

CHAPTER 8

HAND MODIFICATION

Hand or Handle are the terms used to describe how a fabric drapes around an object or feels to the touch. When the fabric becomes stiffer or bulkier, the hand of the fabric is said to be built. Chemicals that accomplish this are called *Handbuilders*. When the hand is made to drape more or to feel silkier, the fabric is said to have been softened. Chemicals that do this are called *Softeners*. Many softeners are derived from naturally occurring *Fats, Oils and Waxes*. Sources and reactions of fats, oils and waxes have been discussed in a Chapter 3. Some softeners are derived from synthetic raw materials. Many of the compounds that work as softeners also function as surfactants or water repellents. These topics are covered in greater detail in other sections. It is hoped that the reader will come to appreciate that certain chemicals can serve many functions as textile finishes and processing auxiliaries.

I. HANDBUILDERS

The purpose of applying handbuilders is to add bulk, weight or stiffness to a fabric. For some fabrics, this change must be permanent and withstand washing and dry-cleaning. In other applications, the change is temporary so handbuilders are classified as either durable or nondurable.

A. Non-durable

Non-durable handbuilders are used to impart better over-the-counter appearance to many fabrics. Starched fabrics have a greater consumer appeal than limp fabrics. They also improve the handling of flimsy fabrics in cutting and sewing operations since stiff fabrics are easier to manipulate than limp fabrics. Another reason for non-durable handbuilders is that some fabrics are traditionally expected to be stiff. For example, consumers expect Denim jeans to be stiff and boardy. They expect jeans to break in, become soft and comfortable and fade with repeated washing.

Most water soluble film forming polymers can serve as non-durable handbuilders. However starch and polyvinyl alcohol are the ones used most often.

1. Starch

Thin boiling starches and dextrin are preferred as finishes because high solids solutions can be prepared without the viscosity becoming so high that they cannot be applied with conventional paddlers. The starches used for finishing do not retrograde. The chemistry of starches has been discussed in detail in Chapter 1.

2. Polyvinyl Alcohol

When used as finishes, fabric stiffness can be achieved with higher molecular weight polymers at lower add-ons. However, increased bulk and weight can be obtained with higher add-ons of lower molecular weight polymers without over stiffening the fabric.

B. Durable

Durable handbuilders are used to improve the aesthetics of rayon fabrics. Fabrics made from conventional rayon fibers are limp and raggy and are very much improved with melamine resins. Durable handbuilders are also used to increase a fabric's weight and to improve toughness and abrasion resistance.

Thermosetting and thermoplastic polymers can serve as durable handbuilders. Finishers have many options to choose from to develop fabric hand. Cost, ease of application and ultimate fabric properties are factors to consider when choosing the appropriate material.

1. Thermosetting Polymers

Urea/formaldehyde and in particular, melamine/formaldehyde are thermosetting resins that stiffen fabric. The chemistry of these two have been described Chapter 7. While used primarily for crosslinking cellulosic fibers, they can also be used on other fibers as handbuilders.

a. Melamine/Formaldehyde

These resins form three-dimensional cross-linked polymers that impart bulk and resilience to fabrics. They are used on synthetic fibers, e.g. polyester, nylon acrylics, as well as cellulose and are durable to repeated laundering and dry cleaning.

b. Urea/Formaldehyde

Alkylated U/F's, e.g. butylated U/F are thermosetting hand builders. They are often used on rayon fabrics. However, the U/F's are not as durable to repeated

laundry as are the M/F's.

2. Thermoplastic Polymers

Stable water dispersion of high molecular weight thermoplastic polymers. serve as durable handbuilders. Vinyl and acrylic polymers are available as latexes or stable water dispersions and come as very high molecular weights materials with a wide range of Tg's. They can also be tailored to be crosslinkable. These products are usually engineered for other end-uses, e.g. non-woven binders, pigment binders, adhesives, carpet backing, paint binders etc. so there is an endless variety to chose from. The property of the dried film mainly depends on the combination of monomers used in the polymerization step. Film hardness, stiffness, flexibility, elasticity, adhesiveness, color, solvent resistance etc. are all a function of the monomers.

As finishes, film properties of the latex can be used to engineer the fabric hand. For example, polymers with a very high Tg add stiffness without adding weight. Poly(methylmethacrylate) latexes dry down to form very stiff films so it doesn't take much add-on to stiffen a fabric. On the other hand, ethyl or butyl acrylate polymers dry down into softer, flexible films. They can be used to build-up weight without making the fabric excessively stiff.

Suitable Monomers/Comonomers

- Vinyl acetate
- Acrylonitrile
- Vinyl chloride
- Propylene
- Acrylate esters
- Styrene
- Vinyl ethers
- Methacrylate esters
- Butadiene
- Ethylene

Reactive Ter-Monomers

- Acrylic acid
- Hydroxyethyl acrylate
- Glycidyl methacrylate
- Methacrylic acid
- N-methylol acrylamide
- Acrylamide

II. FABRIC SOFTENERS

A *Softener* is a chemical that alters the fabric hand making it more pleasing to the touch. The more pleasing feel is a combination of a smooth sensation, characteristic of silk, and of the material being less stiff. The softened fabric is fluffier and has better drape. Drape is the ability of a fabric to follow the contours of an object. In addition to aesthetics (drape and silkiness), softeners improve abrasion resistance, increase tearing strength, reduce sewing thread breakage and reduce needle cutting when the garment is sewn. Because of these functional reasons,

softener chemicals are included in nearly every finish formulation applied to fabrics. Softeners are also applied by the consumer after fabrics are laundered. Here the softeners are either included in the rinse cycle or as dryer added sheets.

