



Type and application of some common surfactants

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ABSTRACT

Surfactants are characterized by the possession of both hydrophilic (polar) and hydrophobic (non-polar) groups on the same molecule. The hydrophobic portion has very little attraction for water and the hydrophilic portion has a strong attraction for water. As surfactant concentration increases in water, surfactant molecules form aggregates (micelles) and the hydrophobic inner portion of a micelle creates a non-polar environment, thus, there are the following surfactants: non-ionic, anionic, cationic, amphoteric and reactive. Surfactants are widely used in the detergent industry, lubrication, softening finishes, sewage sludge, herbicide dispersions, situ flushing to a diesel contaminated site and petroleum Industry. Most of the applications surfactants are softening products present analogous characteristics to a detergent a long aliphatic chain and a hydrophilic part. Its classification is usually based on characteristics from the hydrophilic part. This review paper focuses on the some types of surfactants and their applications.

Keywords: Surfactants, Micelles, Detergents, Lubricant.

INTRODUCTION

The best way to start an introduction to such a subject would be to back up just a little and explain some terms used in the industry and define the origin of surface-active agents. The components of a synthetic detergent can be classified in two categories. The surface active agent is the principal component of a synthetic detergent but is also assisted in its cleaning agent role by the builders used (sometimes called built detergents). Builders such as the phosphates, met silicates and carbonates aid in emulsifying soils and suspending dirt in aqueous solutions the definition for a detergent is a cleaning agent. The main cleaning agent used in earlier days was soap that discovered 40 years ago. In the figure 1 shows the soap structure [1]. This term means a compound formed from the reaction of a fatty acid with a base such as caustic soda, forming the sodium soap of the acid. The more commonly used cleaning agent in this day and age is the synthetic detergent (SYNDET) which is a formulation such as TIDE or FAB. The essential difference between the soaps and the newer synthetic detergents lies in the fact that the soap molecule occurs readymade in nature. As we have seen above, it consists of a long-chain fatty acid modified only to the extent that the acidic hydrogen is replaced by a sodium atom from caustic soda [2]. The synthetic detergents are not derived directly from natural products but are tailor-made, or built up artificially, synthesized in the laboratory. These synthetic detergents are made from a wide variety of raw materials such as certain petroleum constituents, coal tar derivatives, compounds derived from cracking gases, chemically modified fatty acids, and a host of others. The surface-active agents are compounds that have two groups present in the molecule one being hydrophobic in nature and one being hydrophilic in nature [3]. In this review we will focus on the major surfactants, types and their

applications. A surfactant molecule is composed of a hydrophilic head and a hydrophobic tail (Figure2). The head can be an anionic, a cationic, a zwitterion, or a nonionic group while the tail is a nonpolar hydrocarbon chain.



Figure 1.chemical structure of soap

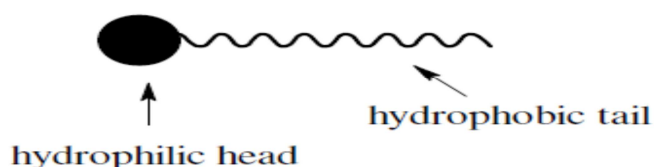


Figure 2. Schematic of a surfactant molecule

These molecules are surface active as a result of the combination of the hydrophobic and hydrophilic properties. They have affinity for two immiscible phases, one of which is water. A zwitterion surfactant (figure 3) has both a positive and negative charge in the head group. This charge separation causes a dipole moment to be present in the head group. Therefore, the head group is polar and soluble in water.



Figure 3.Schematic of a zwitterion surfactant

2.TYPES (CLASSES) OF SURFACTANTS

Surfactants fall in the following classifications according to the nature of the hydrophilic group:

- A:Anionic
- B:Cationic
- C:Nonionic
- D: Amphoteric
- E:Reactive

2.1. Anionic: hydrophilic head is negatively charged

In solution the head is negatively charged. This is the most widely used type of surfactant for laundering, dishwashing liquids and shampoos because of its excellent cleaning properties and high. The surfactant is particularly good at keeping the dirt away from fabrics, and removing residues of fabric softener from fabrics. Anionic surfactants are particularly effective at oily soil cleaning and oil/clay soil suspension. Still, they can react in the wash water with the positively charged water hardness ions (calcium and magnesium), which can lead to partial deactivation. The more calcium and magnesium. Molecules in the water the more the anionic surfactant system suffer from deactivation. To prevent this, the anionic surfactants need help from other ingredients such as builders (Ca/Mg sequestrates)and more detergent should be dosed in hard water. The most commonly used anionic surfactants are alkyl sulphates and sulfonates, alkyl ethoxylatesulphates and soaps petroleum, lignin sulfonates, phosphate esters, sulfosuccinate esters and carboxylates [4].

