

CHAPTER 3.

SCOURING

Natural fibers contain oils, fats, waxes, minerals, leafy matter and notes as impurities that interfere with dyeing and finishing. Synthetic fibers contain producer spin finishes, coning oils and/or knitting oils. Mill grease used to lubricate processing equipment mill dirt, temporary fabric markings and the like may contaminate fabrics as they are being produced. The process of removing these impurities is called *Scouring*. Even though these impurities are not soluble in water, they can be removed by *Extraction*, dissolving the impurities in organic solvents, *Emulsification*, forming stable suspensions of the impurities in water and *Saponification*, Converting the contaminates into water soluble components.

I. COMPOSITION OF NATURAL FIBERS

The contaminates found in natural fibers are the ones that are the most difficult to deal with in fabrics that need to be scoured. Table 3 lists the components found in ginned cotton while table 4 shows the composition of raw wool.

Table 3.
Composition of Ginned Cotton

Constituent	% Dry Basis	Water Soluble
Cellulose	88 - 96	no
Protein Matter	1.1 - 1.9	some
Pectin	0.7 - 1.5	no
Minerals	0.7 - 1.6	some
Wax	0.4 - 1.0	no
Notes (Immature fibers clinging to crushed seed)		

Table 4.
Composition of Raw Wool

Constituent	Approximate Amount	Water Soluble
Keratin	33	no
Wool grease	15	no
Suint (Dried Sweat)	26	yes
Dirt	24	no
Mineral Matter	1	some
Vegetable Matter	1	no

II CHEMISTRY OF OILS, FATS AND WAXES

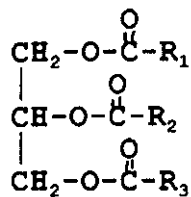
Many of the contaminants removed in scouring, both natural and man made are fats, oils or waxes. Many useful products, some used in scouring, are derived from them. This section will review some of the pertinent chemistry.

A. Fats

Chemically, fats and waxes are esters of fatty acids; fats are triesters of glycerine and waxes are monoesters of fatty alcohols. Fats, also known as triglycerides, are abundantly produced by nature as vegetable oils (corn, olive, coconut, linseed, castor and soy bean oil) and, as fatty deposits in animals (beef, mutton, pork and fish). Marine animals produce both fats and waxes while land based animals produce only fats. Another source of waxes is vegetable matter, predominately the hard shiny outer coating on tropical leaves.

B. Triglycerides

Regardless of whether it is of vegetable or animal origin, a fat can be either liquid or semi-solid. A major factor in determining the physical nature of the fat is the makeup of the fatty acid components. Figure 23 shows a generalized structure of a triglyceride. R_1 , R_2 and R_3 are used to indicate various combinations of fatty acids.



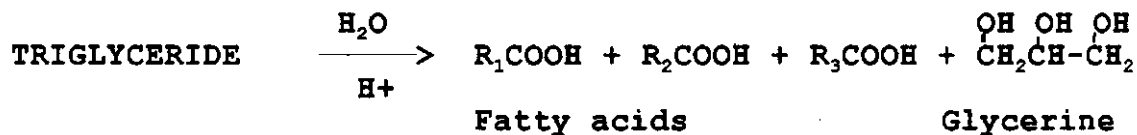
A triglyceride

1. Hydrolysis of Triglycerides

When a triglyceride is hydrolyzed, the reaction products consist of three moles of fatty acid and one mole of glycerine. The reaction is either acid or base catalyzed. Acid hydrolysis is used to manufacture free fatty acids whereas base hydrolysis is called saponification, the process for making soap.

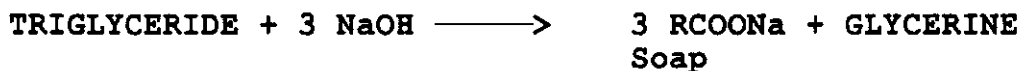
a. Acid Hydrolysis

The hydrolysis is catalyzed by strong acids to yield free fatty acids which are separated by fractional distillation under reduced pressure. Fatty acids are important starting materials for many useful products and this point will be discussed in greater detail in later sections.



b. Saponification

The hydrolysis can also be carried out under alkaline conditions where one mole of alkali is consumed per mole of fatty acid. The alkali salts of fatty acids are called soaps. Laundry and toilet soaps are made this way.



C. Fatty Acids

Fatty acids are long chain alkyl carboxylic acids. The alkyl radical can be either completely saturated (saturated fatty acids) or unsaturated (unsaturated fatty acids). The most common chain length found in nature is C_{18} . There can be 1, 2 or 3 double bonds in the alkyl portion of the molecule. Triglycerides composed of acids containing 2 or 3 double bonds are called polyunsaturated fats. Some common and important fatty acids are:

Table 5.

Saturated Fatty Acids

Acid	No. of C atoms	Formula	M. P. °C
Butyric	4	$\text{CH}_3(\text{CH}_2)_2\text{COOH}$	-4.7
Caproic	6	$\text{CH}_3(\text{CH}_2)_4\text{COOH}$	-1.5
Caprylic	8	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$	16.5
Capric	10	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$	31.3
Lauric	12	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	43.6
Myristic	14	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	58.0
Palmitic	16	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	62.9
Stearic	18	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	69.9
Behenic	22	$\text{CH}_3(\text{CH}_2)_{20}\text{COOH}$	80.2

Table 6

Unsaturated Fatty Acids

Acid	No. of C atoms	Formula
Palmitoleic	16	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Oleic	18	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Ricinoleic	18	$\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{OH})\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Linoleic	18	2 $-\text{CH}=\text{CH}-$ @ C_9 and C_{12}
Linolenic	18	3 $-\text{CH}=\text{CH}-$ @ $\text{C}_9, \text{C}_{12},$ and C_{15}

III. SOURCES

A. Vegetable Sources

Fats and oils are triglycerides which differ only in fatty acid composition. Animal fats are solid or semisolid because they contain a high percentage of saturated fatty acid and saturated alkyl chains can pack more closely together. This accounts for the solid nature of the fat. Vegetable oils are high in unsaturated fatty acids. The substituents around the double bond are arranged in the *cis* configuration which cause the molecules to occupy a larger volume. This accounts for their liquid state. Most natural fats are mixtures, each source contains a different ratio of chain

lengths and a different ratio of saturated to unsaturated fatty acids. There are many literature references that give comprehensive reviews of the composition of fats and oils. The reader is urged to consult these for greater depth. Listed below is a select few.

■ **Castor Oil:** The major fatty acid (90%) in this oil is ricinoleic acid. Hydrogen bonding through the hydroxyl group on C₂, is responsible for the oil's high viscosity and solubility in alcohol. The oil is sulfated to become an important anionic surfactant (turkey red oil). Ricinoleic acid is also the starting material for making sebacic acid and capryl alcohol. It is cleaved with sodium hydroxide. Sebacic acid is a C₁₀, dibasic acid used to make Nylon 6,10.