A. Coefficient of Friction

Softeners act as fiber lubricants and reduce the coefficient of friction between fibers, yarns, and between a fabric and an object (an abrasive object or a person's hand). Whenever yarns slide past each other more easily, the fabric will be more pliable and have better drape. If some of the lubricant transfers to the skin and the fabric is more pliable, the fabric will feel soft and silky. Lubricated fabric sliding against lubricated skin gives rise to lower coefficients of friction and a silky sensation. Tearing resistance, reduced abrasion and improved sewing characteristics are also related to lower coefficients of friction. Fabric tearing is a function of breaking yarns, one at a time, when tearing forces are applied to the fabric. Softeners allow yarns to slide past each other more easily therefore several yarns can bunch up at the point of tear. More fiber mass is brought to bear and the force required to break the bunch is greater than the force required to break a single yarn. Sewing problems are caused by the friction of a needle rapidly moving through the fabric. Friction will cause the needle to become hot and soften thermoplastic finishes on the fibers. The softened finish accumulates in the eye of the needle restricting the passage of the sewing thread creating more sewing thread breaks. A softener will reduce needle heat buildup, provide a steady source of needle lubricant and thus reduce thread breakage.

B. Viscosity

The viscosity of softener materials range from water like (machine oil) to semisolids (waxes). All are capable of reducing coefficient of friction and therefore are effective in overcoming sewing problems, improving tear, and improving abrasion resistance. However the lower viscosity oils are the ones that impart the soft silky feel and improve drape. The textile finisher has a vast array of softener materials to choose from. Since softeners are nearly always needed to improve physical properties, the variable in softener selection is the final fabric hand. When improved sewing, tear and abrasion properties are desired without the pliable, soft silky feel, hard or semi-solid wax lubricant such as paraffin or polyethylene will be appropriate. However if silkiness and drape are important, lower viscosity oils are the materials of choice.

C. Other Points of Concern

There are other important points to consider when selecting the appropriate material as a softener.

Color: Some softener materials are dark in color to begin with while others become dark when exposed to heat, light, oxygen, ozone, oxides of nitrogen or other airborne gases. These might not be a problem on dark shades but they are to be avoided for pastel shades and whites.

Odor: Some softeners develop odor with age. Fat based softeners develop a rancid odor (associated with aged fats) and should be avoided whenever possible.

Bleeding: Some lubricants are good solvents for surface dyes. Disperse dyes, as a class, are particularly prone to dissolve in softener materials. Color from darker yarns will migrate (bleed) to stain adjacent lighter yarns like might be found in a striped pattern.

Spotting: The volatility of softeners is also important. Softener materials that have low smoke points will condense and drip back onto the fabric causing unsightly spots. Smoke from heated oils and waxes are droplets of oil suspended in air. These droplets will condense when they come in contact with cooler surfaces and eventually drip.

Soiling: Cationic softeners tend to attract soils making them harder to remove. This tendency must be compensated for by the use of soil release finishes.

Lightfastness: Certain softeners will diminish the lightfastness of some direct and fiber reactive dyes. This tendency must be checked out and compensated for.

D. Softener Selection Summary

- The physical state of the softener/lubricant will govern the corresponding hand of a fabric. Low viscosity lubricants are responsible for soft, pliable silky feel while solid waxes provide low coefficient of friction without changing the fabric's hand.
- The softener material's initial color and/or propensity to develop color when heated or aged must be considered when selecting the class of material to use.
- The softener material's smoke point may cause processing problems.
- Fabric odors may be caused by certain class of softener materials.
- Softeners can alter the shade of the fabric. Some react with the dye to change it's lightfastness properties while some will cause the shade to become darker (the same phenomenon that makes wet fabric look darker).

- Softeners can be responsible for poorer crockfastness by dissolving surface dye. Some may migrate onto adjacent light colored yarns causing them to be stained.

E. Raw Materials

Hydrocarbon radicals having a total of 8 to 20 carbons are the most effective molecular group used in textile softeners. Commercially, there are two main sources of raw material supply that are inexpensive and available in large quantities: 1. Fat derived raw materials, triglycerides obtained from animal and vegetable fats and oils and 2. petrochemical raw materials based on crude oil and natural gas. Natural fats and oils consist of triglycerides, triesters of glycerine and fatty acids. Because of their physical nature, fats and oils are lubricants and function as softeners. In their natural state, they are not easily miscible with water so in order to make them useable, they are chemically modified to make them water dispersible. More importantly, fats and oils are sources of fatty acids which are intermediates for synthesizing derivatives that are extremely good softeners. The reader is referred back to the section on Fats, Oils and Waxes in Chapter 3. Petroleum based raw materials start with aliphatic and aromatic hydrocarbons which are converted into effective softeners. Hydrocarbons such as mineral oil and paraffin are effective lubricants and too function as softeners. Again, being water insoluble, hydrocarbons can be modified so that they are water miscible and therefore become more useful. Ethylene and propylene are also good starting materials to make softener bases.

1. Raw Material Sources

a. Fat Derived Raw Materials

1. Fatty acids
2. Fatty acid monoesters
3. Fatty acid ethoxylates
4. Fatty amines
5. Fatty alcohols

b. Petrochemical Derived Raw Materials

1. Long chain hydrocarbons
2. Short chain hydrocarbons
3. α Olefins
4. Long chain alcohols
5. Alkyl aromatics
5. Ethylene, propylene oxides
7. Amines

III. SOFTENER CLASSIFICATIONS

Softeners are divided into three major chemical categories describing the ionic nature of the molecule, namely *Anionic*, *Cationic* and *Nonionic*. Nearly all surfactants are softeners; however, not all softeners are surfactants. Surfactants are two-ended molecule, one end being lyophilic and the other hydrophilic. The lyophile is usually a long hydrocarbon chain, the essence of most lubricants. The ionic portion is responsible for water solubility, (a necessary feature for applying the softeners) and as will be discussed later, in how the molecule aligns itself at the fiber surface. This section will be devoted to describing the chemical structures of important softeners, some of their properties and their fabric uses. It is well to remember that the same chemical structure may describe a surfactant used for other purposes such as detergents, wetting agents, emulsifying agents etc.

