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The use of cationic surfactants in the textiles industry

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Abstract

extile processing involves the use of different types of specialty chemicals during the course of the conversion of textiles into finished fabrics, a large number of which generally are surface active agents, so much so that textile specialty chemicals are considered synonymous with surface active agents. This review discusses the theory of surface tension, and the classification of surfactants Highlights concerning cationic surfactants is also mentioned

Keywords: Textile printing, "cotton fabric", printing techniques, Inkjet, Discharge, Resist, and Transfer Printing.

Introduction

Textiles that are primarily used for their performance or functional properties and not for their appearance or aesthetics are known as technical textiles. The industrial fabrics that are used for various industrial applications are also classified as technical textiles. Not only a great variety of raw materials but a multitude of processes are employed for manufacturing technical textiles, including basic processes like weaving and knitting and more advanced processes from stitch bonding, chemical and thermal bonding to needle punching, and many more. All these processes result in various products such as fibers, yarns, and threads that are further used for making the finished technical textiles. [1, 2]

Not only this, but many processes also lead to the manufacture of end products like ropes, cords, bags, belts, etc. A textile fabric undergoes a series of wet processing operations to make it functional. Wet processing has been and will remain an important operation in the textile value chain; however, economic forces, market demands, and environmental concerns will shape the direction of wet processing in the foreseeable future. [3] Unlike apparel and furnishing fabrics, function is the most important attribute of technical textiles. Another way of categorizing technical textiles is by application. A distinction is generally made between fabrics for automotive, construction, safety, medical, geological, and agricultural applications. Technical textiles are used for a wide range of applications and are expected to meet very high-quality standards and demand specifications for coloration and finishing. Specialty surfactants play a key role during pre-treatment, dyeing, and finishing in meeting these standards of the finished fabrics. [4]

The various unit operations of technical textile processing offer numerous opportunities for the use of surface active agents. Beginning with the invention of sulfated oils about 1870, and continuing to the present decade, a wide range of surface active products has been developed with a view towards specific processing applications. [5] During the conversion of textile fibers into various forms of textiles, from scoured fibers or filaments to yarns or fabrics, many processes involve fabric 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

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surfactant for a particular purpose depends on its ability to interact with fibers and/or other components in the system. [6]

Textile processing consists of the following unit operations: desizing, scouring, bleaching, dyeing, printing, and the application of functional finishes. Finishing compounds for softening, crease resistance, water repellency, etc., contain surfactants as their active ingredient. [7] The fact that a finishing compound happens to be surface active has little to do with its application or its utility as a finish. To make a fabric water-repellent or to give it a soft handle, it is necessary to incorporate long-chain fatty or oily compounds into 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. [8, 9]

The Role of Surfactants in Surface Activity

Surfactant is a contraction of 'surface active agent'. It has come to be used interchangeably with detergent, particularly when applied to cleaning products such as fabric washing powders, soaps, hard-surface cleaners, and the many other products used for cleaning in and around the home. Solutions of surfactants exhibit one or more of the properties of detergency, foaming, wetting, emulsifying, solubilizing, and dispersing. [10]

Liquids, including water, exhibit surface tension at the liquid-air interface, and interfacial tension at the liquid-liquid or liquid-solid interfaces. This interfacial tension hinders water from penetrating textiles. [11] As water molecules are dipoles, there are physical electrical forces (van der Waals and dipole bonds) as well as hydrogen bonds between the molecules and the water. In a body of water, these electrical forces of attraction operate in all directions and each molecule is held in equilibrium. At the surface of the water, however, no forces are acting from the air outside, and hence the equilibrium is disturbed. The energy accumulated in the surface molecules of water is manifested as surface tension. So, molecules at the surface tend to be drawn inwards until the surface area is minimum. [12] Surface tension forces the surface of water in a measuring cylinder into a convex profile, and drops of water into a spherical form. Surface tension is measured in units of newtons per meter and the surface tension of water is 0.073 N/m. [13, 14]

Surface active agents, wetting agents, detergents and washing-off agents reduce the surface tension of water. When added to water, these agents more or less cover the liquid surface. They are not as strongly attracted to the inner water molecules as the water molecules were previously, hence the surface tension of water is reduced to 0.030 N/m in the presence of a surface active agent. [15] Hence surfactants are a very important group of textile auxiliaries. They find use as wetting agents, softeners, detergents, emulsifiers, and defoaming agents, to name a few applications. Commercial products rarely contain a pure compound, but rather mixtures or blends of surfactants to tailor their properties to the tasks in demand. [16]

Classification of surfactants

From the commercial point of view, surfactants are often classified according to their use. However, this is not very useful because many surfactants have several uses, and confusion may arise from that. The most accepted and scientifically sound classification of surfactants is based on their dissociation in water. [17]

