the detergent industry has devoted considerable energy to finding cost effective replacement. The surfactants used in early synthetic detergents were prepared by reacting benzene with propylene tetramer to form the alkyl aryl group, which was then sulfonated. These materials are so called hard ABSs (alkyl benzene sulphonates), were highly branched and non-biodegradable. Overtime they accumulated in the environ-

ment to such an extent that foaming resulted in some sewage treatment plants and waterways. In 1965, the U. S. detergent industry voluntarily withdrew hard ABSs from the market, replacing them with biodegradable linear chain analogs. In the mid in 1970s, the introduction of ion exchange materials and zeolites as detergents builders led to a gradual movement away from phosphate technology.

At the time of conversion to compacts the most widely used surfactants in synthetic powder detergents were the anionic, linear alkyl aryl sulfonates (LASs), and long chain fatty alcohol sulfates (ASs), to a lesser extent, long chain fatty acids, and the nonionic alkyl ethoxylates. With the recent change in formulations and manufacturing processes precipitated by a transition to compact detergents, the major U. S. manufacturers took the opportunity to formulate out of phosphate together.

Importantly this was achieved without compromising performance or consumer value. Today the conversion of the U.S. detergent market to nil phosphate formula is virtually complete, 32% of European powders are zeolite based, Canada is about 50% converted whereas Latin America and many of the Pacific region geographies remain largely phosphates.

However, the move to nil phosphate builder system increased the overall complexity of powdered detergents. In addition to binding hardness ions, phosphate provides a number of other functions that are critical to efficient soil removal and cleaning. These include soil peptization or breakup, soil dispersion, suspension and pH buffering. Removing phosphate from detergent formulas required manufacturers to identify other actives that could fulfill its multifunctional role. Today nil phosphate powders contain zeolites and/or layer silicates for hardness control, polycarboxylates polymers for soil suspension, citric acid for soil peptization and dispersion as well as pH control and carbonate for calcium control and buffering.

3 COMPOSITION OF LAUNDRY DETERGENTS

3.1 Surfactants⁷

The term surface-active agent represents a heterogeneous and long-chain molecule containing both hydrophilic and hydrophobic moieties. By varying the hydrophobic and hydrophilic part of a surfactant, a number of properties may be adjusted, e.g. wetting ability, emulsifying ability, dispersive ability, foaming ability and foaming control ability.

One of the characteristic features of the surfactant is their tendency to adsorb at the surface/interfaces mostly in an oriented fashion. The orientation of the surfactant molecules at the surface/interfaces, which in turn determines how the surface/interface will be affected by the adsorption of surfactant, either it will become more

hydrophilic or hydrophobic. These properties provide information on the type and the mechanism of interactions involving the surfactant molecules at the surface/interface and its efficiency as a surface-active agent.

The surfactant or surface active agent is perhaps the most important ingredient present in every laundry detergent formulation because:-

The surfactant:

- 1) Improves the wetting ability of water
- 2) Loosens and removes soil with the aid of wash action
- 3) Emulsifies, solubilizes or suspends soils in the wash solution

Laundry detergents may contain more than one kind of surfactants. These surfactants differ in their ability to remove certain types of soil, in their effectiveness on different fabrics and in their response to water hardness. Surfactants are classified by their ionic (electrical charge) properties in the water. The following major categories are used in laundry products:-

3.1.1 Cationic surfactants

Cationic surfactants are compounds with a positively charged nitrogen atom and at least one hydrophobic, long chain substituent in the molecule. The most common cationic surfactants are the quaternary ammonium compounds^{8,9)} with the general formula $R'R''R'''R''''N^+X^-$, where X^- is usually chloride ion and R represents alkyl groups. A common class of cationic surfactants is the alkyl trimethyl ammonium chloride, where R contains 8-18 C atoms, e.g. DDTMAC (dodecyl trimethyl ammonium chloride), $C_{12}H_{25}(CH_3)_3NCl$. Another widely used cationic surfactant class is that containing two long-chain alkyl groups, i.e. DADMAC (dialkyl dimethyl ammonium chloride), with the alkyl groups having a chain length of 8-18 C atoms. These dialkyl surfactants are less soluble in water than the monoalkyl quaternary compounds, but they are commonly used in detergents as fabric softeners. A widely used cationic surfactant is alkyl dimethyl benzyl ammonium chloride (sometimes referred to as benzalkonium chloride and widely used as bactericide)

3.1.2 Anionic surfactants

Anionic surfactants, such as soap, often have a sodium, potassium, or ammonium group, as in sodium stearate. These are the most widely used class of surfactants^{10,11)} due to their relatively low cost of manufacture and they are used in practically every type of detergent. For optimum detergency the hydrophobic chain is a group with a chain length in the region of 12-16 carbon atoms. Linear chains are preferred since they are more effective and more degradable than branched ones. The most commonly used hydrophilic groups are carboxylates, sulphates, sulphonates and phosphates. A general formula may be ascribed to anionic surfactants as follows:

- Carboxylates: $C_nH_{2n+1}COO^- X^+$

- Sulphates: $C_nH_{2n+1}OSO_3^- X^+$
- Phosphates: $C_nH_{2n+1}OPO(OH)O^- X^+$
- Sulphonates: $C_nH_{2n+1}SO_3^- X^+$

In water, their hydrophilic portion carries a negative charge, which can react in the wash water with the positively charged water hardness (calcium and magnesium) ions that tend to deactivate them. These surfactants are particularly effective at oily soil cleaning and clay soil suspension. But, to different degrees (depending on their chemical structure), they need help from other ingredients to prevent partial inactivation by water hardness ions.