A. Anionic Softeners

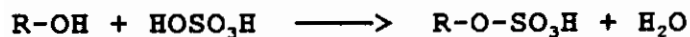
Anionic softeners and/or surfactant molecules have a negative charge on the molecule which come from either a carboxylate group (-COO⁻), a sulfate group (-OSO₃⁻) or a phosphate group (-PO₄⁻). Sulfates and sulfonates make up the bulk of the anionic softeners. Some phosphates, and to a lesser extent the carboxylates, are used as softeners.

1. Sulfates

Sulfate esters are made by the reaction of sulfuric acid with hydroxyl groups or the addition of H₂SO₄ across a -C=C- group. Starting materials for making anionic softeners are fatty alcohols, unsaturated fatty acids or their corresponding esters and triglycerides containing unsaturated fatty acid acids. Oils rich in triolein are excellent bases for making sulfated triglycerides. Castor oil, being rich in ricinoleic acid which contains both a double bond and a hydroxyl group, is a popular starting material for making sulfated triglycerides.

a. Fatty Alcohol Sulfates

Fatty alcohol sulfates are made by the reaction of the appropriate hydrophobe with sulfuric acid.



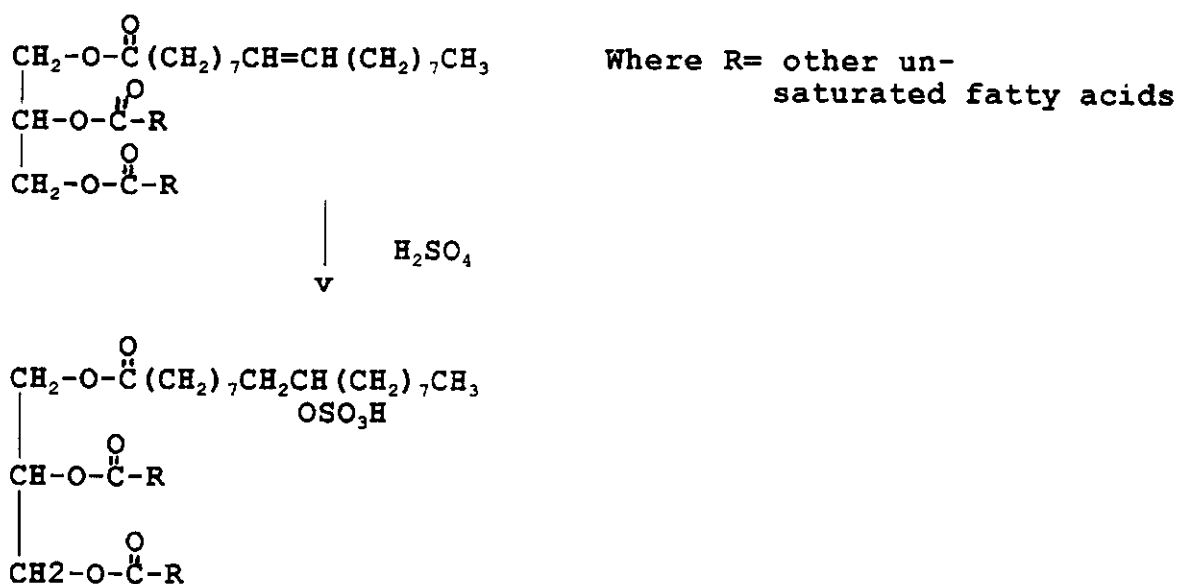
Typical products are sulfated fatty alcohols and sulfated ethoxylated fatty alcohols.

b. Sulfated Fatty Acid Esters

Addition of sulfuric acid across double bonds also lead to sulfate esters.

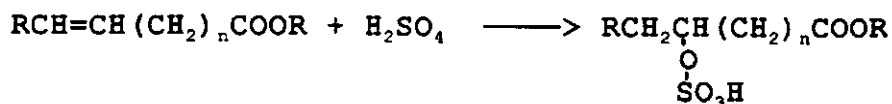


Sulfated Triglycerides. Source of fat will determine the degree of sulfation. The higher the degree of unsaturation, the greater the potential for sulfation. The hydrophilic character of the fat will depend on the number of sulfate attached to the triglyceride. Products ranging from slightly water soluble to highly soluble are made. The best softeners are the ones containing the fewest sulfate groups because the molecule becomes more ionic and a poorer lubricant as the number of sulfate groups increase. The lightly sulfonated oils are sometimes called *self-emulsifying* because they form turbid water solutions. They are easily removed from fiber or fabric without the need of an auxiliary surfactant.



Turkey Red Oil is sulfated castor oil. Ricinoleic acid, the major acid in castor oil has both a hydroxyl group at the C₁₂ position and a C=C at the C₉ position. Both of these groups are converted to sulfate ester linkages so castor oil can have a degree of substitution up to 6.

Sulfated Fatty Acid Esters. Methyl, propyl, butyl and stearyl esters of oleic and linoleic acids are the usual starting materials. The degree of sulfation is controlled by the unsaturated fatty acid. Oleic acid yield monosulfonated esters while linoleic acid can add up to two moles.