2.1.1.Soap and other carboxylates

Strictly speaking the term soap refers to a sodium or potassium salt of a fatty acid. By extension the acid may be any carboxylic acid, and the alkaline metal ion may be replaced by any metallic or organic action[5].

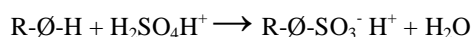
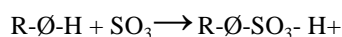
2.1.2. Sulfonation and sulfation

2.1.2.1. Sulfonation mechanisms

Sulfonation of an aromatic ring takes place according to an electrophilic substitution, to produce an intermediate sigma complex that rearranges as an alkyl benzene sulfonic acid.



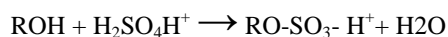
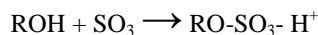
Where Ar-H represents the aromatic ring and X an electrophilic group: SO₃, H₂SO₄, etc. Symbol Ar-X + H⁺ is used because the sulfonic acid is a strong acid, i.e., completely dissociated, even at low pH. With alkyl benzene R-Ø-H the reaction will be:



There exist other mechanisms, such as the addition on the double bond of an olefin or an unsaturated acid, or the nucleophilic substitution (S_N2) in Alfa position of a carboxylic acid [6].

2.1.2.2. Sulfatation Mechanisms

Sulfatation is the esterification of an alcohol by one of the two acidities of sulfuric acid or anhydride. It results in an alkyl ester monosulfuric acid.



As for sulfonates, the salt (sulfate) is obtained by neutralization with a hydroxide. The product is called alkyl-sulfate. However, this is a misleading term and it is better to name it alkyl ester-sulfate in order to remember the existence of the ester bond, particularly because it is the one which is likely to break by hydrolysis, especially at acid pH. This is quite a difference with the sulfonates in which the C-S bond is quite resistant. It is worth remarking that since the esterification-hydrolysis reaction is equilibrated, a small amount of alcohol will be always present, even at alkaline pH. This is why the most employed alkyl-sulfate, e.g., lauryl sulfate, always contains at least traces of dodecanol, which affects its properties. As a matter of fact, an ultrapure lauryl sulfate is a poor former, and it is well known that the traces of lauryl alcohol produce a considerable foam boosting effect [7].

2.1.3. Sulfates

Sulfates are the oldest surfactants. They are excellent foaming and wetting agents, as well as detergents, and they are included in many different products for domestic and industrial use.

2.1.3.1. Alkyl Sulfate (or better Alkyl-Ester-Sulfate)

They are very common, particularly the dodecyl (or lauryl) sulfate, as a sodium, ammonium or ethanolamine salt, which is the foaming agent found in shampoos, tooth paste, and some detergents. They are prepared by neutralization of the alkyl-ester-sulfuric acid by the appropriate base.



The sodium lauryl sulfate is an extremely hydrophilic surfactant. Lesser hydrophobicity can be attained with a longer chain (up to C₁₆) or by using a weaker hydroxide (ammonia, ethanolamine).

2.1.3.2. Alkyl Ether Sulfates (or better Alkyl-Ethoxy-Ester-Sulfate)

They are similar to the previous ones, but this time the sulfatation is carried out on a slightly ethoxylated (2-4 EO groups) alcohol.

For instance sodium laureth sulfate C₁₂H₂₅-(O-CH₂-CH₂)₃-O-SO₃⁻ Na⁺

The presence of the EO groups confers some nonionic character to the surfactant and a better tolerance to divalent cations. They are used as lime soap dispersing agents (LSDA) in luxury soap, bath creams and shampoos. The ethoxylation step results in a mixture of oligomers and the final product contains species having from 0 to 5 EO groups. This allows for a more compact packing of the polar heads at the air-water surface, in spite of the charge, a characteristic which is associated with the excellent foaming ability of these surfactants [8].

