Part 1:

Part 2:

1-4- Surfactants in Textile Processing

1-4-1-Introduction

The Various unit operations of textile industry offer numerous opportunities for advantageous use of surface-active agents. As a consequence, a large number of such products is used in textile processing than in any other industry. Beginning with the invention of the sulfated oils about 1870, and continuing to the present decade, almost all new surface active products have been developed with a view toward specific textile applications [2].

During the conversion of textile fibers into various forms of textiles, from scoured fibers or filaments through to yarns or fabrics, some processes involve treatments in aqueous solutions. The use of water as a medium for textile processing ideally requires that liquid wets the fiber surfaces quickly and uniformly, and here surfactants play a useful role. In addition, surfactants may be required for detergency, achievement of level dyeing, and so on, and the choice of a particular surfactant for a particular purpose depends on its ability to interact with fibers and/or other components in the system [6].

Textile finishing is any treatment applied to fabric (after weaving process) to improve its properties such as desizing, scouring, beaching, dyeing, printing, specific finishing (softening finishes, crease resistant finishes, water repellent finishes,…). Active matters of most textiles finishing processes are surfactants [2,7]. In most instances, the fact that the finishing compound happens to be surface active has little to do with its application or its utility as a finish. In order to make a fabric water-repellent or to give it a soft handle, it is expedient to apply long-chain fatty or oily compounds to the fiber surface. One of the practical methods for depositing and attaching fatty chain compounds on a fiber surface is to introduce a solubilizing group into the fatty molecule. The resulting compound is then water-dispersible and can be applied from an aqueous medium in controlled concentrations. The introduction of certain solubilizing groups may even confer substantivity, thus facilitating and strengthening the attachment of the finish to the fabric [7].

1-4-2-Surfactants Applications in Textile Processing

Some of most important applications of surfactants in textile processing are:

1-4-2-1-Wetting

When treating textiles by immersion in aqueous solutions it is essential to ensure that air be displaced quickly and thoroughly from between the fibers or filaments so as to establish contact between the textile surfaces and the treatment bath. Success depends on a number of factor [6]:

1- Different fibers vary in wettability because of their different chemical structures. For example, according to presence of polar groups in cotton fibers, they wet easily but polyester filaments are wetted only with difficulty.

2- Geometric arrangements of fibers in yarn and fabric influence wettability of the material. Wetting of compact fabrics is more difficult.

3- Presence if impurities (wax, soils, …) influence wettability of fabrics. For example, while raw cotton contaminated with wax is very difficult to wet, scoured and bleached cotton is wetted very easily.

Some commercially available wetting agents which are used in textile processing (Sizing, Dyeing, Printing, …) include surfactants in their compositions [11]:

1. **Phosphoric Esters**
2. **Alkylaryl Ethoxylates**
3. **Diisooctyl Sulfosuccinates**
4. **Fatty Alcohol Ether Sulfate**
5. **Alkylaryl Polyglycol Ether Sulfate**

…

1-4-2-2-Detergency

Scouring processes remove foreign materials from the fibers and are more difficult for natural fibers such as cotton and wool than synthetic fibers. For example, impurities of cotton (sizing agents, wax, pectines,…) are up to 20% and for wool (wax, grease, dust, soil,…) are up to 50% of weight of fibers [11,12].

Surfactants constitute the most important group of detergent components, and they are present in all types of detergents. [3,5].

Some commercially available detergents which are used in textile processing (scouring,…)

include anionic and nonionic surfactants in their compositions [11]:

1. **Carboxylic Acids and Salts**
2. **Sulfuric Acid Derivatives**
3. **Sulfonic Acids and Salts**
4. **Alkoxylated Alcohols**
5. **Alkanolamides**
6. **Ethoxylated Fatty Acids**

…

1-4-2-3-Dispersing Agents

Insoluble dyes applied in the form of aqueous dispersions are used in a large number of dyeing and printing processes. Dispersants are required to produce the dye preparation for these processes and to stablize the finely dispersed state during application. Powdered dispersion and vat dyes contain 50-80% of these products. To maintain the stability of the dispersion throughout the dyeing or printing process, additional dispersant is added to the dye bath.

The dyes in print pastes must be in a completely dissolved or very finely divided form, otherwise problems could arise during the printing processes, resulting in uneven prints. Dispersing agents can cause insoluble dyes to become finely dispersed during the preparation of the print paste, and stablize this state of dispersion.