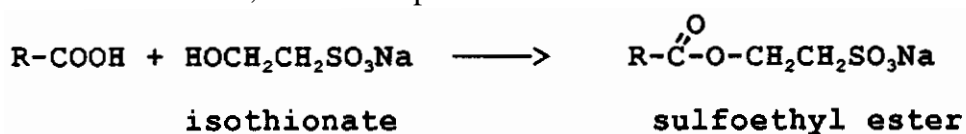


2. Sulfonated Fatty Amides and Esters

Sulfonates differ from sulfates. A sulfonate (-CH₂-SO₃H) has the sulfur atom attached directly to the carbon atom whereas the sulfate (-CH₂-O-SO₃H) is linked to the carbon through an oxygen. This linkage difference changes the stability of the molecule to hydrolysis. Sulfates readily hydrolyze back to the starting alcohol and sulfuric acid whereas sulfonates are much more resistant to hydrolysis.

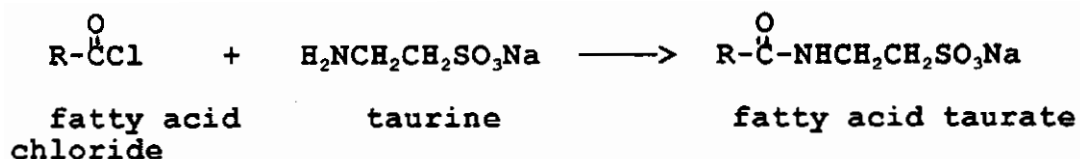
a. Sulfoethyl Fatty Esters (IGEPO A)

This line of surfactants is made by reacting fatty acids with sodium isethionate to yield a sulfo-ethyl ester of the acid. Isethionic acid is made by reacting ethylene oxide with sodium bisulfite, both inexpensive chemicals.



b. Sulfoethyl Fatty Amides (IGEPO A)

Sulfoethyl amides are made by reacting taurine with fatty acid chlorides. Acid chlorides react more easily than the free acid. Taurine is made from isethionic acid.



3. Properties of Anionic Softeners

Anionic softeners impart pliability and flexibility without making the fabric feel silky. They are used extensively on fabrics to be mechanically finished, e.g napped, sheared or Sanforized. A good napping lubricant, for example, provides lubrication between the fabric and the napping wires yet at the same time provides a certain amount of cohesiveness between fibers. If the fibers are too slippery, the napping wires will overly damage the yarn. Sulfonated oils (eg Turkey Red Oil) impart a soft raggy hand, sulfonated tallow a full waxy hand and sulfonated fatty esters a smooth waxy hand.

a. Advantages

Most anionic softeners show good stability towards heat and some are resistant to yellowing. Anionic softeners do not interfere with finishes to be foamed, in fact

like defoamers and are deleterious for foam finishing. Anionic softeners have good rewetting properties and are preferred for those fabrics that must adsorb water such as bath towels.

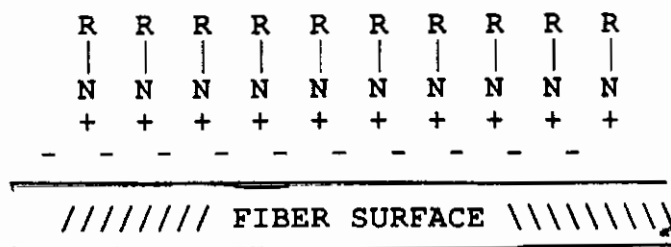
b. Disadvantages

The degree of softness with anionics is inferior when compared with cationics and some nonionics. Generally speaking, more anionic product must be used and even then, the cationics and some nonionics impart a softer, fluffier feel to the fabrics. Anionics have limited durability to laundering and dry-cleaning. Anionics will not exhaust from a bath, they must be physically deposited on the fabric. Anionics tend to be sensitive to water hardness and to electrolytes in finish baths. Anionics are incompatible in some finish baths containing cationically stabilized emulsions.

B. Cationic Softeners

Cationic softeners are ionic molecules that have a positive charge on the large part of the molecule. The important ones are based on nitrogen, either in the form of an amine or in the form of a quaternary ammonium salt. The amine becomes positively charged at acidic pHs and therefore functions as a cationic material at pH below 7. Quaternary ammonium salts (hereafter referred to as QUATS), retain their cationic nature at all pHs. The important types will be described in this section. An important quality of cationic softeners is that they exhaust from water onto all fibers. When in water, fibers develop a negative surface charge, setting up an electronic field for attracting positively charged species. These forces causes the cationic softener to deposit in an oriented fashion, the positive end of the softener molecule is attracted to the fiber surface forcing the hydrocarbon tail to orient outward. The fiber now takes on low energy, nonpolar characteristics; therefore, the fiber has the lowest possible coefficient of friction. Cationics are highly efficient softeners. The ionic attraction causes complete exhaustion from baths and the orientation on the fiber surfaces allows a monolayer to-be as effective as having more lubricant piled on-top.

Figure 50. Adsorption on Fiber Surface

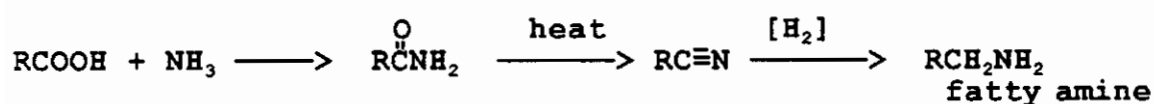


1. Amine Functional Cationic Softeners

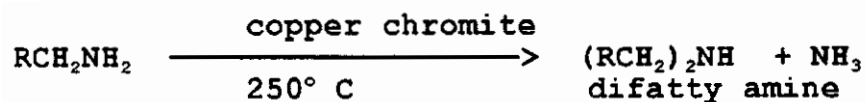
Long chain amines are not water soluble at neutral and alkaline pH; however, when converted to their acid salt, they develop a cationic charge and become water soluble. They exhaust and become excellent softeners under acidic conditions,. The cationic charge on a given hydrophobe is proportional to the number of amino groups, therefore the attraction of the cationic proton to the fiber surface increases as the number of amine groups increase.

