Chemistry & Technology of Fabric Preparation & Finishing

by

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PREFACE

Global competition has caused the US textile industry to modernize and become cost competitive because developing nations have discovered that exporting textile products to the USA is an attractive way to enhance their economic growth. Their low labor costs have pressured domestic producers into replacing labor intensive manufacturing equipment with automated, sophisticated, efficient, high-technology machinery. The industry has focused on reducing costs, improving quality and developing quick turnaround and response scenarios. These forces have impacted the number and quality of the technical work force. Graduates with a background in computers and information management are making up a larger portion of the entry-level technical staff. Process engineers dedicated to improving quality and efficiency make up the rest. Most of the entry level work force has little or no exposure to textile education or training, they have to rely on experienced technologists to guide and train them. Unfortunately as the older technologists retire, they take with them valuable technical knowledge and know-how leaving the skeletal remains technically unsupported. Most of the technical information is in the form of supplier technical bulletins or in the files of one or two key old-time technologists. Very little is in written form, and what does exist, is not easily accessible to others needing the information. The new-hires are expected to perform their job assignment without the benefit of having trained under a technologist who understands the fundamentals of the process.

There are many references dealing with the subject of textile wet processing. Some are text books describing particular aspects of bleaching and dyeing. There are also a few volumes describing chemical finishing. These books, while filled with valuable information, are old and limited to fibers, fabrics and processes important at the time they were written. Some up-to-date information can be found in specific, single topic papers or bound compilation of research and technical conferences papers. Other sources are specific technical support bulletins issued by chemical or fiber companies. The literature is devoid, however, of books that survey the whole field in one volume and stress fundamentals rather than specific recipes and procedures.

The idea for this book started with the need to provide students in textile chemistry written material to support courses in dyeing and finishing, in particular fabric preparation and fabric finishing. I was disappointed that there was no single volume reference book which adequately covered the information I deemed important. In the beginning, course material was a compilation of class notes gathered from a multitude of sources. It soon became clear that a more complete, written monograph was needed to adequately convey the important chemistry and technology. There have also been numerous requests from industrial contacts for single volume reference material for people entering the field.

At the urging of my colleagues and industry peers, I have been persuaded to publish this collection of information so that anyone may have access to it without the laborious and time-consuming efforts required of me. As a reference source, I have used published information where possible. The book is arranged in two parts, preparation and finishing. In both sections, I have attempted to describe both the mechanical and process parameters, as well as the underlying chemistry behind each process. The major focus in describing the underlying chemistry is the fiber/chemical interaction; however, where possible, I have provided a brief review of the appropriate chemistry behind the various classes of chemical auxiliaries. Each part of the book is subdivided into a part that describes equipment and a part that describes unit operations. Some attempt is made to describe the stages in sequence, one that a typical greige fabric may follow. However, it is important for readers to understand that there is no one single correct way to perform textile wet processing. Each dyehouse has its own character, depending largely on the type of equipment and type of fabric it processes. This makes the selection of operating parameters dyehouse-specific and one may be faced with having to select from several options to achieve the desired end-product. Regardless of which option selected, the same final fabric properties must be met. To this end, I have stressed the objectives and fundamentals of each process. It has been my opinion over the years, that those operations with a technical staff well grounded in the fundamentals, ran more smoothly than one who relied on trial and error as a means of setting up their process.

Fabric preparation has been subdivided into singeing, desizing, scouring, bleaching, mercerizing, carbonizing and heat setting. Finishing is broken down into chemical and mechanical. Chemical finishing covers those treatments that alter the performance of the textile fabric where the chemical is the major component of the change. Mechanical finishing refers to certain types of mechanical devices that physically alters the fabric.

Contributing to the existence of this monograph is the age of computers and word processing. I would have never undertaken this task without the convenience and ease of compiling and moving the information about, something I would have never done by hand. It is my sincere hope that you will find the book valuable, and I welcome comments and suggestions for future revisions.