3.1.3 Nonionic surfactants:

Nonionic surfactants do not ionize in solution. Lack of charge enables them to avoid water hardness deactivation. They are especially good at removing oily type soils by solubilization and emulsification. Nonionic surfactants are frequently used in some low sudsing detergent powders and in general purpose liquid detergents. Nonionics may be mixed with anionics in some powder or liquid detergents.

The most common nonionic surfactants are those based on ethylene oxide, referred to as ethoxylated surfactants¹²⁻¹⁴⁾. Several classes can be distinguished: alcohol ethoxylates, alkyl phenol ethoxylates, fatty acid ethoxylates, monoalkanolamide ethoxylates, sorbitan ester ethoxylates, fatty amine ethoxylates and ethylene oxide-propylene oxide copolymers (sometimes referred to as polymeric surfactants).

Another important class of nonionics is the polyhydroxy products such as glycol esters, glycerol (and polyglycerol) esters, glucosides (and polyglucosides) and sucrose esters. Amine oxides and sulfonyl surfactants represent nonionics with a small head group.

3.1.4 Amphoteric surfactants¹⁵⁾

These are surfactants containing both cationic and anionic groups. The most common amphoteric surfactants are the N-alkyl betaines, which are derivatives of trimethyl glycine ($CH_3)_3NCH_2COOH$ (described as betaine). An example of betaine surfactant is laurylamidopropyldimethylbetaine $C_{12}H_{25}CON(CH_3)_2CH_2COOH$. These alkyl betaines are sometimes described as alkyl dimethyl glycinate. The main characteristic of amphoteric surfactants is their dependence on the pH of the solution in which they are dissolved. In acid pH solutions, the molecule acquires a positive charge and behaves like a cationic surfactant, whereas in alkaline pH solutions they become negatively charged and behave like an anionic one. A specific pH can be defined at which both ionic groups show equal ionization (the isoelectric point of the molecule) (described by Scheme 1). Amphoteric surfactants are sometimes

Scheme 1

referred to as zwitterionic molecules.

They are soluble in water, but the solubility shows a minimum at the isoelectric point. Amphoteric surfactants show excellent compatibility with other surfactants, forming mixed micelles. They are chemically stable both in acids and alkalis. The surface activity of amphoteric surfactants varies widely and depends on the distance between the charged groups, showing maximum activity at the isoelectric point.

Another class of amphoteric is the N-alkyl amino propionates having the structure $R-NHCH_2CH_2COOH$. The NH group can react with another acid molecule (e.g. acrylic) to form an amino dipropionate $R-N(CH_2CH_2COOH)_2$. Alkyl imidazoline-based products can also be produced by reacting alkyl imidazoline with a chloroacid. However, the imidazoline ring breaks down during the formation of the amphoteric. The change in charge with pH of amphoteric surfactants affects their properties, such as wetting, detergency, foaming, etc. At the isoelectric point (i.e.p.), the properties of amphoteric surfactants resemble those of nonionics very closely. Below and above the i.e.p. the properties shift towards those of cationic and anionic surfactants, respectively.

3.2 Builders^{16,17)}

Builders are the second most important ingredient of detergent because they enhance or "build" the cleaning efficiency of the surfactant. Builders are designed to do the following:

1. Soften water by binding the hard water minerals
2. Prevent water hardness ions
3. Help surfactants concentrate on removing soil from fabrics
4. Increase the efficiency of the surfactant
5. Provide a desirable level of alkaline to aid in the cleaning process
6. Disperse and suspend soils so they cannot redeposit themselves on the clothing.

Builders are used in general purpose laundry powders and liquids but not in light duty detergents (powders or liquids). Most general purpose liquids contain builders such as citrate, but some are unbuilt. The unbuilt liquids use surfactants which are less hardness sensitive, instead of including a builder to minimize interactions with water hardness minerals. The general purpose liquids should not be confused with light duty liquids, which are designed primarily for washing dishes by hand. Builders soften water by sequestration, precipitation or ion exchange.

3.2.1 Sequestering builders

Sequestering builders, such as polyphosphates, inactivate water hardness mineral ions and hold them tightly in solution. Another builder, citrate, while not as strong a sequestrant as phosphate, contributes to detergency performance in some types of heavy duty liquid detergents.

3.2.2 Precipitating builders

A precipitating builder, such as sodium carbonate or sodium silicate, removes water hardness ions by a nonreversible reaction, forming an insoluble substance or precipitant. They are especially effective on calcium ions.

3.3 Antiredeposition agents¹⁸⁾

Anti-redeposition agents' aid in preventing loosened soil from redepositing on cleaned fabrics. Carboxymethyl cellulose (cmc) is the most popular antiredeposition agent which is derived from natural cellulose, but is very soluble in water, sodium polyacrylate, polyethylene glycol polymers are also sometimes used to prevent dirt from redepositing on the clothes. These anionic polymers adsorb on the soils and substrates and give them negative charges. The steric effect of nonionic polymers on the stability of dispersions is also utilized for antiredeposition.