There are several routes for making aminofunctional cationic softeners. One route is to convert fatty acids to mono and difatty amines. These intermediates can function either as softeners or be used to make other derivatives. A second method of making aminofunctional molecules is to make aminoesters or animoamides of fatty acids. The box below details a number of materials in this class.

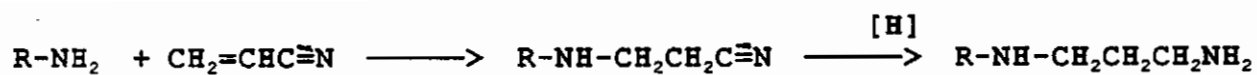
a. Primary Fatty Amines



b. Difatty Amines



c. Fatty Diamines



d. Cationic Amine Salts

Fatty amines derived from tallow fatty acids are called tallow or di-tallow amines, those made from coconut acids would be called coco amines or di-coco amines. Fatty amines become cationic when neutralized with one mole of acid.



2. Fatty Aminoesters

Aminoesters are made by reacting alkanol amines with fatty acids. Aminoesters containing one or more amine groups are commercially available. These materials too become cationic under acidic conditions, the strength of the cationic

charge is proportional to the number of amino groups. Examples of alkanol amines are ethanol amine, diethanol amine and hydroxyethyl-ethylene diamine. Disadvantage of esters is poor hydrolytic stability under alkaline conditions.

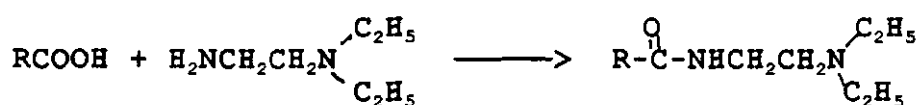
a. Synthesis



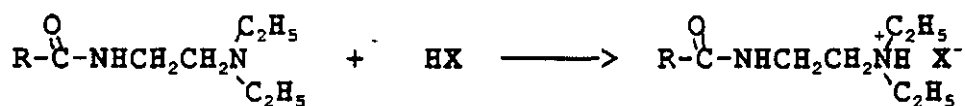
3. Fatty Amidoamides

Aminoamides are made by the condensation of polyamines with fatty acids. Ethylene diamine, N,N-diethylethylene diamine and diethylene triamine are examples of polyamines that are condensed with fatty acids. Usually, the fatty acids are commercial grades such as would be derived from tallow or coconut oil. The products would then carry a generic name such as tallow aminoamides or coco aminoamides. The aminoamides are neutralized with a variety of acids and sold as the salt. Acetic acid, hydrochloric acid, sulfuric acid and citric acid salts of many of them are commercially available for use as softeners. The acid salts are water soluble or water dispersible making them much easier to use.

a. Synthesis of Amidoamides



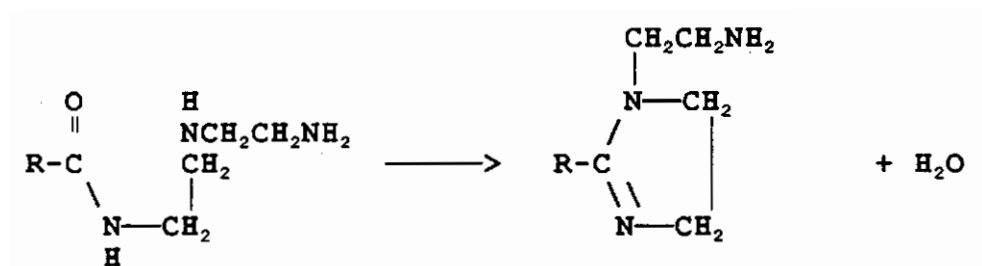
b. Synthesis of Amidoamide Salt



4. Imidazolines

Aminoesters and aminoamides are converted to cyclic imidazolines by heating them under reduced pressure to split out a second mole of water. One nitrogen in the ring reacts as a simple amine so it can form acid salts to become cationic or it can be quaternized. The imidazolines are less viscous than their parent aminoamide and therefore have better softening properties. Imidazolines are less likely to discolor with age than their corresponding parent compound.

a. Synthesis

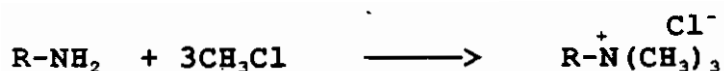


5. Quaternary Ammonium Salts

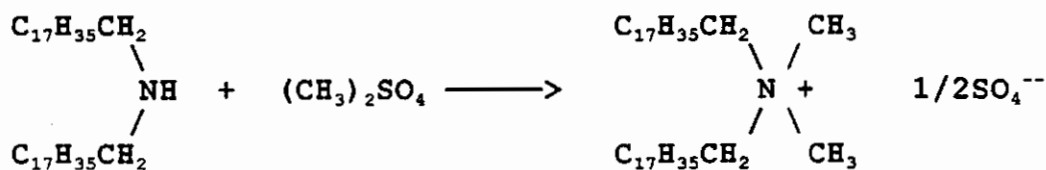
Quaternary ammonium salts are extremely important fatty acid derivatives. The quat's cationic charge is permanent, being maintained at all pHs. In addition to imparting softness, quats reduce the static charge on synthetic fabrics and inhibit the growth of bacteria. Quats are therefore used as antistats and germicides as well as softeners. Cationics containing two C_{18} fatty tails attached to the nitrogen impart very soft, fluffy hand to textile products. Cationics based on di-tallow amine are used as home laundry rinse-added and dryer-added fabric softeners as well as mill applied softeners.

a. Synthesis of Monofatty Quats

Quats are made by reacting fatty amines with alkylating agents such as methyl chloride or dimethyl sulfate. Quaternary chloride salts are derived from methyl chloride while quaternary sulfates are made with dimethyl sulfates. Monofatty amines react with three moles of methyl chloride to give fatty-trimethylammonium chloride. Examples are quats derived from coco, palmito and tallow fatty acids.