■ **Coconut Oil:** The major fatty acids found in this oil are lauric (48%) and myristic (18%). Both acids have shorter length chains (C₁₂ and C₁₄) and are saturated. The lauric chain length is ideal for high foaming soaps. Its potassium salt has higher water solubility acids and is used to make liquid soap products.

■ **Corn Oil:** Corn oil has a high unsaturated acid content (46% oleic and 42% linoleic acids). It is used extensively for cooking, as salad oil and for making oleo-margarine. Because of the high amount of poly-unsaturated, its use leads to lower cholesterol levels in humans.

■ **Cottonseed Oil:** Cottonseed oil contains 27% oleic, 50% linoleic and 21% palmitic acid. It too is used for food purposes like corn oil.

■ **Olive Oil:** Olive oil contains 82% oleic acid and 8% linoleic acid. It is virtually pure triolein. It is a high grade salad oil, remaining liquid when refrigerated. It is also highly prized as a cooking oil.

■ **Palm Oil:** Palm oil has a high content of a C₁₆ saturated acid (40% palmitic acid). It also has a high content of oleic acid, 43%. This combination of fatty acids is ideal for making good toilet soaps.

■ **Linseed Oil:** Linseed oil is high in linoleic (60%) and linolenic acid (25%). These oils will polymerize through the double bonds to form hard lustrous finishes on wood. Their major uses are as wood and furniture finishes and in oil based paints.

■ **Tall Oil:** Tall oil is a by-product obtained from converting wood pulp to paper. The black liquor contains a mixture of triglycerides (about 50%) and rosin (about 45%). The triglyceride portion becomes an important source of fatty acids after it is properly refined.

■ **Bayberry Wax:** Bayberry wax is obtained from the candleberry plant and is chemically a fat. However its wax-like nature stems from the fact that it is mainly

made up of stearic, palmitic and myristic triglycerides. It is used in textile sizing compositions because it can be easily saponified during the desizing operation.

■ **Japan Wax:** Japan wax is a triglyceride. It is obtained from the sumac tree's berries and is high in palmitic acid. Its wax like properties makes it useful for candles, textile finishes, crayons, cosmetics and the like.

B. Animal Sources

Animals produce triglycerides as fatty deposits within their body. The physical nature of these deposits range from hard to very soft. The fatty acids making up the triglyceride is responsible for this.

■ **Tallow:** Tallow is the hard fatty deposits in beef and mutton. It contains of 30% palmitic, 14% stearic and 48% oleic acid. Its hard, solid, physical state comes from the high saturated acids content. It is an important source of many softeners because of its abundance and low price. Tallows are often hydrogenated to increase the saturated acid content giving rise to a class of materials called *hydrogenated tallow*.

■ **Lard:** Lard is the soft, white fatty deposit found in hogs. The best grade is called leaf lard and is used for frying foods. The difference between lard and tallow is the presence of the polyunsaturated linoleic acid which is responsible for the softer physical state. The fatty acid composition is 43% oleic, 10% linoleic, 27% palmitic and 14 % stearic acid.

■ **Whale Oil:** Sperm oil is a liquid wax occurring in the head of a sperm whale. Cetyl alcohol is the major fatty alcohol component of the wax ester while the acids are oleic (14%), palmitoleic (17%), palmitic (11%) and linoleic (9%). The wax oil is very stable to hydrolysis and to oxidation. Its viscosity is low so it makes an excellent lubricant. It was once the main ingredient in synthetic fiber spin finishes.

C. Chemical Wax

Chemical wax is defined as the mono-ester of a fatty acid and a fatty alcohol. It is found in nature as coatings on leaves, stems and berries. Nature's role for these waxes is to reduce the evaporation of moisture from plants, which is very important for those growing in tropical climates. True waxes are less easily hydrolyzed and do not form acrolein when heated. Acrolein is a toxic compound formed when glycerine is overheated.

1. Fatty Alcohols

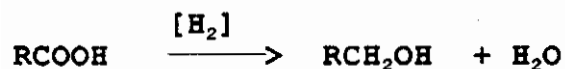
The similarity between fatty acids and fatty alcohols is the long alkyl chain. While some fatty alcohols occur in nature as a part of the ester linkage in natural waxes, the bulk of the industrially important ones are made synthetically.

Table 7
Fatty Alcohols

Name	Structure
Cetyl alcohol	$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{OH}$
Oleyl alcohol	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_2\text{OH}$
Stearyl alcohol	$\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{OH}$
2-Octanol	$\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{OH})\text{CH}_3$
2-Ethylhexanol	$\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OH}$

a. Sources of Fatty Alcohols

1. Reduction of fatty acids.



This process allows for converting any readily available fatty acid to the corresponding alcohol. There are several other industrially important methods for making specific alcohols.

2. Capryl alcohol,(2-octanol) is made from the cleavage of ricinoleic acid. Sebacic acid, an important industrial dibasic acid, is the by-product

3. 2-Ethyl-1- hexanol is made by the Aldol condensation of acetaldehyde.

4. Straight chain primary alcohols ranging from C_6 to C_{24} are made by the Alfol process, a catalytic polymerization of ethylene.

5. Cetyl alcohol is found in spermaceti oil. Chemically, spermaceti oil is a wax and is the mono-ester of palmitic acid and cetyl alcohol.

D. Mineral Wax

1. Paraffin

Paraffin waxes come from a purified mixture of solid hydrocarbons obtained from the distillation of petroleum. This mixture contains C_{23} to C_{33} hydrocarbons. Straight chain hydrocarbons are solids, branched ones are oils. The distillate fraction contains both straight and branch chain isomers since they have identical boiling points. When the distillation fraction is chilled, the straight chain hydrocarbons solidify and can be filtered from the oil. The solid is called **Slack Wax** while the liquid is called **Dewaxed Oil**. The slack wax will contain some occluded oil. The branched isomers can be separated from the solid by a process called **Sweating**. Blocks of wax are placed in an oven where the temperature is increased very slowly. The oil will migrate to the surface of the block and form beads of sweat which drain away by gravity. The procedure can be repeated several times to produce different grades of paraffin, based on melting point. Paraffin waxes produced this way form large, hard white crystals melting between 120 to 140° F. The melt viscosity is low.

2. Microcrystalline Wax

Microcrystalline waxes are higher melting (150° F), have higher melt viscosity and are soft microcrystals obtained by subjecting the wax distillation residue to a solvent crystallization process. The residue is dissolved in a mixture of benzene and methylethyl ketone and then allowed to crystallize.

E. Synthetic Wax

There are a number of synthetic materials that possess wax-like properties.

- **Fatty Acids:** Most saturated fatty acids have wax-like properties. Stearic, palmitic and myristic acids function as waxes.
- **Fatty Alcohols:** Long chain alcohols are waxy in nature.
- **Polyethylene Glycols:** Higher molecular weight polyoxyethylene analog are wax-like.
- **PEG Esters:** Polyethylene glycol esters of fatty acids have wax like properties.