3.4 Zeolite¹⁹⁾

Zeolite is a sequestering agent for multivalent metal ions. Calcium and/or magnesium ions in hard tap water form a salt with anionic surfactants whose krafft point is much higher than ambient temperature. The surfactant salt of high krafft point precipitates out of the cleansing solutions, thus losing its surface active properties. Zeolite sequesters the multivalent ions and prevents the anionic surfactants from precipitating out of the solutions.

3.5 Alkaline agents¹⁷⁾

An alkaline condition in a cleansing solution is useful to give negative charges to the soils and the substrates. Sodium carbonate and sodium silicates are typical examples of such alkaline agents. Oily soil containing fatty acids can be spontaneously removed in alkaline solutions owing to the formation of soaps in the dirt.

3.6 Corrosion inhibitor

Corrosion inhibitor, usually sodium silicate, helps protect washer parts from corrosion. Light duty liquids designed for hand dishwashing do not contain corrosion inhibitors as they are not intended for use in a washing machine.

3.7 Processing aids

Processing aids cover a considerable list of ingredients such as sodium sulfate, water, solvents like alcohol, or xylene sulphonate. They provide the product with the right physical properties for its intended use. Sodium sulfate, for example, helps provide crisp, free-flowing powders. Alcohols are often used in liquid products where they serve as solvents for the detergent ingredients, adjust the viscosity and prevent product separation. Since the water content of liquids is fairly high, alcohols also provide protection to the product under extremely cold storage conditions by lower-

ing the freezing point.

3.8 Colorants²⁰⁾

Colorants are added to lend individuality to the product or dramatize a special additive contributing to product performance. Additionally, blue colorants may provide a bluing which imparts a desirable blue/white color to white fabrics

3.9 Fragrances²¹⁾

Fragrances provide three functions, regardless of the scent used. They cover the chemical odor of the detergent and the odor of soils in the washing solution. Plus, they impart a pleasant scent to fabrics, thus reinforcing the clean performance. Additionally, a fragrance contributes to the character of the product. Some detergents are offered in unscented versions, appealing to consumers who prefer low or no scent on laundry. They may also appeal to people whose skin is sensitive to fragrance ingredients.

3.10 Oxygen bleach¹⁷⁾

Oxygen bleach provides the detergent with an all-fabric bleaching action for stain and soil removal. Oxygen bleaches are available in both a dry and liquid form. All dry oxygen bleaches contain inorganic peroxygen compounds, such as sodium perborate tetrahydrate and sodium percarbonate. When dissolved, the inorganic peroxygen compounds convert to hydrogen peroxide (the oxidizing agent) and the residue of the compound (e.g., sodium borate or carbonate). Liquid oxygen bleaches contain hydrogen peroxide, which supplies the oxidizing agent directly. The hydrogen peroxide reacts with the soil and organic materials in the wash to either decolorize or break them up. Hydrogen peroxide provides a more gentle bleaching action than sodium hypochlorite used in chlorine bleaches.

3.11 Suds control agents

Suds control agents are used as suds stabilizers or suppressors. Suds stabilizers are limited to detergents, such as light duty products, where lasting, voluminous suds are desirable. Suds suppressors inhibit sudsing or control it at a low level. Special long chain soaps are one class of compound used to control sudsing in powder and liquid laundry detergents.

3.12 Opacifiers

Opacifiers provide a rich, zeamy opaque appearance to liquid products.

3.13 Bleaching agents²¹⁾

Bleaching agents and activators are used to make white clothes clean. Oxygen bleach provides detergents with an all-fabric bleaching agent for stain and soil removal. Sodium percarbonate or sodium perborate and the liquid products that contain hydrogen peroxide are also used for this

purpose.

3.14 Enzymes¹⁷⁾

Enzymes are now very popularly blended into detergent formulations. Enzymes aid in breaking down complex soils, especially proteins such as blood and grass, so they can be more easily removed from fabrics. Protease and lipase are used to digest the soils of proteins and lipids, respectively. Cellulose is recently developed as an enzyme component of a detergent that attacks a substrate (cotton) to remove the soils.

3.15 Other ingredients

Other ingredients added to laundry detergent as needed to provide a specialized outcome or as a convenience to consumers. Some laundry detergents contain "optical brighteners". These are fluorescent dyes that glow blue-white in ultraviolet light. The blue-white color makes yellowed fabrics appear white.

4 TYPES OF LAUNDRY DETERGENTS

4.1 Heavy duty detergents¹⁷⁾

The surfactants used in heavy duty detergents are mainly anionic ones such as linear alkylbenzene sulfonates, alkyl sulfates, alkyl polyethoxyethylene sulfates etc. Soaps are sometimes used as a foam controlling agent. Polyoxyethylene alkyl ether, a nonionic surfactant shows strong detergency for oily dirt.

Heavy duty High efficiency laundry detergent is a superior blend of synthetic detergents, water conditioners and fast acting soil specific enzymes. These enzymes work quickly to break down a variety of stains including blood, grass, cooking oil, organic grease, ink and food soils and works in hot and cold water. A free-flowing granular heavy duty high efficiency laundry detergent is made by blending with a detergent builder (e.g. Zeolite A) and optional other ingredients a discrete tertiary amine.