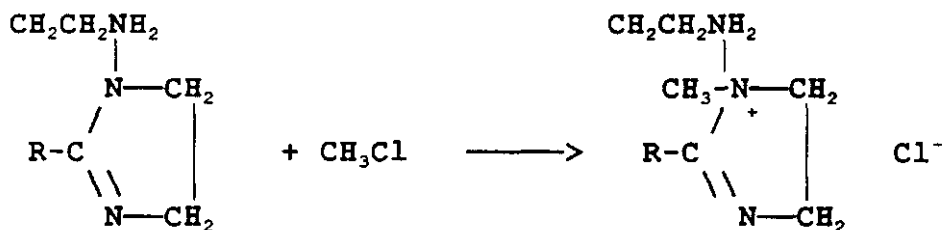
b. Synthesis of Difatty Quats



Tallow amines are commonly used to make very effective softeners. Both the ditallowdimethylammonium chloride and corresponding sulfate salts find use as

mill-applied and home-laundry applied fabric softeners. Quats containing two C₁₈ fatty tails attached to the nitrogen impart very soft, fluffy hand to textile products.

c. Synthesis of Imidazoline Quats



6. Properties of Cationic Softeners

a. Advantages

Cationic softeners impart very soft, fluffy, silky hand to most all fabrics at very low levels of add-on. Cationics will exhaust from dyebaths and laundry rinse baths making them very efficient materials to use. Cationics will exhaust from acidic solutions. Cationics improve tear resistance, abrasion resistance and fabric sewability. Cationics also improve antistatic properties of synthetic fibers. They are compatible with most resin finishes. They are good for fabrics to be napped or sueded.

b. Disadvantages

They are incompatible with anionic auxiliary chemicals. They have poor resistance to yellowing. They may change dye shade or affect light fastness of some dyes. They retain chlorine from bleach baths. They adversely affects soiling and soil removal and may impart unwanted water repellency to some fabrics.

C. Nonionic Softeners

Nonionic softeners can be divided into three subcategories, ethylene oxide derivatives, silicones, and hydrocarbon waxes based on paraffin or polyethylene. The ethylene oxide based softeners, in many instances, are surfactants, and can be tailored to give a multitude of products. Hydrophobes such as fatty alcohols, fatty amines and fatty acids are ethoxylated to give a wide range of products. Silicones too can be tailored to give several different types of products. Polyethylene wax emulsions, either as high density or as low density polymers, are commercially available. Different types of emulsifiers can be used when making the emulsion so that products can be tailored to meet specific needs. This section will discuss some of the more important nonionic surfactants.

1. Polyethylene Emulsions

Polyethylene emulsions dry down to form hard, waxy films. When the emulsion is applied to fibers, a waxy coating deposits on the surface reducing its coefficient of friction. These coatings offer good protection against needle cutting and thread breakage and improve abrasion resistance and tearing strength.

a. Composition of Polyethylene Emulsions

To be emulsifiable, the polyethylene polymer is first oxidized by passing air through the melt. Oxidation converts some polymer end groups to -COOH and the quantity of carboxyl groups is controlled. Both low and high density polyethylene are processed this way. A number of grades of polyethylene polymers are available differing in melting point, melt viscosity, molecular weight and carboxyl content. Dispersions with anionic, nonionic and cationic character are made by selecting appropriate auxiliary emulsifier. Selecting an emulsion with the proper ionic character is important otherwise the finishing bath will become unstable and break out. Stable water emulsions with solids up to 20% are commercially available. The alkali salt of the polymer's carboxyl group is an important factor in the stability of the dispersions.

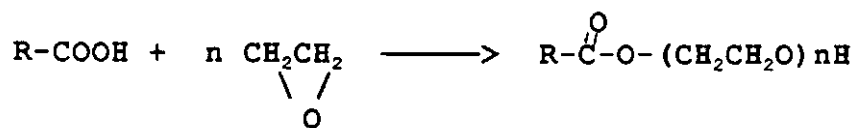
Typical Composition

Polyethylene Wax	20 %
Emulsifier	5 %
KOH	0.5%
Water	74.5%

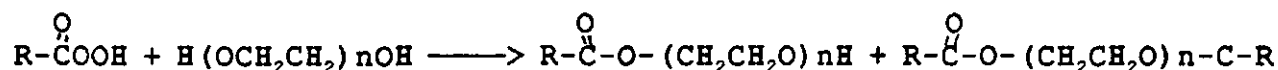
2. Ethoxylated Nonionic Softeners

Many polyethylene glycolated hydrophobes are oily or waxy in nature and function as non-ionic fabric softeners and fiber lubricants. They are important components of fiber spin finishes because of their dual ability to lubricate and function as as antistats. Additionally, they are easily removed in downstream processing. There are two main route for making this family of products, direct ethoxylation of the hydrophobe, or the reaction of fatty acids with polyethylene glycols. The former method gives mainly monofatty derivatives whereas the second method gives a mixture of mono and difatty derivatives.