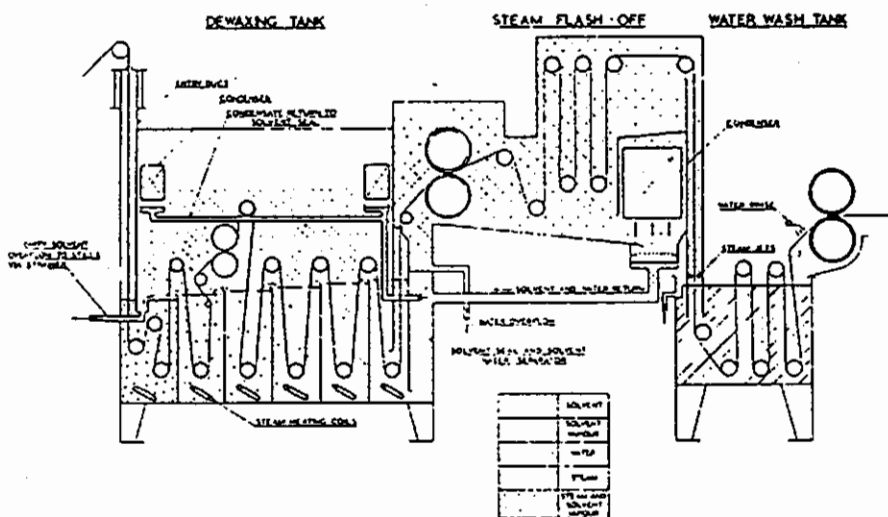
III SOLVENT SCOURING

Certain organic solvents will readily dissolve oils fats and waxes and these solvents can be used to purify textiles. Removal of impurities by dissolution is called **Extraction**. There are commercial processes where textiles are cleaned with organic solvents. Fabrics processed this way are said to be "**Dry Cleaned**". Although not widely used as a fabric preparation step, it is an important way of removing certain difficult to remove impurities, where a small amount of residuals can cause downstream problems. Garment dry-cleaning is more prevalent.

For fabrics that do not have to be desized, solvent scouring is an effective way of removing fiber producer finishes, coning and knitting oils. Knitted fabrics made from nylon, polyester, acetate and acrylics, are particularly amenable to this method of preparation. Wool grease is effectively removed by solvent scouring. Solvent Extractions are particularly useful in the laboratory for determining the amount of processing oils added to man-made fibers and the residual amounts of oils and waxes left by aqueous scouring. Properly controlled, fabrics can be produced with very little residual matter.

Figure 17 shows a schematic of a continuous, solvent scouring range. The entire range is enclosed so the vapors are contained and not allowed to escape into the atmosphere. Recovery units are installed on the range to insure that none of the solvent is allowed to vent to the environment. Usually carbon adsorption towers are use for this. Also a solvent distillation unit is needed to reconstitute the pure solvent and separate the removed contaminants.

Figure 17. Schematic of a Continuous Solvent Scouring Range



The term *solvent scouring* is also used to describe processes where amounts of organic solvents are added to aqueous scouring formulations to assist in the removal of oils and waxes. This technique is widely used and a more in-depth discussion will be found elsewhere. Organic solvents have a number of advantages that make them particularly useful for wax removal.

A. Advantages and Disadvantages

Solvents dissolve almost all oils and waxes. They have low liquid surface tensions and quickly and easily wet out and penetrate fabrics with waxes. They are much easier to evaporate than water, requiring less time and energy. On the negative side hydrocarbon solvents are flammable and present explosion hazards. Most chlorinated solvents are proven or suspect carcinogens and some are known to contribute to atmospheric ozone depletion. Chlorinated hydrocarbons thermally decompose to form phosgene and hydrochloric acids. These decomposition by-products are corrosive to metals and also damage cellulosic fibers. Solvents are expensive so they must be recovered and purified by distillation requiring special equipment. The distillation residue becomes a solid waste disposal problem. Solvents do not aid in the removal of moles, metal ions, starch and other solvent.

B. Common Solvents

Listed below are some of the more common solvents used commercially. These are among the safest as they are generally non-flammable. However they must be handled with care because the chlorinated ones are on the suspect carcinogen list of regulated chemicals.

1. Solvent Properties

- **Boiling Point:** Temperature at which solvent is converted from liquid to a gas.
- **Specific Heat:** The amount of energy needed to raise one gram of solvent one degree centigrade (Calories/gram/^oC).
- **Latent Heat of Evaporation:** The amount of energy needed to vaporize one gram of solvent (Calories/gram).

2. Non-flammable Solvents

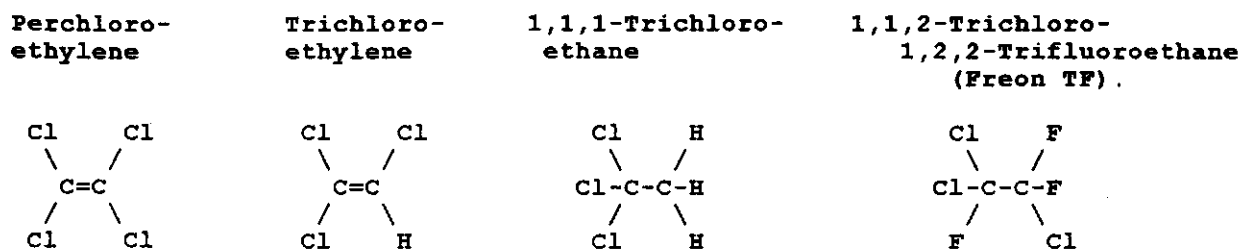


Table 8

Comparison of Properties

	B.P °C	Latent Heat of Evap (Cal/g)	Specific Heat (Cal/g/°C)	Surface Tension (Dynes/cm)
Water	100	545.1	1.0	72.0
Trichloroethylene	87	57.3	0.22	32.0
1,1,1-trichloroethane	74	58.5	0.25	26.4
Perchloroethylene	121.2	50.1	0.21	32.3
Trichlorotrifluoroethane	47.6	35.1	0.21	17.3

IV. AQUEOUS SCOURING

Aqueous scouring is the preferred way of scouring fabrics because water is non-flammable, non-toxic, plentiful and cheap. When preparing woven goods, the scouring step follows desizing and wet fabric proceed to the scouring range without drying in between. The components in the scouring bath must be selected with the fiber in mind. For example strong alkali can be used for scouring cotton, but wool and rayon are damaged by it. Wool can withstand acids whereas cotton, rayon and nylon cannot.