Nonionic Surfactants come as a close second with about 45% of the overall industrial production. They do not ionize in aqueous solution, because their hydrophilic group is of a nondissociable type, such as alcohol, phenol, ether, ester, or amide. [18] A large proportion of these nonionic surfactants are made hydrophilic by the presence of a polyethylene glycol chain, obtained by the polycondensation of ethylene oxide. They are called polyethoxylated nonionic. In the past decade glucoside (sugar-based) head groups, have been introduced in the market, because of their low toxicity. [19] As far as the lipophilic group is concerned, it is often of the alkyl or alkyl benzene type, the former coming from fatty acids of natural origin. The polycondensation of propylene oxide produces a polyether that (in opposition to polyethylene oxide) is slightly hydrophobic. This polyether chain is used as the lipophilic group in the so-called polyEOpolyPO block copolymers, which are most often included in a different class, e.g. polymeric surfactants, to be dealt with later. [20]

Anionic Surfactants are dissociated in water in an amphiphilic anion, and a cation, which is in general an alkaline metal (Na+, K+) or a quaternary ammonium. They are the most commonly used surfactants. They include alkyl benzenesulfonates (detergents), (fatty acid) soaps, lauryl sulfate (foaming agent), di-alkyl sulfosuccinate (wetting agent), lignosulfonates (dispersants), etc... Anionic surfactants account for about 50 % of the world production. [21]

Cationic Surfactants are dissociated in water into an amphiphilic cation and an anion, most often of the halogen type. A very large proportion of this class corresponds to nitrogen compounds such as fatty amine salts and quaternary ammoniums, with one or several long chains of the alkyl type, often coming from natural fatty acids. These surfactants are in general more expensive than anionics, because of the high-pressure hydrogenation reaction to be carried out during their synthesis. [22] As a consequence, they are only used in two cases in which there is no cheaper substitute, i.e. (1) as a bactericide, (2) as the positively charged substance that can adsorb on negatively charged substrates to produce antistatic and hydrophobic effects, often of great commercial importance such as in corrosion inhibition. [23]

When a single surfactant molecule exhibit both anionic and cationic dissociations it is called **amphoteric or zwitterionic**. This is the case with synthetic products like betaines or sulfobetaine and natural substances such as amino acids and phospholipids. [22]

Some amphoteric surfactants are insensitive to pH, whereas others are cationic at low pH and anionic at high pH, with an amphoteric behavior at intermediate pH. Amphoteric surfactants are generally quite expensive, and consequently, their use is limited to very special applications such as cosmetics where their high biological compatibility and low toxicity are of primary importance.[24]

A surfactant reduces the surface tension of a liquid in which it is dissolved. Since surfactants exhibit other properties, they are often labeled according to their main use, e.g. soap, detergent, wetting agent, dispersant, emulsifier, foaming agent, bactericide, corrosion inhibitor, anti-static agent, etc. They are also described according to the form they take, e.g. membrane, microemulsion, liquid crystal, liposome, gel, etc. Surfactants are amphiphilic in their molecular structure, that is, their molecules are composed of two groups with contrasting solubility. When molecules of this structure are introduced to an oil-water interface, they align themselves at that interface, with the hydrophilic group being solubilized into the aqueous phase and the hydrophobic group being solubilized into the organic phase. [25, 26]

Not all amphiphiles display such activity: only amphiphiles with hydrophilic and lipophilic properties are likely to migrate to the surface or interface. If the amphiphilic molecule is too hydrophilic or too hydrophobic, it stays in one of the phases. If the surfactant molecular structure is linear, as in the case of sodium dodecyl sulfate (SDS), a planar monolayer of surfactant molecules is formed at the interface. [27] With more active shearing and mixing, these types of surfactants can form oil-inwater (O/W) and water-in-oil (W/O) dispersions by forming droplet structures called micelles of one phase dispersed within the other. The reduction in surface free energy due to surfactant saturation and the preference for adopting a radius of curvature explains this behavior. The equilibrium interfacial free energy in such systems is extremely low, and the combined surface free energy of the micellar

structure, though positive, is counterbalanced by the entropy of dispersion of the structures within the continuous phase. [28]

Fluid surface tension is the tangential force that keeps a fluid together at the air/fluid interface. It is the intermolecular force of attraction between adjacent molecules, expressed in force per unit width, as dynes/centimeter (dynes/cm) or millinewtons/meter (mN/m). Water, at ambient temperature, has a high surface tension in the range of 72 dynes/cm, while alcohols are in a low range of 20 to 22 dynes/cm. Solvents, typically, are in the 20 to 30 dynes/cm range. [29]

Surface tension: If any formulation changes at the molecular level then the surface tension will change. If the formulation changes due to the addition of another chemical, the addition of a surfactant, or any fluid in question, then the surface tension will change as explained in Fig. 1. Measuring surface tension is a direct indicator of the quality of any chemical and any formulation. Surfactants reduce the surface tension of solvents, water, and waterbased solutions, inks, fountain solutions, adhesives, and other coating formulations to a great extent. To reduce the surface tension, however, the surfactant molecules have to migrate to the interface, and this takes a finite amount of time. [30, 31] Given enough time. the formulation will eventually reach equilibrium (static) surface tension. This takes several seconds or even several minutes depending on the type of surfactant and the concentration. If enough time for the solution to reach equilibrium is not allowed, then it is operating in a dynamic zone and the measurement parameter is called 'dynamic surface tension'. [32]