4.2 Liquid detergents⁶⁾

The liquid detergents commonly contain at least some water to help liquify the other additives and still have the detergent pourable. The liquid detergents may also have other solvent liquids, such as alcohol or a hydrotrope, to help blend all the additives together. Especially effective on food and greasy, oily soils. They are also good for pretreating spots and stains prior to washing.

4.3 Powder detergents²²⁾

Ideal for general wash loads. Powders are especially effective at lifting out clay and ground-in dirt.

4.4 Ultra detergents⁶⁾

Ultra detergents are more concentrated and can be added in smaller amounts. The detergent can be added onto the laundry or to the wash water at the start of the wash, or it can be added beforehand or soon after starting the wash. These ultra detergents are available in liquid or powder forms. They come in smaller packages, yet are designed to offer the same cleaning power as similar products in larger packages and are needed in lesser amount.

4.5 Single-use detergents⁶⁾

Compacted and/or concentrated powder, liquid, or tablet detergents that come in unit-dose sizes for measuring accuracy and laundering convenience.

4.6 Soap bars¹⁷⁾

Soaps are the oldest cleansing agent generally made from fatty acid of tallow or a combination of fatty acids of tallow and cocoa (coconut oil). Palm oil fatty acids have also been used recently. Soaps are the precursors of the chip and powder forms of detergent.

4.7 Combination detergents⁶⁾

Laundry detergents combined with a bleach alternative, color-safe bleach or fabric softener were developed to respond to consumer needs for easy-to-use, effective products and may eliminate the need to buy two products. The detergent/bleach combination products utilize new technology which has provided more effective, low-temperature bleaching systems in response to the lower wash temperatures used in today's washloads. Combination detergents are the mixture of liquid or powder detergents with built-in fabric softeners that have high foaming property and give different feelings during washing and rinsing.

5 MECHANISM OF SOIL REMOVAL BY LAUNDRY DETERGENT/SURFACTANT

Surfactants can work in three different ways: roll-up, emulsification, and solubilization.

5.1 Rolling-up mechanism

The roll up mechanism of oily soil is reviewed by Miller and Raney²²⁾. The driving force causing the oily soil to separate from the fiber surface is the roll-up results from tension at the interfaces between oil, water, and the fiber. In the presence of surfactant, the apparent contact angle of the oil on the fibers increases from 0° to 90° and 180°, and the oily soil rolls up. The surfactant helps an oily soil to roll up by lowering the water/fiber and water/oil interfacial tensions.

David *et al.*²³⁾ studied the rolling up mechanism of surfactants and described that surfactant enhanced soil washing can result from a mechanism that is an outgrowth of

fundamental surfactant property occurs below the CMC (critical micelle concentration) (roll-up mechanism). In the roll-up mechanism, the contact angle becomes larger when the surfactant is added to the water phase, and the oily dirt easily removed (Fig. 1)¹⁷⁾. The surfactant accumulation at the oil-water interface increases the contact angle between the oil and the cuttings. The repulsion between the monomer head group and the solid surface promotes separation of the oil from the cuttings. The roll-up mechanism is augmented by reduction in oil/water interfacial tension because the oil droplet becomes elongated and is more easily ruptured by macroscopic forces like agitation or shear from scrubbing. Since ease of emulsification is inversely correlated to oil/water interfacial tension, interfacial tension reduction generally enhances detergency by the roll-up mechanism.

Figure 2 shows oil/water interfacial tension for low surfactant concentrations (0.025 wt %) as a function of electrolyte (NaCl) concentration for three surfactants²³⁾.

1. The Isofol 145-4PO is a branched alcohol propoxylate sulfate purchased from Condea Vista.
2. The surfactant purchased from Lubrizol is an alkyl succinic anhydride-taurine adduct.
3. Steol is a propoxylated sulfate with a linear alkyl tail.

The isofol 145-4PO effected the lowest oil/water interfacial tensions for sub-cmc concentrations, and it was therefore chosen for sub-CMC washing experiments using the roll-up mechanism.

Figure 3 shows results of washing drill cuttings with a low concentration of isofol (0.1 wt%). Washing experiments compare the low isofol solution to water alone (no surfactant) for two initial oil contents of 10 wt% and 20 wt%. The vast majority of liberated oil using sub-CMC [surfactant] is free phase as opposed to solubilized/emulsified when using supra-CMC [surfactant]. For both initial oil contents of 10 wt% and 20 wt%, the final oil contents are the same (8.0 wt%). The enhancement of sub-CMC [isofol] over water alone is evident for both initial oil contents²⁴⁾.

The roll-up mechanism using only sub-CMC surfactant and appropriate electrolyte reduces the oil content of the cuttings to 8% while solubilization reduces the oil content of the cuttings to 0.1%. Thus, solubilization reduces the oil content to a value that is two orders of magnitude lower than the roll-up mechanism using only surfactant and electrolyte. For an initial oil content of 20 wt%, water-only washing reduces the oil content to 14% demonstrating that sub-CMC surfactant is a great improvement over water alone.

5.2 Emulsification²⁵⁾

Emulsification is of key importance for a large number of processes such as oil recovery, detergency and the preparation of foodstuffs. Emulsion is the main application of surfactant adsorption at liquid/liquid interfaces. An emulsi-

Fig. 1 The Rolling Up Process of Oily Dirt¹⁷⁾.