A. Typical Formulation for Scouring Specific Fibers

1. Cotton

The characteristic speckled look of cotton greige fabrics is caused by cotton motes that were not removed during the yarn making process. Mote removal is a major objective in scouring cotton. Another objective of scouring is to remove minerals, waxes and pectines and to improve absorbency. There are three components in a cotton scouring bath: **caustic**, to swell and dissolve the motes and to saponify oils and waxes, **surfactant**, to lower the bath's surface tension so it can wet-out the fabric faster and to emulsifies oils and waxes and **chelating agent**, to form water dispersible complexes with heavy metals.

a. Batch Scouring Procedure

1. Run fabric in a bath containing :

NaOH	3.0 %
Surfactant	0.2-0.4 %
Sequestrant	0.1-0.2 %

2. Process fabric at 212°F in beck or jet for one hour.
3. Rinse thoroughly.

b. Continuous Scouring Procedure

1. Saturate fabric with:

NaOH	6.0-8.0 %
Surfactant	0.2-0.4 %
Sequestrant	0.1-0.2 %

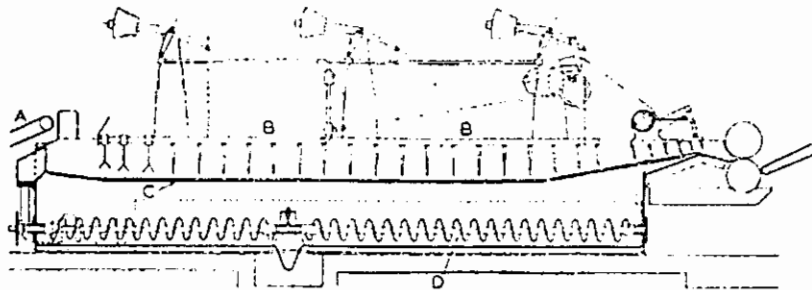
2. Steam fabric one hour at 212°F in J-box or steamer.
3. Rinse thoroughly at 160°F

2. Wool

Wool scouring differs from cotton in two essential respects; raw wool contains a large amount of wool grease in comparison with 0.5 percent oils and waxes in cotton and wool is rapidly degraded by alkali. Sodium hydroxide is never used, instead, sodium or ammonium carbonate are preferred.

Raw wool must be scoured before it can be spun into yarn. This is accomplished in a machine which consists of a long trough provided with rakes, a false bottom and an exit wringer as seen in figure 17.

Figure 18. Typical Wool Raw Scouring Bowl



a. Wool Raw Stock Scouring

1. The trough is filled with scouring liquor containing soap and sodium carbonate at a temperature of 35 to 40° C. 2. The rakes reciprocate pulling the stock from one end of the trough to the other. As the wool leaves the trough, the excess liquor is squeezed back into the trough. 3. Solid matter (dirt) falls through the perforations in the false bottom and the wool grease is suspended in the scouring solution as an emulsion. 4. Since all of the contaminants are not removed in the first pass, additional troughs (called bowls) are arranged in sequence. Each bowl contains either additional scouring chemicals (soap and soda ash) or plain water to effect rinsing. 5. A system of counter flow movement is maintained in this process. Fresh chemicals or water are added to the exit bowls where the wool is the cleanest. The solution from each bowl is pumped into the bowl preceding it. This assures that the wool exits from the cleanest solution and the partially clean solution is reused until it becomes heavily contaminated before it is discharged as waste. 6. The spent liquor is sent to a wool grease recovery unit before it is dumped into the sewer. Wool grease, lanolin, has commercial value of its own.

Wool fabrics contain 2 to 3 % processing oils so scouring will precede dyeing. The fabrics are usually handled, in rope form, in becks. Mild chemicals are used because of wool's sensitivity to alkali. Mechanical agitation in the presence of soap and water will cause wool fabrics to felt. Felting occurs because wool fibers have scales on the surface and the fibers can slip past each other in one direction but not in the other - the scales latch together preventing moving in one direction. Felting causes the fabric to become thicker as it shrinks in width and length.

3. Silk

Silk is scoured (degummed) to remove sericin, a gummy deposit on silk fibers. The process involves "boiling-off" silk in a 0.75 % soap solution at a pH of 10. Sericin is soluble at pH 10. and the excessive amount of soap is there to buffer the solution's pH.

4. Blends

Scouring fabrics with a blend of fibers requires consideration of the sensitivities of each fiber to scouring chemicals and to process conditions. Sensitivities to consider when scouring blends are:

- **Cotton:** Resistant to strong alkali. Degraded by acid.
- **Rayon:** Sensitive to alkali. May be dissolved by hot alkali.
- **Wool:** Degraded by alkali.
- **Acetate:** Hydrolyzed by alkali.
- **Polyester:** Hydrolyses under extreme conditions of alkali and heat.

B. Test for Effective Scouring

1. AATCC Test Method Number 79

Properly scoured fabric should wet out faster and be more water absorbent. *AATCC Test Method No. 79* is used to measure fabric wetting. A drop of water is placed on the fabric and the time it takes for the drop to penetrate the fabric is recorded. The faster the wetting time, the more absorbent the fabric.

VI. WATER AS A RAW MATERIAL

A abundant supply of clean water is necessary in order to run a dyeing and finishing plant. Dye houses are usually located in areas where the natural water supply is sufficiently pure and plentiful. A knowledge of the impurities and how to remove them is important. This section will briefly discuss some of the more important water purification methods. More emphasis will be placed on dealing with trace amounts of certain metal ions which are especially troublesome.

Rivers, lakes and wells represent the major sources of fresh water available for use in wet processing. Rain inevitably finds its way into rivers, streams and lakes, all classified as surface water. When water passes over the surface of the earth, it carries with it organic matter in various stages of decay and dissolves and/or

suspends a certain amount of minerals, depending upon the nature of the soil or rock with which it has come in contact. Well water is surface water which has percolated through soil or rock formations. Subsoil water is usually free of suspended matter but is rich in dissolved carbon dioxide. Dissolved carbon dioxide will convert insoluble calcium carbonate (limestone) into soluble calcium bicarbonate.

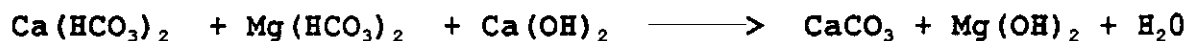
Presence of calcium and magnesium ions in process water is undesirable because these ions are responsible for hardness in water and lead into the formation of insoluble precipitates of soaps and dyestuffs. The bicarbonate salts of calcium and magnesium are called *Temporary* hardness because boiling will liberate carbon dioxide and precipitate calcium carbonate. Chloride salts of calcium and magnesium are called *Permanent* hardness because boiling will not cause a precipitate.

A. Water Softening

There are three methods of removing hardness from water; the lime soda process, cation exchange and sequestration.

1. Lime Soda Process

Calcium and magnesium ions are precipitated as water insoluble salts. Salts settle out and soft water is drawn off. Hydrated lime ($\text{Ca}(\text{OH})_2$) and sodium carbonate (Na_2CO_3) are the chemicals used.



The lime soda process eliminates alkalinity and reduces total solids to 25-40 ppm. Distilled water has 10 ppm solids so this process produces pretty soft water.

2. Cation Exchange

In this processes water passes through a cationic resin bed. One of the most popular ion exchange resins in made from vinylbenzene sulfonic acid crosslinked with divinyl benzene. The sulfonic acid exchanges H^+ ions for calcium or magnesium ions. Once the resin becomes saturated with calcium and magnesium, it is reconstituted by back flushing with acid. The resin can be reused over and over again.