2.2. Cationic: hydrophilic head is positively charged

Cationic are formed in reactions where alkyl halides react with primary, secondary, or tertiary fatty amines. Here the water-insoluble part of the molecule has a positive charge and the water-soluble part of the molecule is negatively charged, thus giving it the name of a cationic surface-active agent. Cationic surface-active agents reduce surface tension and are used as wetting agents in acid media. However, a disadvantage of a cationic surface-active agent is that they have no detergent action when formulated into an alkaline solution such as quaternary ammonium salts [9].

2.2.1. Nomenclature for Amines and Non- Cyclic Ammoniums

Most used cationic surfactants are fatty amines, their salts and quaternary derivatives. Actually fatty amines are not cationic but anionic surfactants. However, they are generally classified with cationic because they are mostly used at acid pH, in which their salts are cationic. The amine is labeled as primary, secondary or tertiary respectively when the nitrogen is linked with 1, 2 or 3 alkyl groups. If the nitrogen possesses 4 bonds with C atoms, the compound is called a quaternary ammonium. In an ammonium structure, the nitrogen atom gives two electrons to ensure the fourth bond, and thus remains with a positive charge. Alkyl-ammonium ions are produced in acid medium by the reaction of a proton with the amine. The resulting salt (in general chloride or bromide) is soluble in water thanks to the cation solvation [10].

2.2.2. Fatty Amine Synthesis

There are several methods. The mostly used in practice starts from a fatty acid and transforms it into amide, nitrile, primary amine, secondary amine, tertiary amine and finally quaternary ammonium [11].

2.2.3. Uses of Cationic Surfactants

It can be concluded from the previous sections that the attainment of an amine or alkyl ammonium surfactant requires a chain of chemical reactions which are more or less selective and not necessarily complete. Consequently, only a small part of the original raw material ends up as the desired product. This is why cationic surfactants are in general more expensive than anionic such as sulfonates or sulfates. Hence, cationic surfactants are used only in applications in which they cannot be substituted by other surfactants, i.e. those which require a positive charge or a bactericide action. They are found as antistatic agents in fabric softeners and hair rinse formulas [12]. They are used in textile manufacturing to delay dye adsorption. In this application they compete with dye and thus slow down their adsorption and help attaining a uniform coloration. Their action as corrosion inhibitor in acid environment is similar, but in this case they compete with H^+ ions. Collectors for mineral floatation are often ammonium salts or quats. Asphalts emulsions for roadway pavement and protective coatings and paints are often stabilized by fatty amine salt salts (at acid pH) or quats (at neutral pH). Benzalkonium and alkyltrimethyl ammonium chloride or bromide is used as antiseptic agents, disinfectants and sterilizing agents. They are also incorporated as additive in nonionic detergents formulation for corrosion inhibition purposes, and (in very small quantity) in anionic powdered formulas to synergize detergency [13].

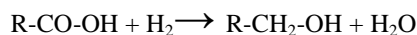
3. Nonionic: hydrophilic head is polar but not fully charged

Nonionic surfactants have diverse uses in textiles and the volume used is large of the several types of nonionic surfactants. The alcohols ethoxylated acids, alkanolamides, ethoxylated amines, amine oxides, polyoxyethylenated alkyl phenols and the poly oxyethylenated linear are the most common. The properties of a nonionic surfactant can be tailored somewhat for a particular use by controlling the relative amounts of hydrophilic and hydrophobic character [14-18].

3.1. Ethoxylated Alcohols and Alkylphenols

3.1.1. Ethoxylated Linear Alcohols

Alcohols come from various origins, but today the main point is to select those with linear alkyl groups. Primary alcohols have their -OH group at the end of the chain. They are generally prepared by moderate hydrogenation of fatty acids, so called catalytic hydrogenolysis (150 °C, 50 atm H_2 , and copper chromite catalyst):



They can be prepared too by Ziegler hydroformylation of olefins (OXO process) or Controlled oxidation of paraffin's. Secondary alcohols, which have their hydroxyl group attached on the second carbon atom of the alkyl chain, are produced by hydration of alpha-olefins in sulfuric medium. The polycondensation of ethylene oxide on anhydrous alcohol is carried out in presence of an alkaline catalyst (NaOH, KOH, Na metal), in absence of air and with caution. Since the probability of condensation is the same for the unreacted alcohol as for already ethoxylated molecules, there is a large distribution of oligomers. The most used alcohol is the so-called tridecanol, actually a C12-C16 mixture. The ethoxylation degree ranges from EON = 6-10 for detergents, EON > 10 for lime soap dispersants, wetting agents and emulsifiers. Foaming ability passes through a maximum for a proper ethoxylation degree. For dodecanol, it is EON = 30.[19,20]

3.2. Ethoxylated Alkyl- Phenols

Phenol (or hydroxybenzene) is mostly prepared as a sub product of acetone manufacturing via the peroxidation of cumene (isopropyl benzene).