Some of the most important surfactants used as dispersing agents are listed below [5,11]:

1. **Alkali Metal Derivatives of Unsaturated and Aromatic Hydrocarbons**
2. **Alkali Metal Alcoholates**
3. **Anhydrous Alkali Metal Soaps of Higher Fatty Acids**

…

1-4-2-4-Antistatics

The rapid growth of the synthetic fiber industry has greatly emphasized the importance of antistatic finishes. Cotton and viscose rayon under normal humidity conditions do not generate static electricity to any troublesome extent. Acetate rayon and wool generate static electricity more readily, and necessitate precautionary measures in the mills where they are fabricated. Different types of antistatic finishes are based on increasing of the electrical conductivity of the fiber surface. Antistatic compounds are not only applied at the mill but are also sold for use by laundries and dry cleaners and for home use, to be applied as a final rinse after laundering. Antistatic compounds are also used for spray application to rugs, carpets, upholstery, auto seat covers, etc. [7].

Similarly charged textiles repel each other and are attracted by conductors nearby, by machine parts, or by the human body, in which the opposite charge is produced by induction. The latter effect is well known to occur in underwear made from man-made fibers and charges are induced in adjacent garments, causing them to stick to the body. By walking over non-conducting floor covering, the body potential can be raised and an electric shock may be felt when an earthed object is touched. Small and harmless though these shocks are to human beings, they may cause difficulties in the operation of electronic equipment [6].

Cationic surfactants are quite widely used as antistatic agents. Commercial antistatics are included surfactants with following structures [5,7,11]:

1. **Cationic or Neutral Nitrogenous Compounds**
2. **Polyhydroxy and Polyethenoxy Nonionic Compounds**
3. **Long Chain Phosphates, Phosphonates Derivatives**
4. **Sulfonated Oil and Sulfonated Ester Emulsions**

…

1-4-2-5-Softeners

Softeners are of great importance in textile processing and, these days, almost every single textile piece leaving a textile mill is treated with a softener. The aim of this treatment is to achieve a soft handle to facilitate the processability and improve wearability.

The chemical nature of softeners can either be cationic, anionic or non-ionic. Most of the long-chain quaternary ammonium salts, particularly those in which the straight C_{18} chain is present, have a marked softening action on cellulosic fabrics [16].

1. **Cationic Surfactants (** $R-NH_2.HX, RN(R_1)(R_2).HX, RN^{+}(R_1)(R_2)(R_3).X$ **)**
2. **Anionic Surfactants (** $R-SO_3.M, R-OSO_3.M$ **)**
3. **Nonionic Surfactants (** $R(OC_2H_4)_nOH$ **)**

R=Alkyl or Aryl X=Chloride, Acetate, Glycolate M=Na,K

1-4-2-6-Leveling Agents for Dyeing

Leveling agents promote uniform distribution of the dye in the textile in the exhaustion dyeing process, so that the dyeing is level, with a uniform shade and depth of color. Leveling agents act mainly by reducing the dyeing rate, increasing the rate of migration of the dye within the textile, and improving the compatibility of dyes.

$$H_3{}^{+}N-R-COOH$$

$$\uparrow A^{-}, \uparrow S^{-}, \uparrow R^{-}$$

A=Acid, S=Surfactant, D=Acidic Dye (Anionic)

Fig. 2- Competition of Acid, Surfactant and Anionic Dye ions for cationic charged sites of wool

Another example of using leveling agents "retarders" are in dyeing of polyacrylonitrile fibers with cationic dyes. Cationic surfactants (quaternary ammonium salts in which the alkyl chain contained $C_{12}-C_{18}$) are recommended for this purpose. These cationic surfactants compete with cationc dyes for anionic dye sites of fibers, so retard dye sorption [6,11].

The most important leveling agents (surfactants) for different fibers are listed below:

1- Leveling agents for dyeing cellulose fibers with vat and direct dyes
Ployglycol Ether
Phosphoric Esters
Alkyl aryl Sulfonate
…

2- Leveling agents for wool dyeing with acid dyes
Alkyl Amine Ployglycol ether sulfate
Ethoxylated fatty acid amide derivative
Alkyl Amine Polyglycol ether
Fatty Amine Polyglycol ether
…

3- Leveling agents for dyeing Polyamide fibers
Fatty Amine Polyglycol Ether
Alkyl Amine Ethoxylate
Polyglycol Ether derivatives and sulfonate
…

4- Leveling agents for dyeing polyester fibers **with disperse dyes**
Modified Phosphoric Acid Esters
Alkyl Phenol and Fatty Acid Ploygl ycol Ethers
Carboxylic Acid Alkyl Esters
…

5- Leveling agents for dyeing polyacrylonitrile fibers with cationic dyes
Quaternary ammonium compound
Quaternary Fatty Acid Amine
...