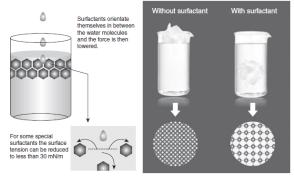


Figure (1) Surface tension and the influence of surfactants on surface tension

Applications of Surfactants in the textile field *Pre-treatment – wetting*

When treating textiles by immersion in aqueous solutions it is essential to ensure that air is displaced quickly and thoroughly from between the fibers or filaments to establish contact between the textile surfaces and the treatment bath. The efficiency of this process depends on several factors: [33] • Different fibers vary in wettability because of their different chemical structures. For example, due to the presence of polar groups in cotton fibers, they wet easily but polyester filaments are wetted only with difficulty.

- Geometric arrangements of fibers in yarn and fabric influence the wettability of the material. Wetting compact fabrics is more difficult.
- The presence of impurities (wax, soils) influences the wettability of fabrics. For example, while raw cotton contaminated with wax is very difficult to wet, scoured and bleached cotton is wetted very easily. [34]

The wetting agents that are used in technical textile processing (sizing, dyeing, and printing) include the following surfactants in their compositions:

- Phosphoric esters
- Alkyl aryl ethoxylates
- Diisooctyl sulphosuccinates
- Fatty alcohol ether sulfate
- Alkyl aryl polyglycol ether sulfate.

Multifunctional specialty surfactants have been developed that allow the combining of two or more operations, thereby saving time, water, and energy. [35]

Scouring

Scouring processes remove foreign materials from the fibers and are more difficult for natural fibers such as cotton and wool than for synthetic fibers. For example, impurities of cotton (sizing agents, wax, pectins, etc.) are up to 20%, and for wool (wax, grease, dust, soil, etc.) up to 50% of the weight of the fibers. Surfactants constitute the most important group of detergent components and are present in all types of detergents. Some of the scouring agents which are used in technical textile processing include

- Carboxylic acids and salt
- Sulphuric acid derivatives
- Sulphonic acids and salts
- Alkoxylated alcohols
- Alkanolamides
- Ethoxylated fatty acids. [36]

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 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. 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 a 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. Cationic surfactants are quite widely used as antistatic agents. [37, 38]

Commercial antistatics are included surfactants with the following structures:

- Cationic or neutral nitrogenous compounds
- Polyhydroxy and polyethylene non-ionic compounds
- Long-chain phosphates and phosphonate derivatives
- Sulphonated oil and sulfonated ester emulsions. [39]

Softening

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. This treatment aims to achieve a soft handle to facilitate processability and improve wearability. 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. The chemical nature of softeners can be cationic, anionic, or non-ionic: [40]

- Cationic surfactants R_NH2.HX, RN (R1) (R2).HX, RN+ (R1) (R2) (R3).X
- Anionic surfactants R_SO3.M, R_OSO3M
- Non-ionic surfactants ROC2H4 (R = alkyl or aryl, X = chloride, acetate or glycolate, M = Na, K). [41]

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: [42]

H3 + N–R—COOH A–S–R Another example of using leveling 'retarder' agents is in the dyeing of polyacrylonitrile fibers with cationic dyes. Cationic surfactants (quaternary ammonium salts in which the alkyl chain contains 12–18 C–C) are recommended for this purpose. [43] These cationic surfactants compete with cationic dyes for anionic dye sites of fibers, so retard dye sorption. The most important leveling agents (surfactants) for different fibers are listed below:

- Leveling agents for dyeing cellulose fibers with vat and direct dyes:
 - Polyglycol ether Phosphoric esters Alkyl aryl sulphonate[44]
- Leveling agents for wool dyeing with acid dyes:
 - Alkyl amine polyglycol ether sulfate
 - Ethoxylated fatty acid amide derivative
 - Alkyl amine polyglycol ether
 - Fatty amine polyglycol ether [45, 46]
- Leveling agents for dyeing polyamide fibers:
 - Fatty amine polyglycol ether
 - Alkyl amine ethoxylate
- Polyglycol ether derivatives and sulphonate[47, 48]
- Leveling agents for dyeing polyester fibers with dispersed dyes:
 - Modified phosphoric acid esters
 - Alkyl phenol and fatty acid ployglycol ethers
 - Carboxylic acid alkyl esters [49, 50]
- Leveling agents for dyeing polyacrylonitrile fibers with cationic dyes:
 - Quaternary ammonium compound
 - Quaternary fatty acid amine. [51, 52]

Water-repellent finishes

The term water repellency, as applied to fabrics, means that the fabric retains its air permeability but resists the passage of liquid water. A large number of variations on the above general principle depend on forming a water-soluble long-chain compound that can be applied to the fabric from an aqueous solution and which is heat labile so that on drying and heating a water-insoluble, water-repellent finish is generated on the 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 non-ionizing group. Some of the most important surface active agents which are used for making fabrics water-repellent are as follows:

- Cationic surfactants: R-CO-NH-CH2-CH2-CH2-NH-(CH3)
- Methylol stearamides: C₁₉H₃₉NO₂
- Ethylene bisstearamide: $(CH_2NHC(O)C_{17}H_{35})_2$
- Lauryl pyridinium chloride: C₅H₅NClC₁₂H₂₅ [53-55]

Cationic Surfactants

Cationic surfactants account for only 5-6% of the total surfactant production. However, they are extremely useful for some specific uses, because of their peculiar properties. They are not good detergents nor foaming agents, and they cannot be mixed in formulations that contain anionic surfactants, except for non-quaternary nitrogenated compounds, or when a catanionic complex synergetic action is sought. Nevertheless, they exhibit two very important features. [56, 57]

First, their positive charge allows them to adsorb on negatively charged substrates, as most solid surfaces are at neutral pH. This capacity confers to them an antistatic behavior and a softening action for fabric. The positive charge enables them to operate as floatation collectors, hydrophobin agents, corrosion inhibitors as well as solid particle dispersants. They are used as emulsifiers in asphaltic emulsions and coatings in general, in inks, wood pulp dispersions, magnetic slurry, etc. On the other hand, many cationic surfactants are bactericides. [58]

Cationic surfactants are dissociated in water into an amphiphilic cation and an anion, most often of the halogen type. Many are nitrogen compounds, such as fatty amine salts and quaternary ammoniums. The standard classification of these surfactants is based on their dissociation in water. The hydroxide used to neutralize the acid is of great importance, because of the hydrolysis reaction which takes place in water. With very alkaline hydroxides, e.g. NaOH or KOH, the pH of the soap aqueous solution is very high. This increases cleaning power but can damage the skin. Selecting the soap cation controls the balance of cleansing action and solubility. [59]

The use of organic hydroxides such as ammonia, amine, amide, or ethanol amine results in a less alkaline soap, although one which is less water soluble. For instance, triethanolamine oleate is a common soap used in cosmetics as well as in dry cleaning formulas. Calcium and magnesium soaps are oil soluble and are used as detergents. Cu soap exhibits fungicidal properties. Cationic surfactants find application as leveling agents in acrylic dyeing with cationic dyes; alkyl dimethyl ammonium chloride is a typical example. They are produced by the benzylation of fatty amines such as cocoamine, lauryl amine, etc., under controlled conditions. [60] The structures of various cationic surfactants are shown in Figs 3–5.

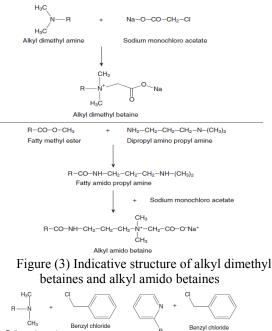
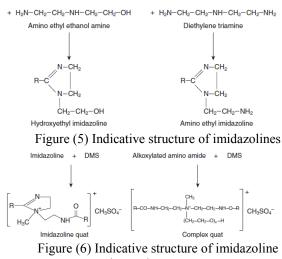




Figure (4) Indicative structure of benzyl quats

R-COOH Fatty acid



and complex quats

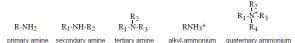
Linear Alkyl-Amines and Alkyl-Ammoniums Nomenclature for amines and non-cyclic ammoniums

The most used cationic surfactants are fatty amines, their salts, and quaternary derivatives. Fatty amines are not cationic but anionic surfactants. However, they are generally classified as cationic because they are mostly used at acid pH, in which their salts are cationic. [61, 62]

Cationic surfactants may be classified as

- I. Amine salts (primary, secondary, and tertiary)
 - The amino group joined directly with the hydrophobic group
 - The amino group joined through an intermediate linkage [63]
- II. Quaternary ammonium compounds
 - Nitrogen joined directly to the hydrophobic group
 - Nitrogen joined through an intermediate linkage [64]
- III. Other nitrogenous bases
 - Non-quaternary bases (e.g. guanidine, thioronium salts, etc.)
 - Quaternary bases. [65]

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 quaternary ammonium. [66]



In an ammonium structure, the nitrogen atom gives two electrons to ensure the fourth bond and thus remains with a positive charge. Alkylammonium ions are produced in the 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. [67]

$$R-NH_2 + H^+C1^- \rightarrow R^-NH_3^+C1^-$$

amine alkyl-ammonium salt

Fatty amines come from fatty acids; hence their chain is linear with an even number of carbon atoms. The IUPAC nomenclature uses common names.

 $C_{12}H_{25}NH_2$ Dodecyl amine or Lauryl amine, or even coco (C12-C14) amine When the substance contains more than one long alkyl group, the longest is named first as in the following substances. [68] $C_{14}H_{29}NHCH_3$ Tetradecyl methyl amine

 $C_{16}H_{33}-N^+(CH_3)_3 Br^-$

Cetyl trimethyl ammonium bromide (CETAB) or Hexadecyl trimethyl ammonium bromide (HTAB)

Another common product is formed with a long alkyl chain and different short substituents such as two methyls and one benzyl group.