Ethoxylated alkyl-phenols are produced by two ways, depending on the available raw material. The first method consists in alkylating the phenol according to classical Friedel-Crafts reaction the second method consists in adding an alpha-olefin such as propylene trimer or tetramer, or isobutylene dimer, on an aromatic ring. This technique results in nonyl, dodecyl and octylphenols, with branched, thus non-biodegradable alkylates. One of the most common alkyl phenol has been for many years the ter-octyl-phenol produced by the Friedel-Crafts alkylation of phenol by isobutylene dimer. As seen in the following formula this substance exhibits two tertiary carbon atoms which are a challenge to biodegradation [21].

3.3. Ethoxylated Thiols

Thiols (the alcohol structure in which the O atom is replaced by a S atom) can be ethoxylated just as alcohols or phenols. The corresponding products are excellent detergents and wetting agents, which are used in industry only, since the possibility of releasing stinking mercaptans bar them from domestic use. Ter-dodecyl mercaptan with EON = 8-10 exhibits a good solubility in both water and organic solvents. Moreover it is an excellent industrial detergent. It is used in raw wool treatment and agrochemical emulsions, in which its wetting ability enhances the cleansing action[22].

4. AMPHOTERIC:

Amphoteric surfactants have both cationic and anionic centers attached to the same molecule. The cationic part is based on primary, secondary, or tertiary amines or quaternary ammonium cations. The anionic part can be more variable and include sulfonates, asinCHAPS(3[Cholamidopropyl]dimethylammonio]-1-propanesulfonate). Other anionic groups are sultaines illustrated by cocamidopropylhydroxysultaine. Betaines, e.g. cocamidopropylbetaine. Phosphates lecithincarboxybetaines and sulfobetaines. In the last years there has been a growing interest in the property of amphoteric surfactants in relation to their applications in personal-care and house hold detergency. An important property of the amphoteric in the ionization state of their molecules, which is dependent on the pH of the solution. One way to determine the ionization state is to experimentally obtain the neutral-ization (titration) curves for the amphoteric surfactant solution [23]. Other methods described in the literature are infrared (IR) and proton magnetic resonance (PMR) spectrometry in particular; the IR spectra exhibit absorption bands due to COO- and N+H2 groups. All these methods give information about the ionization state of the surfactant molecules in the bulk of solution, which could be markedly different from the ionization state of the same molecule when it is incorporated in to an adsorption monolayer properties of this type surfactants are: good detergency foaming properties and foam stabilization hard water compatibility, mild, reduction of irritation of anionic surfactants to skin and eyes, viscosity builder for anionic surfactants solutions. Conditioning effect, compatible with anionic, nonionic and cationic surfactants, applicable in a wide pH range and excellent biodegradability [24-25].

4.1. Amino Propionic Acids

The general formula for amino propionic acids is $\text{RN}^+\text{-CH}_2\text{-CH}_2\text{-COO}^-$. Their isoelectric point is around pH = 4. They are soluble in acid or alkaline solutions. They adsorb on skin, hair, and textile fibers. They are used as antistatic and lubricants for hair and fabrics. The dodecyl amino propionic acid is used in cosmetics as wetting agent

and bactericide. At high pH it is good detergent and foaming agent. However, due to their carboxylic acid groups, these surfactants are sensitive to divalent cations[26].

4.2. Imino Propionic Acids

Their general formula is $\text{HOOC-CH}_2\text{-CH}_2\text{-RN}^+\text{H-CH}_2\text{-CH}_2\text{-COO}^-$. Their isoelectric point is around $\text{pH} = 2\text{-}3$. They are thus more water soluble than the previous ones. They are used as textile softeners. Dicarboxylic compounds of alkyl imidazole, in which the alkyl group is located on the carbon placed between the nitrogen atoms, are used in cosmetics and deluxe soap bars [27].