a. Ethoxylation with Ethylene Oxide



b. Esterification with Polyglycol



c. Typical Ethoxylates

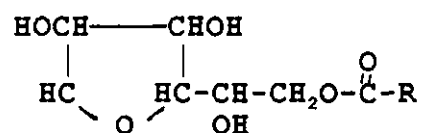
Ethoxylated Fatty Acids: See above

Ethoxylated Fatty Alcohols: $R-\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$

Ethoxylated Fatty Amides: $R-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$

Ethoxylated Fatty Amines: $R-\text{CH}_2\text{NH}(\text{CH}_2\text{CH}_2\text{O})_n(\text{CH}_2\text{CH}_2)\text{OH}$

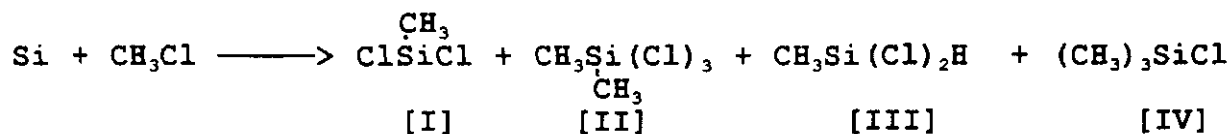
Sorbitan Fatty Esters:



3. Silicone Chemistry

In order to appreciate the role of silicones as fabric softeners, it is necessary for the reader to understand the chemistry leading to this class of polymeric materials. Silicones are *Polysiloxane Polymers* and fall under the class of materials known as organometallics. The element silicon is considered a metal and is found in abundance in nature as silica, SiO_2 . Silicon resembles carbon in that it is tetravalent and forms covalent bond with other elements. Simple tetravalent compounds are called silanes. Silicon forms a stable covalent bond with carbon leading to a class of materials known as organosilanes. For example methyl chloride reacts with silicon to form a mixture of silanes as shown in the box below. The mixture includes silanes containing methyl, chloro and hydrogen groups in varying proportions. Chlorosilanes rapidly react with water to form silanols which further condense to form siloxane linkages. Dimethyldichlorosilane will form linear polysiloxanes which are water clear oils with excellent lubricating properties. The viscosity of the oil will vary with the molecular weight. Utilizing appropriate monomers and reactive groups, polysiloxanes, better known as silicones, are also found as three dimensional resins. and high molecular weight elastomers.

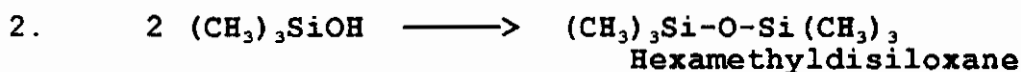
a. Formation of Organofunctional Reactive Silanes



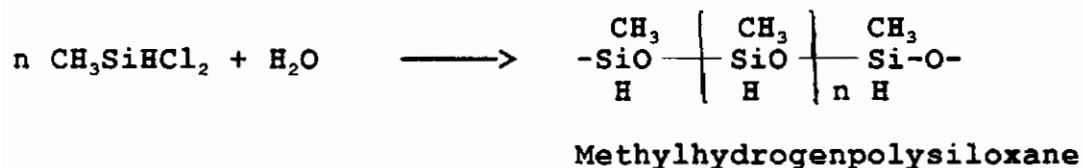
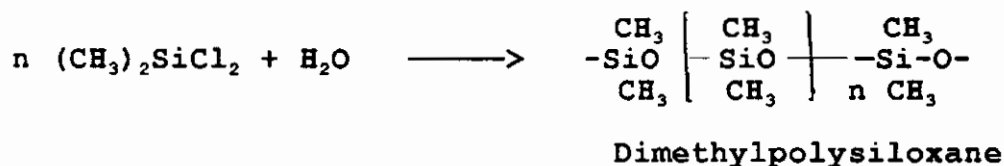
Compound Name

- [I] Dimethyldichlorosilane
- [II] Methyltrichlorosilane
- [III] Methylhydrogendichlorosilane
- [IV] Trimethylchlorosilane

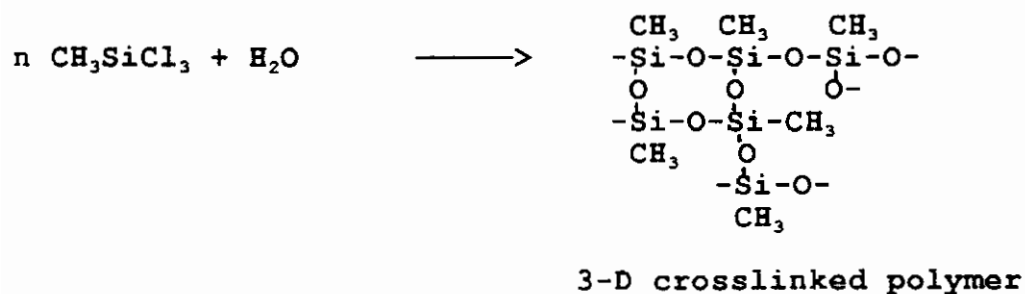
b. Reaction of Monochlorosilanes with Water