Benzalkonium or alkyl dimethyl benzyl-ammonium chloride

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.

$\text{R-COOH} + \text{NH}_3 \rightarrow \text{RCONH}_2 + \text{H}_3$	H ₂ O amide (by dehydration)
$R\text{-CONH}_2 \rightarrow RC=N + H_2O$	nitrile (by heating/dehydration)
$R-C=N + 2 H_2 \rightarrow R-CH_2NH_2$	amine and other products (by hydrogenation)

If the primary amine is transformed into a secondary amine by catalytic removal of ammonia, the two alkyl groups are the same.

$2 \text{ R-NH}_2 \rightarrow \text{ R-NH-R} + \text{ NH}_3$

In general, only one long alkyl group is required. Hence, the secondary amine is obtained by methylation, either by the reaction of methyl amine on nitrile or by reductive methylation with formaldehyde. [69]

Preparation Of Quaternary Alkyl-Ammoniums (Quats)

Primary and secondary amines are quaternized by exhaustive methylation with methyl chloride, with the removal of produced HCl to displace the reaction. $R_1R_2NH + 2 CH_3C1 \rightarrow R_1R_2N^+(CH_3)_2 Cl^- + HCl^{\dagger}$

Another way is to react an alkyl bromide with a tertiary amine. This is the usual way to prepare the cetyltrimethyl-ammonium bromide (CETAB).

 $C_{16}H_{33}Br + N(CH_3)_3 \rightarrow C_{16}H_{33}-N^+(CH_3)_3 Br^-$

If a sulfate anon is required, the quaternization of the tertiary amine is carried out with dimethyl or diethyl sulfate.

 $R_1R_2CH_3 + (CH_3)_2SO_4 \rightarrow R_1R_2N^+(CH_3)_2 + CH_3SO_4^-$

All these methods result in alkyl ammoniums displaying different alkyl groups.

Salts of primary amines: These have the general formula RNH, HX (where R = alkyl, X = chloride, acetate, glycolate). A typical representative of this group is octadecyl ammonium chloride, which can be obtained by neutralizing the corresponding octadecyl amine. Fatty amines are synthesized by hydrogenation of fatty nitriles obtained from the dehydration of fatty amides. Fatty amides can be directly synthesized from the fatty acid and ammonia. Derivatives with chains long enough for imparting adequate lubricity and softness have relatively poor solubility. This group is relatively unimportant for textile operations. [70]

Salts of tertiary amines: These have the general formula RN(R')(R'').HX (where $\mathbf{R} = alkyl$, X = chloride, acetate, glycolate). These derivates can be obtained by converting tertiary amines into the corresponding salts with organic or inorganic acids. The tertiary amines can be obtained by alkylation of secondary amines with fatty chlorides or fatty alcohols. There are several trade-name products that are used as emulsifiers and scouring and wetting agents.

Quaternary ammonium salts: These have the general formula RN(R')(R'')(R)X (where R = alkyl, X = chloride, alkyl sulfate). This well-known group is synthesized by treating a tertiary amine with alkyl halides, alkyl sulfates, etc. A typical representative is distearyl dimethyl ammonium chloride 1. Despite having better solubility than the corresponding salts of primary and tertiary amines, the technical use of this group is limited due to their low biodegradability.

Salts of amino amides: These have the general formula RCON(R')(R'')[N(R''')(R''')]n(-wHhXe re R = H, alkyl, X = acetate, glycolate). These important types of softeners can be prepared either by direct amidation of a polyamine with fatty acids or by aminolysis with triglycerides such as

hydrogenated fat or oil. The use of hydrogenated tallow, which is a 60:40 mixture of stearic and palmitic acid or hydrogenated palm oil, is very common. The most common polyamines are amino ethyl ethanol amine and diethylene triamine, as well as trimethylene tetramine and tetramethylene pentamine. Generally, the solubility in water and mild alkali increases as the number of amino groups increases. All reaction products are neutralized with acids (such as acetic or glyoxalic acid) to form the corresponding salts, which are 'pseudo-quaternary'. These products show excellent softness on many types of textiles. Further improvement of the solubility especially in alkaline solutions can be achieved by alkylation of the amino amides with alkyl halides or alkyl sulfates to form quaternary ammonium salts of amino amides. The degree

of hydrogenation of the fat is very important; the lower the iodine value, the better the softness, and the lower the yellowing after drying. [71]

Salts of imidazolines: Imidazolines are synthesized by reacting fatty amides with polyethylene polyamines under the removal of water. The reaction products can be further alkylated with alkyl halides or alkyl sulfates to form quaternary imidazolines. Residual amino groups in imidazolines can also be neutralized with organic acids to form the corresponding ammonium salts. [72]