4.3. Quaternized Compounds

Quaternized compound have similar structures. The most important are betaines and ulfobetaines or taurines, which have a single methylene group between the acid and the quaternary ammonium [28].

5. REACTIVE

The reactive softeners are usually applied in permanent finishes. They are resistant to washing (on the contrary of others) and react to cellulose fibre. Beyond the soft effect, they have a slight hydrophobic finish.

6. APPLICATION SURFACTANTS

6.1. Softening finishes

Finishing is a comprehensive term referring to the processes which fabrics undergo after production [29]. While resins are applied to nearly all knitted and woven goods during manufacture to add body, some resins and surface-active agents serve to soften fabrics. Textile softeners, a result of chemical technology, have been used industrially for almost 40 years[30]. A fabric softener is one such product designed to increase the consumer's satisfaction with the wash, while most fabrics today receive certain resin finishes and softening agents in the manufacturing process. Softening finishes are among the most important of textile chemical after treatments with chemical softeners; textiles can achieve an agreeable, soft hand (supple, pliant, sleek and fluffy), some smoothness, more flexibility and better drape and pliability. Softeners provide their main effects on the surface of the fibres. Small softener molecules, in addition, penetrate the fibre and provide an internal plasticization of the fibre forming polymer by reducing of the glass transition temperature T_g [31,32]. Softeners, with hydrophobic characteristics confer a pleasingly soft bulky and sometimes fatty to the touch. Softeners, with hydrophilic characteristics, provide generally a drier touch and very often they are designated as less soft. Pharmaceutical. Applications of gemini surfactant. Most of the softening products present analogous characteristics to a detergent. A long aliphatic chain and a hydrophilic part. Its classification is usually based on characteristics from the hydrophilic part [33].

6.2. Surfactants/salt auxiliaries as lubricating agents in warp sizing

Fatty lubricants, such as waxes and oils, are applied to warp yarn to reduce end that fatty lubricants are necessary to prevent wear on machine parts and friction between yarn surfaces and warp-yarn abrasion. Weaving machine accessory surfaces. The removal of fatty lubricants from finishing mills would prefer to have no fabric is a difficult procedure for the fin fats on the woven goods to expedite is her. Both finishers and weavers prefer a lubricant for warps which can be applied in sizing as current lubricants are and which meets the necessary prerequisites of sizing materials for weaving but can be easily washed away during finishing. The use of salts and other electrolytes as additives to reduce interfacial tension in the presence of surfactants is well known with the using surfactant lubricants, enhanced by salt auxiliaries which are well known from detergency theory offers a promising possibility for lubricating warp sizes, enhancing their abrasion resistances in weaving and permitting easier removal in finishing.[34-37].

6.3. Surfactants in sewage sludge

The literature concerning the fate of surfactants in sewage sludge amended soil is heavily biased towards the study of LAS with other surfactants receiving little or no attention. Due to their amphiphilic nature surfactants in raw sewage can adsorb to the surface of resident particulate matter. Surfactants may also precipitate from solution in the presence of metal ions (particularly Ca^{2+}). Such behavior may result in a significant proportion of the surfactant load of raw sewage being associated with the particulate fraction. A common initial step in a WWTP is the removal of particulate matter in primary settling tanks. Sludge collected from these tanks is relatively rich in surfactant. Treatment of such sludge is commonly anaerobic digestion at elevated temperature. Many common surfactants used are easily biodegradable in aerobic conditions but due to restricted metabolic pathways the majorities are not degradable under anaerobic conditions. Therefore, sludge treated anaerobically may still be relatively rich in surfactants post treatment. Matthews [38] reported that during 1977 of the 1.3 M tons of sewage sludge produced in

the UK45% was disposed of as a fertilizer to agricultural land. The remaining 55% was disposed of via landfillsites or incineration. Anaerobically digested sludge (dry weight) can contain 0.3¹.2% LAS [38-42].The addition of anaerobically digested sewage sludge to agricultural land is a large potential source of LAS and other surfactants to the soil environment.

6.4.Particulate soil detergency

Particulate soil and fabric (cotton) normally acquire a negative charge in neutral or alkaline aqueous medium. Cellulosic material (cotton) is a natural polymer, a long chain made by linking of β -D-glucose monomer molecules. The chain length in cellulose varies greatly, from a few hundred sugar unit to 6000 for cotton. The cellulose chain contains polar hydroxyl groups, which develop negative charge in water. The negative charge of soil and fabric is further increased by adsorption of anionic surfactants. The corresponding increase in mutual repulsion is responsible for an increase in the washing effect of detergency.