Fig. 2 Oil (-Olefins)/Water IFT for Sub-CMC Surfactants as a Function of [NaCl].

Fig. 3 Washing Results Using the Roll-up Mechanism for Two Initial Oil Contents. The red are results for sub-CMC [isofol] = 0.1%. The blue is for water only. The final oil content of the cuttings is 8.0 wt% independent of the initial oil contents.

fied mixture of water in oil is commonly called mousse. During laundry, detergent is act as an emulsifier which stabilizes an emulsion and lowers the oil-solution interfacial tension and makes easy emulsification of the oily soils possible. The emulsifying effect of surfactants is important for both cleansing and washing of textiles. Due to the hydrophobic and hydrophilic parts, surfactants can adsorb to non-polar and polar materials at the same time. At low surfactant concentrations, systems that give ultralow oil-water interfacial tensions, usually form micro-emulsions in thermodynamic equilibrium. In such micro-emulsions, an amount of the oil is dispersed in the aqueous phase (or the inverse) in the form of swollen surfactant aggregates or micelles. A second form of dispersion is that these systems can form a third, mixed, oil/water/surfactant phase that can be either a lamellar (L₂) or a sponge (L₃) phase. As for the non-equilibrium process of spontaneous emulsification, the only mechanism that appears to be clearly established so far is due to a (slow) diffusion of either the oil or the aqueous phases in the other phase. The soluble surfactant exhibits an ultralow oil-water interfacial tension (with linear alkanes as the oil) without the addition of co-surfactants, so that the analysis of the phase behaviour is considerably simplified. This can be seen as a result of the nearly balanced hydrophilic and lipophilic parts of the surfactant molecule. Another consequence of the nearly balanced head and tail group areas is that surfactant solutions form vesicular rather than micellar structures. The presence of large vesicles allows us to follow the redistribution of the surfactant during the spontaneous emulsification²⁶⁾. During cleansing and washing, the non-polar materials are kept in emulsions in the aqueous solution and removed by rinsing. Surface active substances (surfactants) can increase the kinetic stability of emulsions greatly so that, once formed, the emulsion does not change significantly over years of storage. Detergents will chemically interact with both oil and water, thus stabilizing the interface between oil or water droplets in suspension.

5.3 Solubilization²⁴⁾

Solubilization is usually describes as the process of incorporation of an "insoluble" substance (usually referred to as substrate or solubilize) into surfactants micelles (the solubilizer). The process of solubilization involves the transfer of co-solute from the pure state, either crystalline solid or liquid to micelles. The co-solute can be either polar or non polar. The solubility however increases when the CMC of surfactant is reached, but above the CMC the increase in solubility of the substrate is directly proportional to the wide range of the surfactant concentrations. This increase of the solubility of solute in the micellar medium is due to the solubilization of the substrate molecules into the micelles.

Due to their amphiphilic properties, possessing both

Fig. 4 Micelle Formation of Surfactant Unimers.

hydrophilic and lipophilic moieties, surfactants tend to accumulate or adsorb at gas-liquid and solid-liquid interfaces. Below the surfactant concentration at which micelles begin to form, the CMC, interfacial adsorption of surfactants typically results in a lowering of both the surface tension of water and the contact angle between the solid and aqueous phases²⁷⁾

The detergent is soluble in water and makes the water wash the laundry better along with agitation or tumbling. The detergent does its work and is needed during the initial “wash” cycle to separate the dirt or soil out from the fabric. The purpose of the rinses which follow is to rinse the detergent residue from the laundry as well as to remove the dirt suspended in the wash water by replacing the initial wash water with fresh water.

6 REMOVING PROCESS OF SOILS AND ITS KINETICS¹⁷⁾

Removing soils from a substrate is the central process of cleansing. The removing of soils is the reverse process of coagulation and adhesion, and it requires energy. The soil must be transferred from the attached state (attached to a substrate) of a lower energy level to the separated state in an aqueous medium of higher energy level. This energy is supplied by its external source, such as washing machine, an ultra-sonicator, or a human hand. In this energy-required state of cleansing, the detergent serves to reduce the amount of energy required and to remove the soils easily. The soil removing process for solid soil particles was first formulated by Lange²⁸⁾ as a reverse process of coagulation. Figure 5 illustrates the mechanism for removing soil particles from the substrate. A soil particle P attached to the substrate spontaneously separated at a tiny distance δ in detergent solutions Step 1 proceeds by the adsorption of surfactant or water molecules onto the soil and/or the sub-

strate surface and the separated distance δ is in a molecular order. The energy requires in step 1 ($A_1 = V_{II} - V_I$) is given spontaneously by the free energy gain of the adsorption process: it need not be supply externally. Step 2 is to carry the soil particle away from the distance δ to infinite one. The energy $A_2 (= V_{III} - V_{II})$ is necessary in Step 2 as a sum, but at higher barrier E becomes presenting the process of this step and must be overcome. A soil particle on the substrate is subjected to van der Waals attraction and electrical forces assuming a sphere plate model presented in Fig. 6. The potential energy of the van der Waals attraction is V_A , The electrical double layer repulsion is V_R and the resultant $V = V_A + V_R$. The curve depicts an energy barrier E , the heights of which depends largely on the zeta potential of fiber and the particulate. The height of this barrier is one of the factors controlling the kinetics of soil removal and redeposition.