3. Sequestration or Chelation

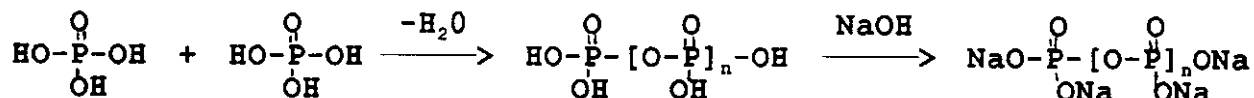
The principles behind sequestration is the formation of a water soluble complex between a sequestering agent and a polyvalent metal ion. The technique can be used for softening water; however, it is more often used as a component in many textile wet processing steps to remove metallic ions that interfere with the process.

VI. CLASSES OF SEQUESTERING AGENTS

A. Polyphosphates

1. Formation of Polyphosphates

Polyphosphates are derivatives of phosphoric acid and are made by reacting phosphorous pentoxide with phosphoric acid. The formation of the polyphosphates can be seen by the following dehydration of orthophosphoric acid.



2. Important Polyphosphates

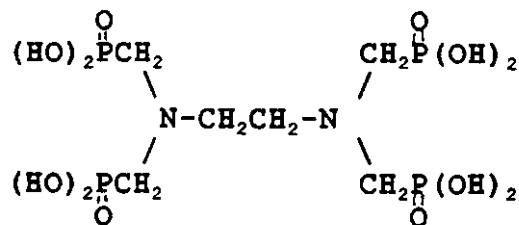
- Tetrasodium pyrophosphate (TSPP). $\text{Na}_4\text{P}_2\text{O}_7$
- (Tripoly)sodium phosphate (TSP). $\text{Na}_5\text{P}_3\text{O}_{10}$
- Sodiumhexameta phosphate. $\text{Na}_6\text{P}_6\text{O}_{18}$

3. Advantages of Inorganic Phosphates

They sequester metal ions and contribute to detergency by suspending and dispersing soils. They require less than the stoichiometric amount predicted to keep ions in solution (threshold effect). They will break down to sodium phosphate in water over time losing their ability to chelate, especially in hot water. They are foods for algae causing rapid growth in streams and ponds. Algae growth depletes stream's oxygen supply causing fish kill.

B. Organophosphonic Acids

1. Ethylenediaminetetra(methylenephosphonicAcid) EDTMP

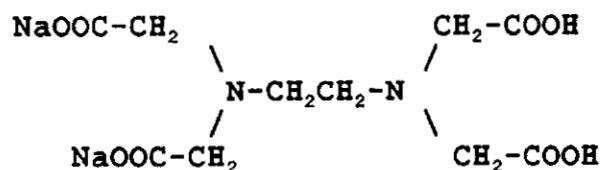


a. Advantages and Disadvantages:

They will sequester metal ions and aid detergency by dispersing and suspending soil. They are more stable than inorganic polyphosphates in hot water and exhibit threshold effect. They are more expensive than inorganic polyphosphates.

C. Aminocarboxylic Acids

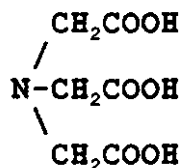
1. Disodium-Ethylenediaminetetraacetic acid (EDTA)



a. Advantages and Disadvantages:

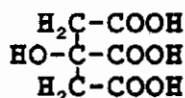
They form very stable complexes with most metal ions. They react stoichiometrically and can be used to quantitatively determine calcium and magnesium by titration. They do not contribute to detergency nor do they exhibit a threshold effect.

2. Nitrilotriacetic Acid (NTA)

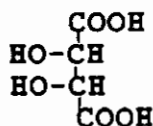


D. Hydroxycarboxylic Acids

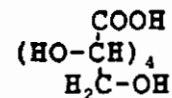
Citric acid



Tartaric acid



Gluconic acid



a. Advantages and Disadvantages:

Hydroxy acids are effective for sequestering iron. They are not effective for calcium or magnesium.

VII. FORMATION OF COMPLEXES

Most polyvalent ions can form complexes with certain ions or molecules. This type of complex formation is called coordination chemistry. The types of molecules or ions that form coordination complexes are called **Ligands**, abbreviated "L". Metal ions are electron acceptors (Lewis Acids) and Ligands are electron pair donors (Lewis Base). The bond that is formed is a **Coordinate Covalent Bond**. **Formation Constant** is a measure of the strength and stability of a complex. It is a measure of the extent the complex will form or dissociate when the system has reached equilibrium. Complex formation is an equilibrium process.

A. Formation Constant



The equilibrium expression is:

$$K = \frac{[ML]^{-}}{[M^{++}][L]}$$

where K = equilibrium constant and log K = formation constant (stability constant). The higher the formation constant, the more strongly held is the metal ion in the complex. Therefore Ligand that give high log K values with a particular metal are very effective sequestering agents. Table 9 lists some formation constants for several chelating agents. The data shows the specificity of some agents, i.e. gluconic acid which is particularly effective for iron. Also the data shows that EDTA is effective across the board.

Table 9.
Formation Constants

	Log K			
	Ca ⁺⁺	Mg ⁺⁺	Fe ⁺⁺	Cu ⁺⁺
EDTA	10.7	8.7	25.1	18.7
NTA	6.4	5.4	15.9	12.9
EDTMP	9.3	8.6	19.6	23.2
Gluconic acid	1.2	0.7	37.2	-

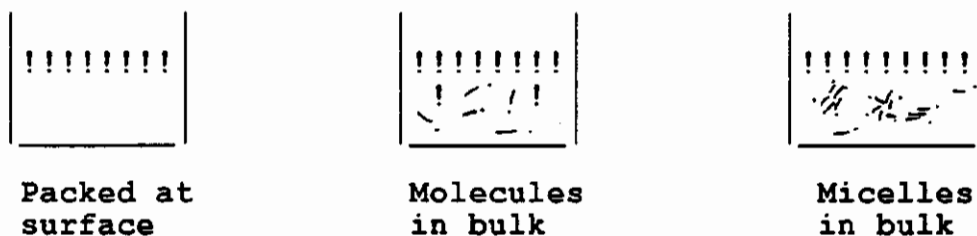
VII. SURFACTANTS

The word *Surfactant* is coined from the expression "surface active agent". As the phrase implies, a surfactant molecule possesses surface activity, a property associated with the chemical structure of the molecule. The characteristic feature of a surfactant molecule is its two ends attached by a covalent bond. The two ends have diametrically opposed polarities. The non-polar end is lyophilic (strongly attracted to organic molecules) while the strongly polar end is lyophobic (having little attraction for organic molecules) yet strongly hydrophilic (water loving). Duality of polarity causes the molecule to align itself with respect to the polar nature of the surfaces it contacts.