Salts of amino esters: These have the general formula RCOOR'N(R')(R)(R)X (where R = alkyl, hydroxyalkyl, X = chloride) These compounds can be obtained by reacting fatty acids with amino alcohol. Triethanol amine is the preferred alcohol, because one, two, or three of its hydroxy groups may be esterified according to the composition of the reaction mixture. Alternatively, di ethanol amine or mono ethanol amine can be used. The corresponding quaternary salts can be produced with alkylating agents like alkyl halides or alkyl sulphates. Therefore this

group is often called 'esterquats'. As in many other cases the solubility, wetting and lubricating properties can be adjusted by the chain lengths of the fatty acids. [73]

Applications of cationic Surfactants

Fabric softeners represent the largest portion of cationic surfactants, accounting for 23% of global consumption (Figure 1). Personal care products are the second largest portion (19%), followed by textile auxiliaries (12.6%), dishwash detergents (10.5%), household cleaners (7.8%), laundry and cleaning products (5.6%) and biocides (4%). Industrial markets such as asphalt emulsifiers, corrosion inhibitors, fuel and plastic additives account for the remainder. [74]

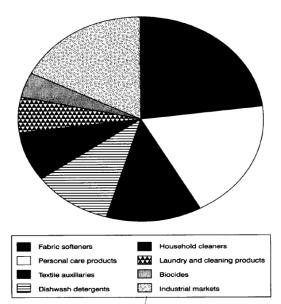


Figure (7) Composition of the various categories of cationic surfactants

Cationic Softener

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. This treatment aims to achieve a soft handle to facilitate processability and improve wearability. Often a pleasantly soft handle of a fabric is the decisive criterion in purchasing a textile article and therefore is often regarded to be the most important factor for saleability.

Softeners are predominantly used for textiles: to apply the desired softness (which can often be described as smooth, supple, supersoft, elastic, dry, or slushy); to influence/improve technical properties such as antistatic, hydrophilicity, elasticity, sewability, rub fastness; and to give synthetic fibers a certain 'natural touch' and enhance the comfort of wearing by promoting secondary effects (moisture regulation, smoothness). Among all the different types of softeners, cationic agents were well-known and mainly used.

Quaternary and pseudo-cationic softeners: According to their chemical nature, pseudo-cationic softeners have a pH-dependent positive charge. The charge of quaternary softeners is not pH-dependent. Due to their charge such products can be used in padders as well as in exhaust processes. They give the best softness and exhaust to almost all fibers, however, a common problem is a poor compatibility with anionic products (such as optical brighteners or dyeing auxiliaries) and the tendency to result in yellowing at higher drying temperatures. Worldwide such products have a significant market share in the softening of dyed textiles. The most common compounds used for special effects are silicones,+ polyethylenes, paraffin, and/or amphoteric. [75]

Components	and	technical	effects	of	the	most
common cationic softeners						

Component	Technical effect	Final result		
Quaternary substances	Quaternary substances	soft handle, volume, body, drape		
Fatty acid esters		Improvement in		
Paraffin	smoothness	sewability, yarn knitting		
Polyethylenes		abrasive & ripping resistance		
Silicones	smoothness,soft	soft handle;		
Silicolles	ness	silicone touch'		
Amphoteric	hydrophilicity, antistatic	absorbancy		

Mechanism of action of cationic softeners

The mechanism of action of fabric softeners involves drying the laundry in air, the laundry acquiring a harsh feel. Adding a liquid fabric softener to the final rinse (rinse cycle softener) results in the laundry that feels softer. Cationic softeners bind by electrostatic attraction to the negatively charged groups on the surface of the fibers and neutralize their charge. The long aliphatic chains then line up towards the outside of the fiber, imparting lubricity. Fabric softeners impart good antistatic properties on fabrics and thus prevent the build-up of electrostatic charges on synthetic fibers, which in turn eliminates fabric cling during handling and wearing, crackling noises, and dust attraction. Also, fabric softeners make fabrics easier to iron and help reduce wrinkles in garments. In addition, they reduce drying times so that energy is saved when softened laundry is tumbledried. [76]

Early cotton softeners were typically based on a water emulsion of soap and olive oil, corn oil, or tallow oil. Softening compounds differ in affinity to various fabrics. Some work better on cellulose-based fibers (i.e., cotton), while others have a higher affinity to hydrophobic materials like nylon, polyethylene terephthalate, polyacrylonitrile, etc. New silicone-based compounds, such as polydimethylsiloxane, work by lubricating the fiber.