Fig. 5 Schematic Representation of the Removing Process of Solid (Soil) Particle (P) from the Substrate (S), V_I , V_{II} and V_{III} are Potential Energies in Step I, II and III Respectively. A_1 and A_2 are work needed to separate the particle in step I, II and III respectively³⁴⁾.

Fig. 6 Potential Energy as a Function of Distance between a Soil Particle and a Substrate³⁴⁾. The soil particle must go over the potential barrier ($A_2 + E$) in the removing process of the particle.

A kinetic study usually involves the determination of soil concentrations on the fabric or in the bath at various times. A plot of soil concentration against time yields a curve that can provide useful information about the detergent process being studied²⁹⁻³²⁾. The kinetics of soil removal is complicated by the heterogeneity of the soil, shape, size, chemical composition and location of soil. In an empirical approach, kinetics of soil removal can be presented mathematically.

$$\frac{dS}{dt} = -K_s S^{n_s}$$

Equation 1

Where S is the amount of soil on the substrate at any time t, n_s is the order of the process, K_s is the average soil removal coefficient. The order n_s is independent of time and the rate coefficient K_s is not a constant, rather, decreases with increasing time. Most of the reported results of kinetics of particulate soil removal follow first order kinetics.

7 ROLE OF DETERGENTS TO PREVENT DIRT FROM BEING RE-DEPOSITED³⁴⁾

Detergents have a vital role to play in preventing the re-deposition of soils like greasy, oily stains and particulate dirt on the surface or fabric from which they have just been removed. This works by electrostatic interactions and steric hindrance.

7.1 Electrostatic interactions³⁵⁾

Surfactants are adsorbed on both the surface of the dirt which is dispersed in the detergent solution and the fabric surface. This creates a negative charge on both surfaces, causing electrostatic repulsions. This repulsion prevents the soil from re-depositing on the fabric.

In the presence of hardness, however, this mechanism acts like a 'bridge' between the suspended soil and the fabric. This is another reason why hardness sequestrants (a chemical that promotes Ca/Mg sequestration) are often used in detergents.

7.2 Steric hindrance

Surfactants like alcohol ethoxylates also adsorb on the dirt. Their long ethoxylated chains extend in the water phase and prevent the dirt droplets or particles from uniting and from depositing onto the fabric surface. Dirt is present in solution. The non-ionic surfactants adsorb to the dirt particles. Their long hydrophilic heads extend in the water phase and as a result, prevent the dirt particles/droplets from uniting and from re-depositing onto fabrics.

8 EFFECTS OF LAUNDRY DETERGENTS ON ENVIRONMENTAL³⁶⁾

Every household, hotel, hospital, nursing home, prison and military base in the developed world uses laundry detergent to clean their garments and linens. Because these chemicals are non-renewable (one-time use), billions of tons of these chemicals get dumped back into the water supply every year. The concern of many environmentalists is that we are poisoning ourselves slowly, and this has been one of the main reasons we have made the transition from drinking tap water, to exclusively drinking bottled spring water over the last 15 years. Much of the fresh water supply has become undrinkable. Because water is the most critical element for human beings in the environment, it is in our best interests to do whatever we can to protect our precious and fragile fresh water supply for the future.

A laundry detergent concentration of only 2 ppm can cause fish to absorb double the amount of chemicals they would normally absorb, although that concentration itself is not high enough to affect fish directly. Commercial laundry operations can have a vast impact on this. Phosphates in detergents can lead to freshwater algal blooms that release toxins and deplete oxygen in waterways.

Surfactants used in household and various industries, are rather toxic; therefore, the accumulation of these compounds in the environment through wastewaters has challenged the problem of their biodegradation.

The effect of different type of detergents on environment is as below:

8.1 Anionic surfactant based detergents

Sulphonates are not degraded significantly under the anaerobic conditions of the laboratory test methods^{37,38)}. In the real environment and also in field system tests, however, oxygen-limited conditions may be more common than rigorously anaerobic conditions. In such conditions sulphonates mineralize even if the rate is not as rapid as that observed under aerobic conditions. Once sulphonate biodegradation has been initiated in aerobic or oxygen-limited conditions, the intermediates can continue to biodegrade anaerobically. This is the reason why in some simulation tests these chemicals can show mineralization results, if some oxygen diffusion had occurred or if limited oxygen conditions had been created^{39,40)}. Sulphonates can also inhibit biogas formation in laboratory tests if present at relatively high concentrations⁴¹⁾. This inhibition starts at sulphonate concentrations with respect to the total solid matter of about 15 g/kg dw in the laboratory tests, where the added products are used as Na salts. In actual anaerobic environmental compartments (e.g. STP anaerobic digester), however, sulphonates have shown to not inhibit biogas formation even at high concentration (>30 g/kg dw) because they are present as Ca salts which are poorly soluble and less bioavailable. It has been recently demonstrated

that not all desulphonation reactions require oxygen. Desulphonation of alkylsulphonates as well as of LAS surfactant has been reported to occur by anaerobic bacteria in the laboratory⁴²⁾.