A. Physical Chemistry of Surfactant Solutions

When soap (sodium oleate) molecules are added to pure water one molecule at a time, the first few molecules align at the air/water interface and the hydrocarbon tails orient toward air. The driving force for this alignment is the non-polar tails seeking to associate themselves with the most non-polar interface it can find, in this case air. As additional molecules are added, they too will align at the water/air interface until all of the surface area is completely packed. As more molecules are added, they are forced into the bulk of the water, floating about as individual molecules until a saturation level is reached. At this point, called the *Critical Micelle Concentration*, soap molecules agglomerate into water soluble clumps (*Micelles*), where the lyophobic tails are associated with themselves and the hydrophilic heads are surrounded by water molecules. This sequence of events are diagrammed in figure 27. The first beaker represents close packing of surfactant molecules at the surface. The second beaker represents the condition before micelle formation. The third beaker shows the formation of micelles.

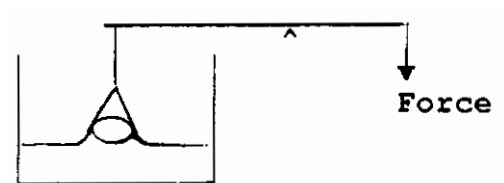
Figure 19. Orientation of Surfactant Molecules in Water



B. Surface Tension

Surface tension is defined as the interfacial tension between a liquid and its vapor. A very simple method of measuring surface tensions is with a du Noy tensiometer. This technique measures the force necessary to pull a platinum ring away from a liquid. For pure water, the force is 72 dynes/cm.

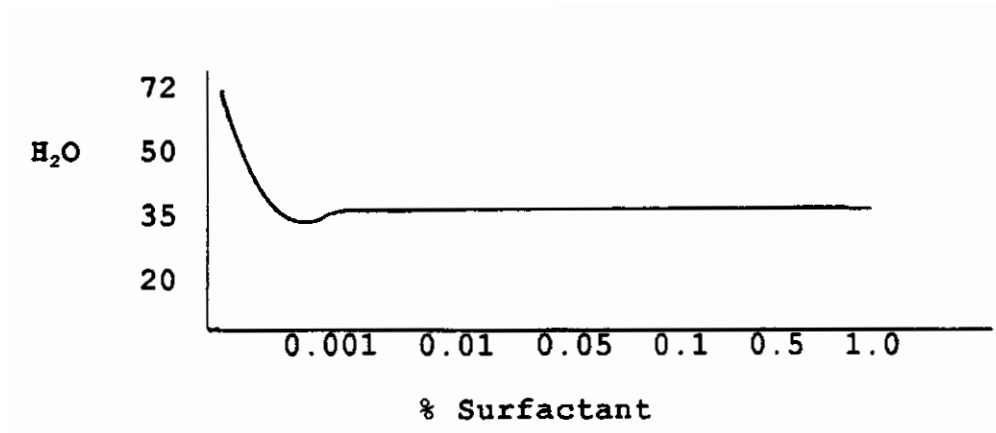
Figure 20. du Noy Tensiometer



C. Critical Micelle Concentration

A plot of soap concentration versus water's surface tension is shown in figure 21. It takes very little surfactant to quickly lower the surface tension. At some low concentration, the plot levels off and maintains the low surface tension value regardless of how much more soap is added. The concentration where the curve levels off is called the critical micelle concentration (CMC). The literal meaning of CMC is the minimum concentration of soap required to form micelles. Increasing the soap concentration beyond this point simply increases the number of micelles in the solution.

Figure 21. Plot of Surface Tension verses Concentration



IX. CLASSIFICATION OF SURFACTANTS

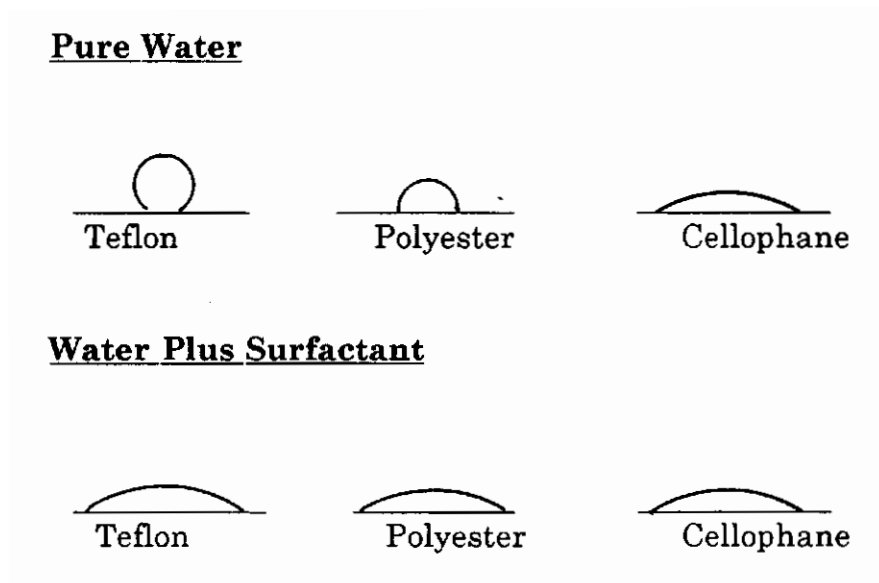
Surfactants are classified according to use, to ionic charge and to chemical structure.

A. By Use

■ **Wetting Agents:** The ability of a liquid to spread on a smooth solid surface is dependent on the polar nature of the solid and the surface tension of the liquid. More about the thermodynamic relationships will be brought up in the chapter on water and oil repellents. A non-polar solid surface such as paraffin wax or Teflon will cause a drop of pure water to bead-up and not spread. Water containing surfactants on the other hand will easily spread on paraffin surfaces and have lower contact angles on Teflon. Surfactants used this way are called wetting agents, or penetrating agents when used to wet out repellent fabrics. This is illustrated in figure 22.

Penetration of fabrics is a function of surface wetting, however fabric assemblies have a volume of air entrapped in the void formed spaces. Before a liquid can move in, the air must move out. Penetrants facilitate this process.

Figure 22. Spreading of Water on Smooth Surfaces



■ **Detergents** are surfactants that help remove soils from solid surfaces. Over and above reducing water's surface tension, detergents must adsorb onto the soil's surface to aid in spontaneous release. Detergents must also keep the soil suspended to prevent redeposition.

■ **Emulsifying Agents** are surfactants that convert water-insoluble oils into stable, aqueous suspensions. The lyophilic part of the surfactant molecule is absorbed by the oil droplet and the lyophobic head is oriented outward, surrounding the droplet with a hydrophilic sheath. Ionic surfactants add another dimension to the stability of emulsions, they set up a charge-charge repulsion field which adds to keeping the droplets separated.

■ **Dispersing Agents** function in a manner similar to emulsifying agents. The difference is that solid particulate matter, rather than insoluble oils, is dispersed. The nature of the lyophilic part of the surfactant molecule must be such that it adsorbs onto the particle's surface. Surfactant molecules must be matched with their intended use.

B. By Ionic Charge

- **Anionic:** Those that develop a negative charge on the water solubilizing end.
- **Cationic:** Those that develop a positive charge on the water solubilizing end.
- **Non-Ionic:** Those that develop no ionic charge on the water solubilizing end.
- **Amphoteric:** Those that have both a positive and negative charged group on the molecule.