Application

There are two principal methods of application of cationic softeners

1. Exhaustion from dilute baths

2. Padding from relatively concentrated solutions

The long bath (exhaustion) process is especially suitable because of the natural substantivity of the softeners and is usually adopted for knitted goods, not requiring resin treatment. With thermosetting resins (urea formaldehyde resin), cation lubricants/softeners are a valuable adjunct to the treatment; since, they are not appreciably removed in the subsequent washing operation and serve to reduce needle cutting during garment manufacture and generally impart improved tear and abrasion resistance. [77]

Laundry Cleaning of Textiles

Cationic surfactants are much less used in laundry detergents, due to their tendency to rapidly adsorb to - and not desorb from- the fabric and the soil (both having negatively charged surfaces under normal conditions). This property of adsorption on fabrics is used in fabric softening, where double longchain surfactant-like molecules are the standard "actives" used in all fabric softener formulations. If this double-long chain cationic actives were used in combination with anionic surfactants, they would also strongly interact with the anionics forming insoluble ion pairs, with negative results on overall detergency. [78]

However, low levels of soluble, single-shortchain cationic can have a positive cleaning effect when mixed with anionic surfactants, for example, by improving the packing of anionic surfactants at the soil interface. Examples of such cationic surfactants are C8-10 alkyl hydroxyethyl dimethylammonium chloride (Figure 8) or C8-10 alkylamidodimethyl propylamine (which will be partially protonated at wash pH). Other surfactants with similar functionality, although formally not cationic under typical wash conditions, are the alkyl dimethyl amine oxides (Figure 9). [79]

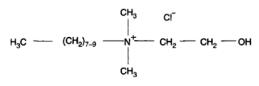


Figure (8): Alkyl hydroxyethyl dimethyl ammonium chloride

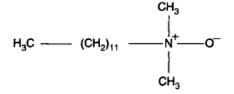
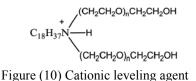


Figure (9): Alkyl dimethyl amine oxide

Surfactants are easier to process and incorporate into liquid formulations than powders, where they (especially the ethoxylated alcohols) can cause stickiness and caking. Thus, today's heavy-duty liquid detergents typically contain higher surfactant levels than powder and generally offer better performance for the removal of greasy/oily stains. [80]

Leveling agents

A cationic polyethoxylated amine can perform strong leveling action. The greater cationic character is a strong complex formation, pronounced retardation of dyeing, and a higher risk of precipitation (Figure 10). The polyethoxylated chain is longer (n > 50), and the dye auxiliary complex is dispersed by the cationic leveling agents. Amphoteric leveling agents have both anionic and cationic groups, so their activation depends on the dye bath pH. [81]



Sasmita Baliarsingh et al studied the role of cationic and anionic surfactants for dyeing silk and cotton yarns using native plant extracts. Results showed that dyes obtained from native plants can be an alternative source to synthetic dyes, with the potential for upgradation from medium to large-scale industrial production and marketing. Natural dyes can be a sustainable alternative to synthetic dyes in developing countries. [82]

Cationic Bleach Activators (CBAs)

Cationic bleach activators have the potential to exhibit inherent substantivity for the fiber which at the same time exhibits the same mechanism of activating peroxide. All of them react with peroxide to produce peracid which has higher efficiency in bleaching compared to the perhydroxyl anion obtained from the dissociation of H_2O_2 under alkaline conditions. [83]

Cationic bleach activators contain at least one cationic group, which can provide high water solubility. Compared to anionic bleach activators, cationic bleach activators have the potential to exhibit better performance because they exhibit inherent substantivity to the negatively charged surface of cellulosic fibers in neutral to alkaline conditions to provide enhanced bleaching efficiency, especially in low temperatures. [84]

Cationic bleach activators can be applied in cold pad batch or rapid hot peroxide bleaching for cotton. N-[4- (triethylammonium ethyl)benzoyl]caprolactam chloride (TBCC, 10) N-[4-(triethylammonium ethyl) benzoyl] butyrolactam chloride (TBBC) are two kinds of cationic bleach activator that exhibited satisfactory bleaching performance in a shorter time and at lower temperatures than conventional peroxide bleaching. This kind of bleach activator may improve the performance of rapid H_2O_2 hot bleaching. [85]

Changhai Xu et al studied the development of Cationic Bleach Activators (CBAs) for textile bleaching and discussed the opportunities and potential hurdles to commercialization. CBAs work by generating more kinetically active bleaching species (CPDC) by reacting with H2O2. The physical interaction between CBAs and cellulosic substrates appears to enhance bleaching. The hydrolytic stability of CBAs is important for practical utility in industrial textile bleaching. Experimental results revealed that the TBBC-activated peroxide system provides satisfactory factory bleaching performance under the conditions of equimolar amounts of TBBC and H2O2, neutral pH, 40-60 minutes dwell time, and 30 minutes dwell time. Further work is needed to investigate the effects of CBA-based bleaching on dyeing performance, pilot plant and full production scale-up, and the potential for improved benefits. [86]

Improved wet fastness

Cationic products for example polyammonium compounds, the so-called polyquats. Many successful products are based on quaternary poly heterocycles such as poly diallyl dimethyl ammonium chloride (DADMAC). They are mostly used for direct and reactive dyed cellulose and improve the wet fastness for about one too, at most, two ratings. The washing fastness is usually more improved than the contact fastness (water or perspiration fastness). Quaternary ammonium polymers are often used to shorten the long washing processes (soaping at the boil) of reactive dyes on cellulosic, thus providing relatively good wet fastness. [87] Their high affinity for cellulose enables exhaust application. But cationic products can cause several problems:

- Insufficient permanence of the effects of repeated washings, caused by salt formation with anionic surfactants and release of the immobilized dyestuff
- Variation of the degree of wet fastness improvement, depending on the specific dyestuff interaction
- Reduced light fastness and color changes, which are also dyestuff specific
- Competition with cationic soft handle products (blocking their uptake)
- Greying and increased soiling when applied in large amounts (cationized cotton)
- Stripping off is only possible with large amounts of anionic surfactants
- Fish toxicity, almost no biodegradation but a high rate of elimination in the wastewater

Mousa et al investigated the dyeing and fastness properties of three mono azo naphthylamide dyes on a polyester fabric in the presence of two Gemini cationic surfactants and a conventional single chain surfactant, dodecyl trimethylammonium bromide (DTAB). The color strength (K/S) of naphthylamide dyes increased in the presence of different cationic surfactants, and the washing and rubbing fastness properties improved with increasing the concentration of surfactants. The sublimation fastness of dye 3 was more than other dyes, and the light fastness of naphthalimide dyes was generally moderate. [88]

S. M. Burkinshaw et al studied The adsorption of a commercial system on both conventional and microfiber nylon 6,6 they found that it was increased with decreasing application pH and increased with increasing application temperature. It was postulated that adsorption involves the formation of multi-layers and forces other than ion-ion contribute to syntaxfiber interaction. The effectiveness of the system in improving the wash fastness of non-metalized acid dyes on microfiber was enhanced by the subsequent application of certain cationic agents. [89]

Antimicrobial Agents

Cationic surface-active (cationic agents surfactants), including particular quaternary ammonium salts (QASs), are important biocides that for many years have been known to be effective antiseptic and disinfectant agents. As antimicrobial agents for textiles, mono ammonium and "Gemini" or "dimeric" ammonium surfactants with an alkyl, alkyl aryl, and perfluorinated hydrocarbon group are used. These are active against a broad spectrum of microorganisms such as Gram-positive and Gramnegative bacteria, fungi, and certain types of viruses. [90]

The antimicrobial activity of QASs depends on the length of the alkyl chain, the presence of the perfluorinated group, and the number of cationic ammonium groups in the molecule. The antimicrobial function arises from attractive interactions between the cationic ammonium group of the QAS and the negatively charged cell membrane of the microbe; these interactions consequently result in the formation of a surfactant–microbe complex. This in turn causes the interruption of all essential functions of the cell membrane and thus the interruption of protein activity. [91]

QASs also affect bacterial DNA, causing a loss of multiplication ability. If the long hydrocarbon chain is bonded to the cationic ammonium in the structure of the QAS, two types of interactions between the agent and the microorganism can occur a polar interaction with the cationic nitrogen of the ammonium group and a non-polar interaction with Penetration the hydrophobic chain. of the hydrophobic the microorganism group into consequently occurs, enabling the alkylammonium group to physically interrupt all key cell functions. [92]

Diz et al. synthesized a new QAC, N-dodecylaminobetaine-2-mercaptoethylamine hydrochloride (DABM). DABM can react with wool utilizing its thiol group, either with cysteine-S-sulphonate residues (Bunte salts) of sodium bisulfite pretreated wool or with the disulfide bond of cystine wool, forming an asymmetrical disulfide bond. Such covalent attachment of the quaternary ammonium surfactant provides antimicrobial activity. [93, 94]

Sun and colleagues have hypothesized that dye molecules may act as bridges to bind functional molecules to the fiber surface. In their studies, the fabrics were first dyed with acid dyes before QACs were applied under alkaline conditions. The ionic interaction between the dye molecules and the QAC was sufficiently strong to provide a semi-durable antimicrobial finish. [95]

Conclusion

Cationic surfactants have relatively limited application due to restricted compatibility and costeffectiveness. Cationic surfactants are mostly used in finishing processes as softening/lubricating and antistatic/antimicrobial agents, for water/oil repulsion, and in dyeing as dye fixative and dye leveling agents. Amphoteric surfactants account for only a small proportion of total textile surfactants.

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استخدام مواد التوتر السطحى الكاتيونية في صناعة المنسوجات

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الملخص

تتضمن معالجة المنسوجات استخدام أنواع مختلفة من المواد الكيميائية المتخصصة أثناء تحويل المنسوجات إلى أقمشة نهائية ، وعدد كبير منها عمومًا عبارة عن عوامل نشطة سطحيًا ، لدرجة أن المواد الكيميائية المتخصصة في المنسوجات تعتبر مرادفًا للعوامل النشطة السطحية. تناقش هذه المراجعة نظرية التوتر السطحي ، كما تم ذكر تصنيف المواد الخافضة للتوتر السطحي.

الكلمات الدالة: طباعة المنسوجات ، "نسيج قطني" ، تقنيات الطباعة) نفث الحبر ، تفريغ ، مقاومة ونقل الطباعة).