There is recent evidence that anaerobic desulphonation can take place. Desulphonation with assimilation of the sulphur moiety by strictly anaerobic bacteria⁴³⁻⁴⁵⁾ was followed by the reduction of the sulphonate as a source of electrons and carbon under anaerobic nitrate-respiring conditions⁴⁶⁻⁴⁸⁾.

LAS data for sludges have been obtained in several countries and range from <500 mg/kg to a maximum value of 30000 mg/kg⁴⁹⁾ depending on STP operating conditions and water hardness. Aerobic stabilized sludge always has a LAS content lower than 500 mg/kg, whereas anaerobic stabilized sludge has a LAS concentration typically in the range 5000 - 10000 mg/kg^{50,51)}. Results are overall quite consistent between different studies, and between the EU and the US. A few studies have attempted to make a LAS mass balance over full scale anaerobic digesters. A low degree of removal is measured, ranging from 0 - 35%^{49,52)}. Which indicate that LAS as well as any other sulphonate surfactants, does not degrade under strictly anaerobic conditions. It is not entirely clear to which process (es) the small degree of removal observed in field systems can be ascribed (binding, humification, co-metabolism, anaerobic desulphonation). While LAS concentrations on a wet sludge basis actually increase in an anaerobic digester due to the dewatering and digestion of solids, there is no evidence that LAS causes any inhibition of the essential processes (biodegradation, biogas formation, dewatering, and digestion) on going in the reactor.

LAS has been found in river sediments. The levels range from zero to a maximum value of 174 mg/kg, believed to be the most reliable one and found just below a STP outfall. Downstream the same STP outfall the LAS concentrations in sediments drop to 5-11 mg/kg⁵³⁾. No mass balancing studies are known to us. Several interesting studies have looked at the levels of LAS and other surfactants in cores or river/lake sediments as accumulated over time. Residual LAS levels can be measured, and in the trends over time (i.e. depth) clear parallels can be seen with changes from branched alkyl sulphonates to LAS^{54,55)}. Another study on anaerobic degradation of sulfonates in full scale systems, not related to LAS but instead to SAS⁵⁶⁾. The SAS monitoring in anaerobic sludge ranges from 270 to 800 mg/kg. Like LAS, there is no evidence for a significant anaerobic degradation of SAS. Primary alcohol sulfates are anaerobically biodegradable, with a conversion to CH₄ and CO₂ (biogas) of 80-94% in tests simulating anaerobic digesters. They are also extensively mineralized (65-88%) in screening tests, although as with other anionic surfactants, the unnaturally high surfactant to biomass ratio means that low biodegradation or inhibition of biogas production are sometimes

observed.

Fewer data are available on the anaerobic biodegradability of ethoxysulphates but the available information indicates that they too are extensively biodegraded (>75%) during anaerobic digestion. Low biodegradation has been reported for lauryl ether sulfate but this can be attributed to the very high test substance to biomass ratio used in the study quoted.

8.2 Nonionic surfactant based detergents

Alcohol ethoxylates (AE) (linear C₉-C₁₈-alcohols) are well biodegradable in anaerobic screening tests. Degradation of usually >70% (biogas) has been reported in digested sewage sludge and freshwater sediment. Degradation >80% (biogas formation and 14C) in digester simulation tests have been reported in the case of lauryl alcohol ethoxylates and stearyl alcohol ethoxylates. Actual data on the AE concentration in digester sludges support the conclusion that AE's are well biodegradable in full scale digesters⁵⁷⁾. Alkylphenol ethoxylates showed poor to moderate mineralization rates (20-50 % biogas formation) in screening and simulation tests. Simulation tests indicated that degradation proceeds via de-ethoxylation to alkylphenol which is poorly degradable. Consequently, high concentrations of nonylphenol (up to 2530 mg/kg DM) were measured in digesters⁵⁸⁾.

Lower concentrations (35-95 mg/kg DM) of nonylphenol in digester sludges were reported recently⁵⁹⁾. Alkylpolyglucosides (C8-C12-linear alkyl) and glucoside fatty acid esters are well degradable in anaerobic biodegradation screening tests (>60 % biogas formation). Glucose Amides showed high mineralization rates (>80%) in a 14C-simulation test. Amine oxides are likely to be anaerobically degradable.

8.3 Cationic surfactant based detergents

Mono-alkyl or dialkyl quaternary nitrogen compounds with straight (C-C) alkyl chains are not anaerobically degradable (e.g. TMAC, DTDMAC, etc).

Esterified mono-alkyl or dialkyl quaternary nitrogen compounds are biodegradable (e.g. MTEA esterquat, DEEDMAC, etc). After ester hydrolysis, both the fatty acid as well as the alcohol cleavage products can be further completely mineralized since only if few compounds have been tested; it is difficult to draw general conclusions for cationics with a high degree of confidence. The effect on the degradability of factors such as the position of the ester bond, the type of substitution on the nitrogen, branching, etc., have not been systematically investigated.

8.4 Amphoteric surfactant based detergents

No data were found.