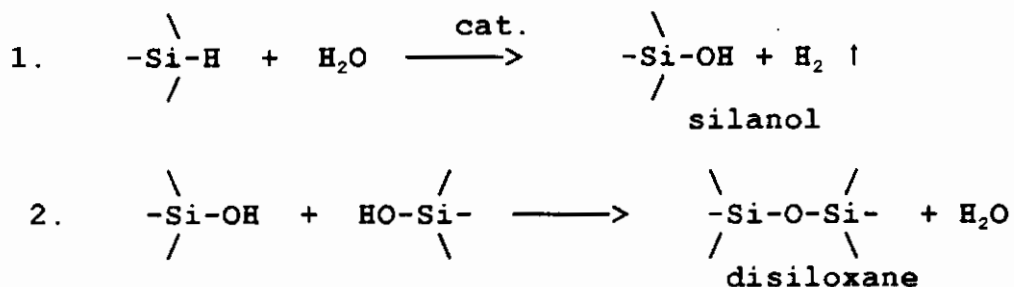
c. Reaction of Dichlorosilanes with Water



d. Reactions of Trichlorosilanes with Water



e. Reaction of Hydrogen Silanes with Water



From the reactions described above, it can be seen that Si-Cl bonds eventually winds up as -Si-O-Si- linkages. Monochlorosilanes lead to dimer whereas dichlorosilanes lead to linear or cyclic polymers. Trichlorosilanes lead to three-dimensional crosslinked resins. Si-H bonds also react with water to form silanols which also lead to siloxane linkages. The reaction is much slower than the chlorosilanes and require a catalyst. This difference in conditions required to form siloxanes is exploited as a means to post crosslink polymers. Methyl hydrogen silane reactivity is utilized in durable silicone water repellent finishes.

4. Silicone Softeners

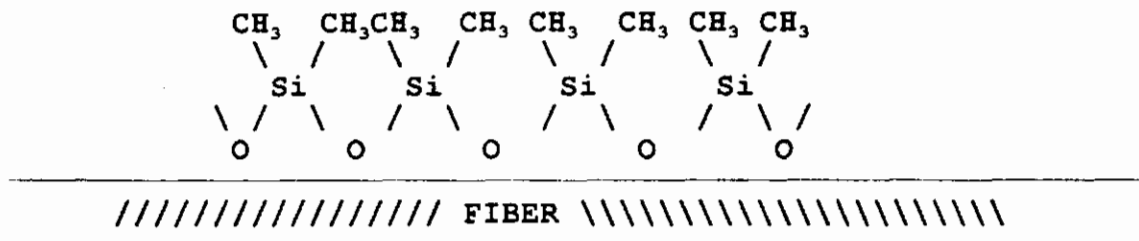
Three varieties of silicone polymers have found use as textile softeners. One variety is based on emulsified dimethyl fluids. Another variety is based on emulsified reactive fluids having Si-H groups dispersed throughout the polymer. The third variety has amino or epoxy functional groups located on the polymer backbone. The amino and epoxy functional silicones have been reported to produce the softest possible hand and to improve the durable press performance of cotton fabrics.

a. Dimethyl Fluids

Dimethyl fluids are made from dimethyldichloro silane. The reaction conditions can be controlled to vary the number of repeat dimethyl siloxane units within the polymer. As the number increase, the viscosity increases so there is a range of commercially available fluids with varying viscosity. Fluids can be emulsified to make stable water dispersions for use as finishes. Fluids are water clear and do not discolor with heat or age. They impart soft silky hands to fabrics. In addition to softening, dimethyl fluids render fabrics somewhat water repellent; however, being fluids, they are not durable.

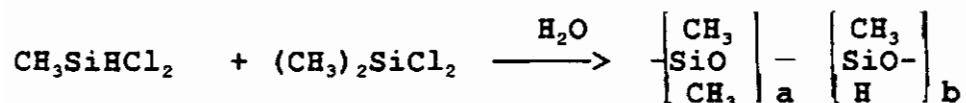


Figure 51. Orientation of Dimethyl Fluids on Fiber Surface.



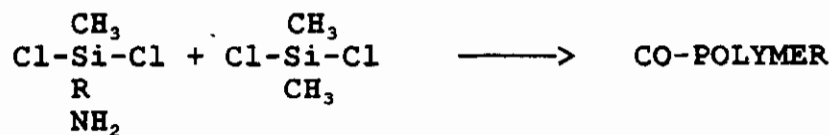
b. Methylhydrogen Fluids

Methylhydrogendichlorosilane offers a route for making a linear polysiloxane fluid with latent crosslinking potential. Hydrolysis of the dichloro groups will occur rapidly with water to form a linear polymer. Stable emulsions can be prepared, as long as the aqueous pH is maintained between 3-4,. When these emulsions are applied to a fabric with a tin catalyst (e.g. dibutyltin-dilaurate), the Si-H group hydrolyzes to the silanol and condenses to form a crosslink. These offer a way of improving durability.



c. Amino Functional Silicones

Amino functional silicones are made by incorporation the appropriate organofunctional chlorosilane to the reaction mix. Amino functional silicones become cationic at acid pHs and exhaust from aqueous baths.



d. Epoxy Functional Silicones

Epoxy functional groups can be incorporated into silicone polymers by incorporating the appropriate group into the silicone polymer back bone. Epoxy functionality offers a non-silanol crosslinking mechanism along with the ability to react with fiber hydroxyls. These softeners are more durable to repeated laundering.

5. Properties

a. Advantages

Silicones are water clear oils that are stable to heat and light and do not discolor fabric. They produce a slick silky hand and are preferred for white goods. They improve tear and abrasion resistance and are excellent for improving sewing properties of fabrics. Amino functional silicones improve DP performance of cotton goods. Epoxy functional are more durable.

b. Disadvantages

The silicones are water repellent which make them unsuitable as towel softeners. Silicones are expensive compared with fatty softeners. Amino functional silicone discolor with heat and aging. They may interfere with redyeing when salvaging off quality goods.

IV. REFERENCES