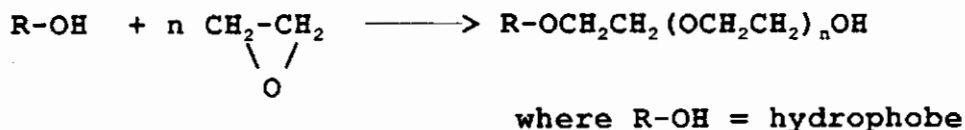
X. NONIONIC SURFACTANTS

Many nonionic surfactants are based on the reaction of ethylene oxide with certain hydrophobes. The word hydrophobe is used to define a water insoluble, lyophilic molecule which will be converted into a surfactant by appropriate reactions. The meaning of hydrophilic/lyophilic balance (HLB), and how HLB can be modified by ethoxylation will be discussed in this section. *Cloud Point* and the relationship between cloud point and surfactant effectiveness will also be discussed.

A. Ethoxylates

Molecules containing active hydrogens will react with ethylene oxide to form poly(ethylene glycol) derivatives. Hydroxyls, carboxyls, amines and mercaptyl groups

are active hydrogen types that can be ethoxylated. The general reaction can be written as:



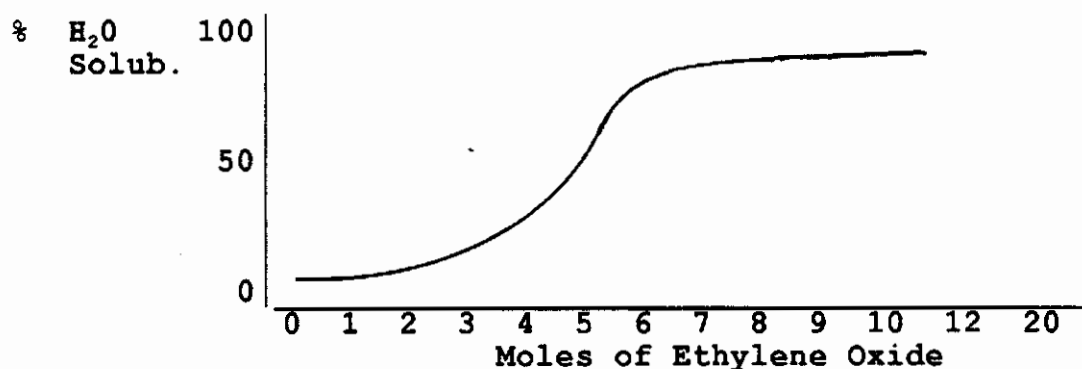
1. Typical Hydrophobes:

- Fatty alcohols such as laurel, oleyl and stearyl
- Alkyl phenols such as octyl and nonylphenol
- Fatty amines
- Fatty acids

2. Water Solubility of Ethoxylated Nonylphenol

Water solubility of ethoxylated compounds is a function of hydrogen-bond formation between water molecules with ether oxygens. The greater the number of ether groups, the greater the number of hydrogen-bonding sites for solubilizing the compound. The relationship between water solubility is shown in figure 23. As the number of moles of ethylene oxide increases for a given hydrophobe, the solubility of the compound increases.

Figure 23. Solubility as a Function of Ethylene Oxide Content

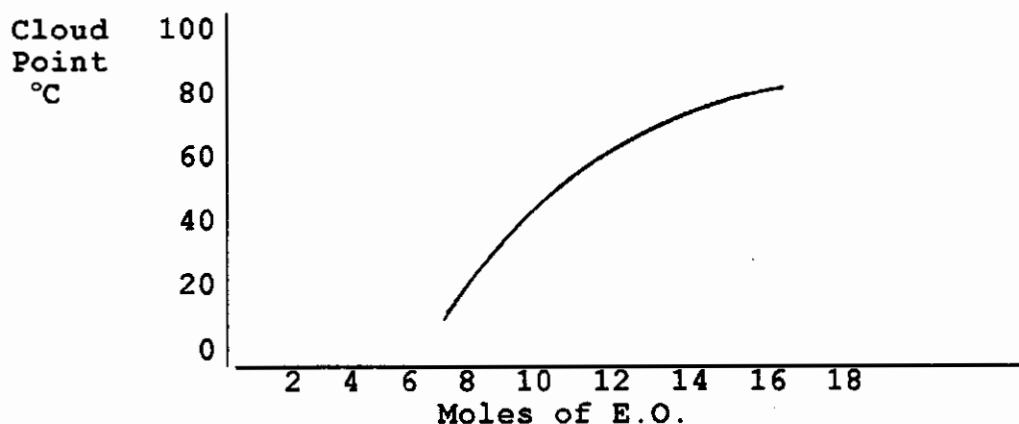


3. Cloud Point

Cloud point is defined as the temperature at which a 1% solution of a nonionic surfactant forms a cloud of insolubility. Cloud point is influenced by the structure of the hydrophobe and the degree of ethoxylation. Temperature too has an influence

on hydrogen bonds, as the temperature increases, H-bonds rupture. At some elevated temperature, enough of them will have broken to cause a cloud of insolubility to form. Eventually the surfactant will separate into an insoluble layer floating on water. Cloud point of a given hydrophobe is influenced by the number of ether units available to hydrogen-bond with water. In figure 24, cloud point is plotted against temperature. For this particular hydrophobe, eight moles of E.O. gives a molecule that is barely soluble at room temperature. Increasing the E.O. content to 16, the new product is soluble up to the boil. This concept is valuable for designing surfactants that work best at given temperatures.

Figure 24. Cloud Point versus Moles of Ethylene Oxide



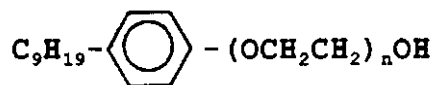
4. Hydrophilic-Lyophilic Balance (HLB)

For a molecule to function as a surfactant, it must have the proper balance of water and oil solubility. The molecule must not be too water soluble otherwise it will not form micelles, yet at the same time it must be sufficiently soluble to do its job. The solubility of a surfactant molecule in water versus oil depends on the water solubilizing group. Ethoxylated nonyl phenol is a good molecule to describe this concept. Nonyl phenol (considered as the hydrophobe), is very slightly soluble in water. It is highly soluble in oils (organic solvents). If one mole of ethylene oxide is added, the water solubility is increased slightly while oil solubility is decreased. As more ethylene oxide is added, water solubility continues to increase at the expense of oil solubility. When 5 to 9 moles of ethylene oxide have been added, the molecule is equally soluble in water and in oil. Above 9 moles of E.O., the water solubility continues to increase at the expense of oil solubility.