8.5 Fatty acid salts based detergents

Fatty acids and their sodium/calcium salts (soaps) are

well biodegradable under anaerobic conditions. This was shown in several laboratory studies using different test methods. The data for dodecanoate and palmitate obtained in the stringent ECETOC (European Centre for Ecotoxicology and Toxicology of Chemicals) screening test showed very high mineralization rates ($>75\%$ $\text{CO}_2 + \text{CH}_4$ formation) within the test period of 4-8 weeks. The bacterial inocula used in these investigations were digester sludges as well as anaerobic sediments from fresh water and marine environments. The data for C_{12-18} fatty acids reported by Madsen and Rasmussen⁶⁰⁾ are lower (40-57%) but this may indicate slower biodegradation kinetics due to the unusually high test substance/inoculum ratio used in the test. The positive evaluation of the anaerobic biodegradability of fatty acids and soaps was confirmed in a digester simulation study using radio labelled palmitate and showing an almost quantitative ultimate degradation to carbon dioxide and methane⁶¹⁾. Additional static and semicontinuous digester simulation tests proved the extensive ultimate biodegradation of Na- and Ca-salts of fatty acids with an alkyl chain length of 8-22 carbons^{62,63)}. While the Ca-soaps (C_{12} , C_{18} , C_{22}) exhibited high gas formation rates ($>85\%$) in the static system within a 10-day test duration, the semi continuously run investigations with Na-soaps showed that the time needed for mineralization was increasing with the chain length and concomitantly with the water solubility. The relatively poor water solubility of Ca/Mg-soaps may also account for the high soap concentrations found in the raw sludges of sewage treatment plants (up to 5% of sludge dry matter); nevertheless, the mass balances of soap based on a monitoring study of the concentrations in sludges of a digester influent and effluent, respectively, showed unequivocally that the removal of soap was about 70%⁶⁴⁾.

9 CONSUMPTION OF DETERGENT AND CLEANING PRODUCTS⁶⁵⁾

The two major markets, household detergents and industrial and institutional cleaning products, consume more than 1 million and more than 200 thousand tons surfactants, respectively, in Europe. The formulations, or products, in which these volumes are used, differ markedly in their contents of surfactants. e.g., a liquid product may contain approximately 50% surfactant compared to less than 25% in powders. The consumption of various household detergent products is estimated below by inclusion of figures from several sources (Table 1).

The diversity of products to perform basic cleaning tasks in the house is growing, and soap and detergent producers renew their product lines by introducing new additives, improved surfactants, or new formulations to enhance performance. Several trends influence the development of consumer detergent products.

Multifunctional chemicals with the ability to serve multiple functions in the product will reduce the number of raw materials and, hence, reduce the formulation costs. Formulation of chemicals that can be used as ingredient alternatives in the products in order to increase flexibility and independence of suppliers. Adjustment of existing formulations, e.g. by introduction of new additives or surfactants, or by utilizing synergistic effects between ingredients.

Mildness is an important property that plays a significant role for the use of surfactants in household products. Today, anionic surfactants are used in the largest volume, but the growth of anionic surfactants is expected to be relatively slow in the next few years, as they are gradually replaced by milder nonionic and amphoteric surfactants. The trend towards milder surfactants has already favoured

Table 1 Estimated Annual Consumption of Household Detergents.

Product	Annual consumption (tons)	
	Denmark (1997)	Europe (1998)
Laundry detergents, powders	28,700	3,100,000
Laundry detergents, liquids	4,900	560,000
Laundry detergents, specialty products	3,200	-
Fabric softeners	9,100	1,000,000
All-purpose cleaning agents	5,100	950,000
Toilet cleaning agents	2,300	400,000
Hand dishwashing agents	6,000	800,000
Machine dishwashing agents	3,800	500,000
Personal care products	14,200	1,900,000

the use of specific surfactant types. Mild components such as the amphoteric surfactants, alkyl betaines and alkylamido betaines, as well as the anionic surfactants, α -olefin sulfonates (AOS), are used in increasing volumes and the con-

sumption of these chemicals is expected to grow. The consumption of surfactants in household and in industrial and institutional detergents is estimated below by inclusion of figures from several sources (Table 2,3).

Table 2 Estimated Consumption of Surfactants in Household Detergents.

Surfactant		Annual consumption 1998 (tons)	
		Denmark	Europe
Anionic surfactants, subtotal		8,700	780,000
	AES	1,800	123,000
	AS	1,000	117,000
	LAS	3,500	330,000
	SAS	600	55,000
	Soap	1,600	134,000
	Other	200	21,000
Nonionic surfactants, subtotal		6,000	530,000
	AE+AA	5,400	455,000
	APG	200	28,000
	FAGA	200	28,000
	Other	200	19,000
Cationic surfactants, subtotal		1,200	98,000
Amphoteric surfactants, subtotal		460	40,000
Total		16,360	1,448,000

AES= Alkyl ether sulfates, AS= Alkyl sulfonates, LAS= Linear alkyl benzene sulfonates, SAS=Sodium alkyl benzene sulfonates, AE= Alcohol ethoxylates, AA=Alkyl amides, APG=Alkyl poly glycosides, FAGA=Fatty acid glucamide

Table 3 Estimated Consumption of Surfactants in Industrial and Institutional Products.

Surfactant		Annual consumption 1998 (tons)	
		Denmark (1997)	Europe (1998)
Anionic surfactants, subtotal		1,400	128,000
	LAS	800	80,000
	Soap	250	22,000
	Other	350	26,000
Nonionic surfactants		1,100	96,000
Cationic surfactants		200	17,000
Amphoteric surfactants		80	7,000
Total		2,780	248,000

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