1-4-2-7-Water-Repellents

The term water-repellents, as applied to fabrics, means that the fabric retains its air permeability but resist the passage of liquid water. A large number of variations on the above general principle depend on forming a water-soluble long-chain compound which can be applied to the fabric from aqueous solution and which is heat-labile, so that on drying and heating a water-insoluble, water-repellent finish is generated on fabric surface. The water solubility of the long-chain compound may be due to a cationic or an anionic solubilizing group or in some cases even to a nonionizing group [2,6,7].

Some of the most important surface active agents which are used for making fabrics water-repellent:

1. **Cationic Surfactants :**

$$RC(O)NH - CH_2 - N^+(R_1)(R_2)(R_3)$$

$$RO - CH_2 - N^+(R_1)(R_2)(R_3)$$

$$R - OC(O) - CH_2 - N^+(R_1)(R_2)(R_3)$$

2. **Methylol Stear Amides , Methylene Distear Amide**
3. **Pyridinium Compounds**

Part 3: Proposal for Ph.D. Project

Gemini surfactants are novel surfactants that are presently attracting considerable interest in the academic and industrial communities working on surfactants. The most important properties of gemini surfactants are lower CMC, higher surface activity (more efficiency in reducing the water surface tension) and special micelle structures. So we can expected lower consumption of the geminis in comparison with the conventional surfactants in a same applications even with better results. Because of the better surface activity, these surfactants can be used in wide range of applications in virtually every major industry (pharmaceutical, food, metal, paint, petroleum, polymer, textile, …) [36,37].

Study of gemini surfactants and investigation of their properties is in progress. Rosen and Tracy in their paper [38] in 1998 listed 60 papers and 40 patents and Zana in his review of dimeric surfactant [37] in 2002 referred to more than 200 papers in this field. Most of these papers are about synthesis, properties and different applications of such materials. But, unfortunately in the field of textile applications of gemini surfactants, there are few papers. Hamada et. Al. investigated solubilization capacity of disperse dyes in the presence of gemini cationic surfactants [95]. In the study of disperse dyeing of nylon and polyester fibers using gemini surfactants, it was concluded that these surfactants are good dispersing agents and can be applied as a controller of dyeing kinetics or an improver of dye uptake [96,97].

General applications of conventional cationic surfactants in the textile processing can be summarized as follows [2,6-8,17]:

1. Softeners
2. Antistatic Agents
3. Leveling agents or Retarder for Dyeing
4. Fastness improver after dyeing
5. Dispersing agents
6. Wetting Agents
7. Biocides
8. Water-Repellents

So, according to advantageous and special properties of cationic gemini surfactants in comparison with conventional ones and possibility of using them in textile processing, we need more and precise investigation in this field.

First step in this proposal is synthesis and purification of some gemini cationic surfactants. Simple cationic geminis can be prepared as shown below by method A or B (with method B being preferable when n=2) [36]:

A) $2R-N(CH_3)_2+Br-(CH_2)_n-Br \longrightarrow R-N^+(CH_3)_2-(CH_2)_n-N^+(CH_3)_2-R$

B) $2R-Br+(CH_3)_2N-(CH_2)_n-N(CH_3)_2 \longrightarrow R-N^+(CH_3)_2-(CH_2)_n-N^+(CH_3)_2-R$

Typically, one boils under reflux a Mixture of the reagents in dry ethanol for two or three days and purifies the product by recrystallization. Method A is attractive when the dibromide is reactive and commercially available. Synthesis procedures of some of gemini cationic surfactants are shown in (Fig. 11).