6.5.Herbicide dispersions

In the present day success of weed control technology in agriculture is attributable to the development and effective use of organic herbicides, then, to the use of herbicide adjutants, particularly, surfactants. Surfactants perform a number of different functions in herbicide dispersions. Surfactants are primarily used in aqueous dispersions where they reduce the surface tension and consequently increase spreading and wetting of the weed surface. This result in a uniform coverage of weed surface, greater absorption, reduced rate of evaporation and other desirable effects) [43]. Surfactants help herbicides molecules to penetrate through the waxy surface of leaf. In nitrogen containing fertilizer (ammonium sulfate) surfactant blends help the nitrogen compound to penetrate through the leaf surface. Generally, mixture of nonionic surfactants is used in these applications.

6.6.Nonionic surfactant-enhanced in situ flushing to a diesel contaminated site

A type of remediation technology, surfactant enhanced flushing is modified from the conventional pump and treat method and is applied in the removal of NAPLs from soil and groundwater.Researches that have achieved well-established success in the cleanup of genuinely contaminated sites are rare [44]. The 2 of NAPL distribution in a contaminated site is essential to attain the highest level of clean up and the most important factors controlling the NAPL distribution in the subsurface are geological heterogeneities. Thus, to achieve a successful cleanup of a contaminated area, the design of a surfactant-enhanced flushing process must take the heterogeneous property of a given site into consideration [45-48].

6.7. Amphoteric surfactants in detergents with indirect UV detection

Using amphoteric surfactants in consumer products containing anionic surfactants (e.g., sodium alkyl ether sulfate),nonionic surfactants (e.g., alcohol ethoxylate) and other additives (e.g., hydrotropes) was performed. The accuracy and precision were tested using commercially available and chemically defined hand dishwashing detergents and shampoo. It should be noted that only the amphoteric peaks were detected and no peak corresponding matrix and other surfactants was observed in the developed method. In this analytical condition, the positively charged amphoteric surfactants migrate toward the catholic end but anionic and nonionic components cannot migrate toward the detector under the very slower electro osmotic flow condition. As a result, the peaks originating only from the amphoteric surfactants were observed though all the products consist of various raw materials. The content values of the amphoteric in the products were found to be from 98 to 102% of the expected values [49].

6.8.Petroleum Industry

Applications of surfactants in the petroleum industry are of great practical importance and are also quite diverse, since surfactants may be applied to advantage throughout the petroleum production process in reservoirs, in oil and gas wells, in surface processing operations, and in environmental, health and safety applications. CMC values are important in virtually all of the petroleum industry surfactant applications. For example, a number of improved or enhanced oil recovery processes involve the use of surfactants including micellar, alkali/surfactant/polymer (A/S/P) and gas (hydrocarbon, N₂,CO₂ or steam) flooding. In these processes, surfactant must usually be present at a concentration higher than the CMC because the greatest effect of the surfactant, whether in interfacial tension lowering [50] or in promoting foam stability [51], is achieved when a significant concentration of micelles is present. The CMC is also of interest because at concentrations. Some examples of surfactant applications in the petroleum Industry in Gas/Liquid systems are producing oil well and well-head foams ,oil flotation process froth distillation and fractionation tower foams ,fuel oil and jet fuel tank (truck) foams, foam drilling fluid, foam acidizing fluid, blocking and diverting foams gas mobility control foams. Some examples in the liquid/liquid systems are

emulsion drilling fluids, enhanced oil recovery in situ emulsions; Oil sand flotation process slurry Oil sand flotation process froths well-head emulsions, heavy oil pipeline emulsions, fuel oil emulsions, asphalt emulsion, oil spill emulsions and tanker bilge emulsions. Liquid/solid systems are reservoir wettability modifiers, reservoir fines stabilizers, tank/vessel sludge dispersants and drilling mud dispersants [52-54].

CONCLUSION

The purpose of this study is introduction surfactants and their application. Surfactants can used in Softening finishes, Lubricating agents in warp Sizing, sewage sludge, and particulate soil detergency. Most using surfactants in the textiles are softeners. A softener's active ingredient or compound deposition in the rinse cycle can be very high; approaching 90% in some cases the rinse deposition provided by a liquid fabric softener provides an advantage over dryer sheet softener deposition.

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