The HLB concept is illustrated in figure 25. which pictures the balance as a teeter board. For this illustration the hydrophobe is nonylphenol. One end of the





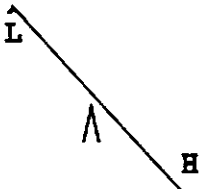
board represents oil solubility while the other end represents water solubility. Figure 25 illustrates the solubility balance of the ethoxylate between the two solvents. The lower ethoxylates are more soluble in oil than in water where the inverse is true of the higher ethoxylates. They become more water soluble and less oil soluble. This balance of solubility is important for any given ethoxylate to perform as a surfactant. For the molecule to affect an interface, it must evenly distribute itself between the two phases, it cannot preferentially be attracted to either phase.

a. Structure of Ethoxylated Nonylphenol



b. Effect of Ethylene Oxide on Solubility Balance

Figure 25. HLB Concept

n	Balance	Solubility
1		Oil soluble
5		Balanced water/ oil solubility Good surfactant at room temp
7		Water soluble
9		More water soluble
16		Highly water soluble

Ionic surfactants are different than nonionic polyethers. Like most water soluble materials, ionic surfactants are more soluble in hot water than in cold. Since more molecules are individually solvated, it follows that a greater amount of surfactant will be needed to reach the critical micelles concentration. Therefore, for ionic surfactants, CMC increases with increasing temperature and the number of available micelles is reduced.

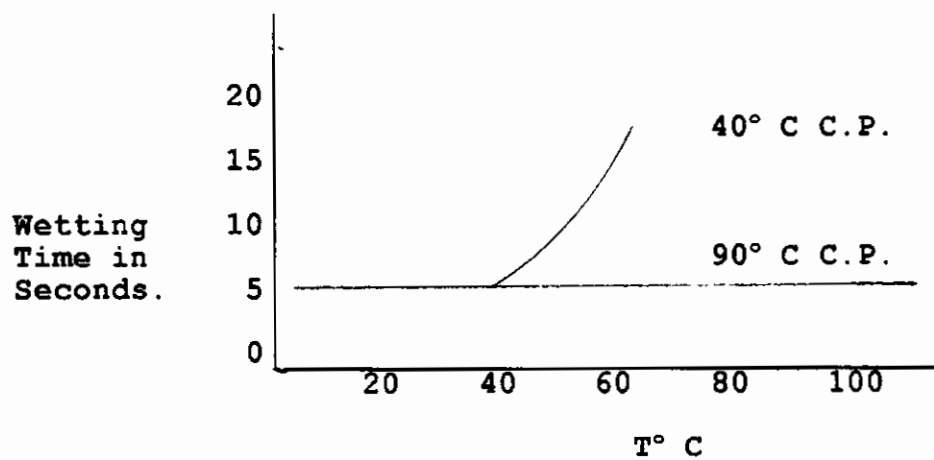
Nonionics are just the opposite. Because they are less soluble hot than cold, more micelles are formed as the temperature is raised. This unique feature gives rise to the fact that nonionics are most effective at temperatures just below their cloud point. At low temperatures, their solubility is higher so a greater number of molecules are needed to reach the critical micelle concentration.

4. Performance

At temperatures above the cloud point nonionics, become insoluble and lose their ability to function as surfactants. This feature can best be illustrated by observing the wetting and detergent characteristics of two nonionics with different cloud points. Figure 34 plots wetting time versus temperature for two surfactants of different cloud points. Both surfactants equally wet out the fabric at room temperature. The 40° CP surfactant however becomes insoluble and loses its wetting-out characteristics at its cloud point. The 90° CP one however is still effective until it reaches boiling temperature.

a. Wetting Times

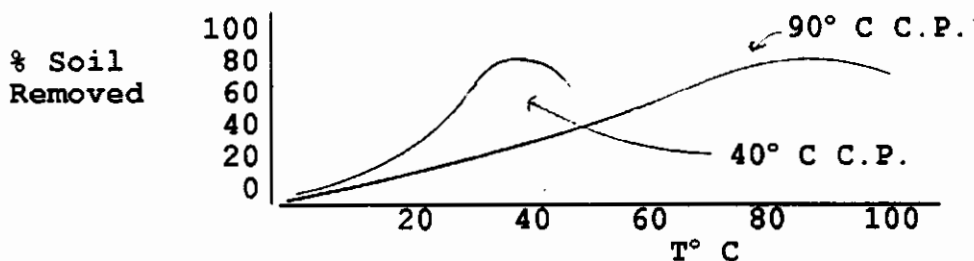
Figure 26. Wetting Times as a Function of Cloud Point



b. Detergency

Figure 26 repeats the comparison, except the surfactants were used as detergents. Again, for soil removal, the 40° CP surfactant was most effective at a temperature just below its cloud point. The 90° CP product, didn't reach its maximum efficiency until the temperature reached the boiling point. At lower temperatures, the 40° CP product removed more soil than the 90° CP product.

Figure 27. Comparison of Cloud Point versus Soil Removal



XI. ANIONIC SURFACTANTS

Many of the structures that function as anionic softeners are also useful as detergents and wetting agents. Anionic surfactants have a negative charge on the molecule. The hydrophilic moiety of anionics are based on carboxylic, sulfuric, sulfonic and phosphoric acids. The surfactants are usually neutral molecules, the acids having been converted to their corresponding alkali salt. Solubility is usually related to the length of the alkyl chain. HLB becomes a function of choosing the proper fatty alkyl group. Listed below are the structure of some of the more widely used anionics.

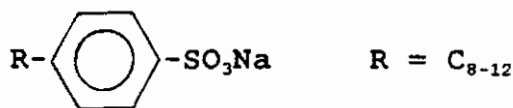
A. Chemical Classification of Anionic Surfactants

1. **Soaps:** Sodium, potassium, ammonium salts of fatty acids. E.g. sodium oleate

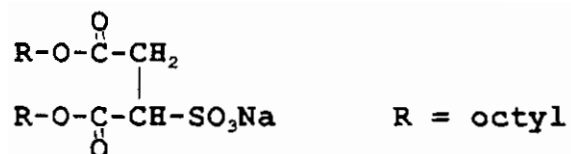


2. Sulfonates:

- a. **Alkylaryl Sulfonates** E.g. Sodium laurelbenzene sulfonate



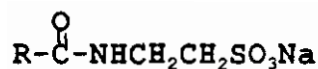
- b. **Sulfosuccinates** E.g. Dioctylsulfosuccinate (DOSS)



- c. **Sulfoethylesters** E.g. (Igepon T)

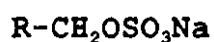


- d. **Sulfoethylamides** E.g. (Igepon A)

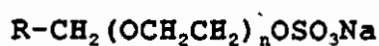


3. Sulfates

- a. **Sulfated alcohols** E.g. Sodium laurel sulfate

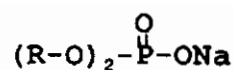
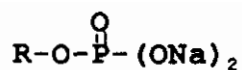


- b. **Sulfated ethoxylated alcohols**



4. Phosphate Esters

- a. **Monoesters and diesters**



XII. CATIONICS

Cationic surfactants are primarily used as softeners, emulsifying agents and dyeing assistants. They are seldom used as detergents and wetting agents. They will be discussed in detail in a latter section.

XIII. REFERENCES