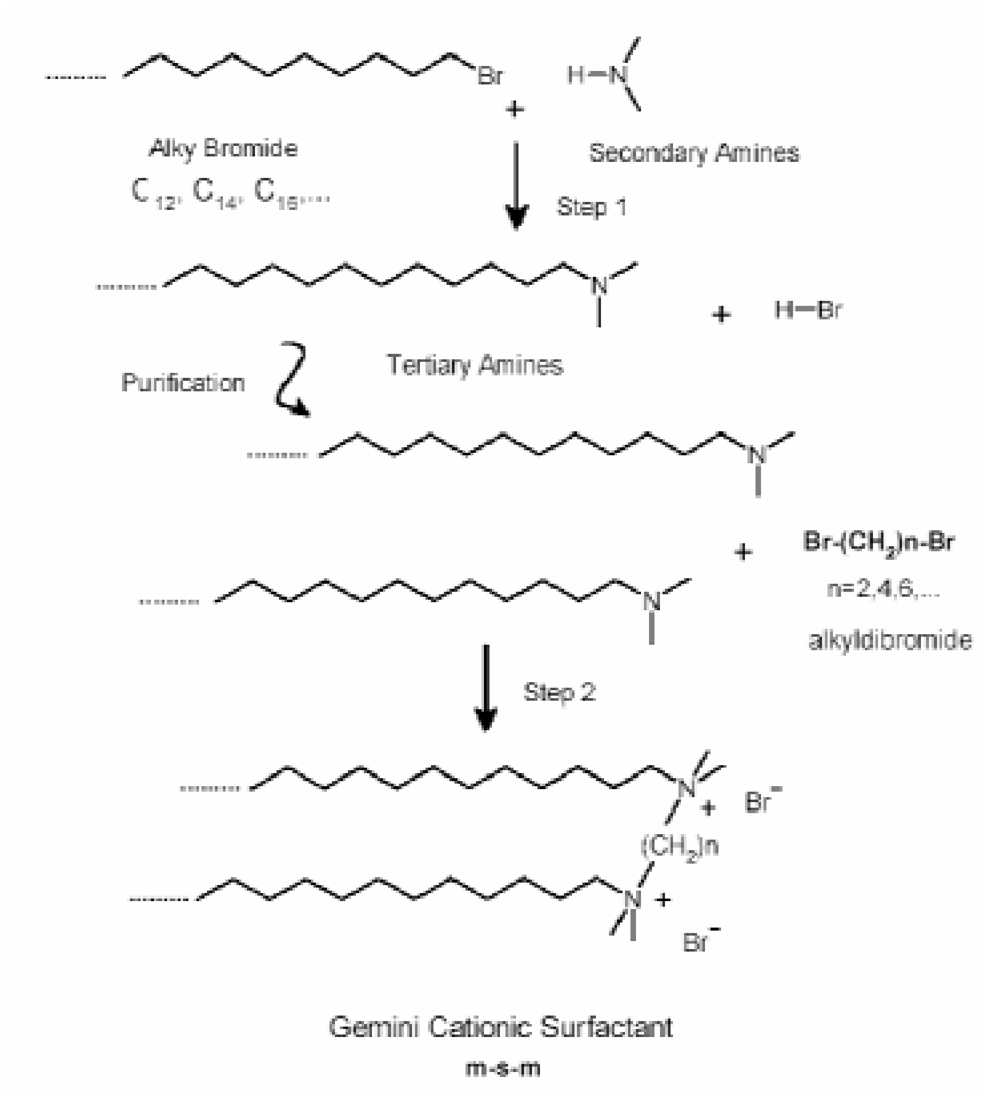

Fig 11. Synthesis procedures of some gemini cationic surfactants

The purification of the crude gemini surfactants is essential, particularly in studies of adsorption and behavior at interfaces. The purification procedures are somewhat easier for the quaternary ammonium gemini surfactants. Sophisticated procedures must often be used. Indeed one (or more) reaction step(s) that leads to gemini surfactants usually involves the two ends of some intermediate compound. This reaction rarely reaches full completion. It results in the formation of a mixture of mono and di functionalize compounds. Their separation is usually achieved through chromatography [37].

As with all surfactants, the purity of the geminis is of critical concern. We characterize them by $({}^{31}P, {}^{13}C, {}^{1}H)NMR$ spectroscopy, mass spectrometry (FAB), and elemental analysis.

Surface active properties of geminis such as CMC, C_{20},… will be determined by measuring surface tension of their solutions. After synthesis and purification, we apply them on different fabrics and investigate their applications in textile processing.

Equipments and instruments needed:

1. UV/Visible Spectrophotometer
2. Reflectance Spectrophotometer
3. Laboratory dyeing machine
4. Oven
5. Equipment for washing fastness investigation
6. Equipment for rubbing fastness investigation
7. Equipment for light fastness investigation
8. Heater stirrer
9. Instrument for measuring fabric hand
10. pH meter
11. Conduct-o-meter
12. Instrument for measuring static electricity of fabrics
13. Rotary-evaporator

…

Steps of this project are summarized in following table:

	Steps of Projects	Time (month)																	
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	Gathering more information	×	×	×															
2	Buying chemicals and other equipment	×	×	×															
3	Synthesis and purification of geminis			×	×	×	×	×	×										
4	Analysis, study purification (NMR,…)						×	×	×	×									
5	Study of surface active properties (CMC, …)										×	×	×						
6	Investigation of textile applications										×	×	×	×	×	×			
7	Writing Ph.D. thesis and papers																×	×	×

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