Charles Tomasino

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PART I

FABRIC PREPARATION

The term "Preparation" has two implications in textile processing. In greige manufacturing, it is used to describe the processes which prepare yarns for weaving and knitting. Mostly, it is used to describe slashing operations that ready warp yarns for weaving. In dyeing and finishing, the term is used to describe those processes that ready fabrics for the steps that follow, coloration and finishing. Fabric preparation is the first of the wet processing steps where greige fabric is converted into finished fabric. The steps that follow, dyeing or printing and finishing, are greatly influenced by how the fabric is prepared. Improper preparation is often the cause of problems encountered in the dyeing and finishing steps. Wet processing technical conferences nearly always have sessions that stress the importance of fabric preparation, seldom is there a conference without topics on how to prepare specific fabrics. There are many different fabrics, many different plant set-ups and many different machines used in wet processing. There is no universally accepted best method for each of the wet processing steps. Nonetheless every set-up is expected to, and more often than not, accomplish the same goals. To deal with this seemingly infinite number of permutations, a fundamental understanding of what happens at each step and how to control the chemical and physical parameters becomes paramount.

The discussions that follows will deal with all of the specific steps that encompass fabric preparation. Fundamental chemical and physical concepts will be stressed. It is important for the reader to understand that not all fabrics undergo each of the steps: however, a specific fabric will be routed through those steps that are necessary to end up with a thoroughly prepared fabric. Chapter 1 will discuss the equipment used to prepare warp yarns, and the equipment used to prepare fabrics for dyeing and finishing, Chapter 2. will cover the chemistry. In wet processing it is generally recognized that the steps encompassing preparation are:

- Singeing: A process where loose fibers and fuzz is burned away to yield a clear and clean fabric surface.

- Desizing: A process where warp size is removed.

- Scouring: A process where mill and natural dirt, waxes and grease are removed.

- **Bleaching:** A process where color bodies are destroyed and the fabric is whitened.

- **Mercerizing:** Caustic treatment of cellulosic fabrics improving luster, water absorbance, dye yield and fiber strength.

- **Carbonizing:** Acid treatment of wool for removing vegetable matter.

- **Heat Setting:** Heat treatment of fabrics containing thermoplastic synthetic fibers. Stabilizes fabric by reducing shrinkage and distortion.

CHAPTER 1

PREPARATION PROCESSES

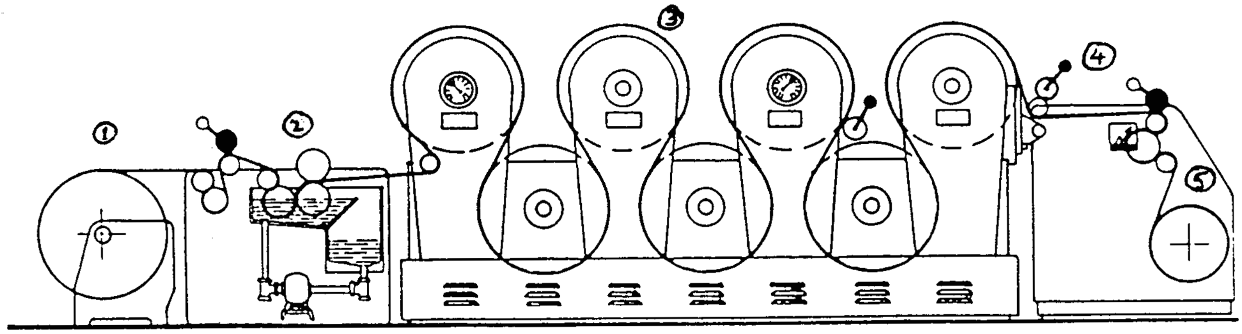
Various types of equipment can be used for preparing fabric. The ultimate goal of any preparation process is to produce fabric that is clean and rid of all impurities that interfere with dyeing and finishing. The preparation steps can be carried out as either batch or continuous processes. The fabric may be transported as a rope or as an open sheet through the equipment. The choice is often predicated on the dye-house itself. The distinguishing feature of batch equipment is that all of the fabric is simultaneously submerged in the liquor. The fabric is agitated by moving it through the liquor. In continuous processes, the fabric passes non-stop through compartments and/or stages so that the fabric is incrementally subjected to the action of the chemicals. The equipment used for dyeing fabrics is also suitable for preparing fabric. In this section, the equipment used to perform fabric preparation will be described.

I. YARN PREPARATION EQUIPMENT

Slashing is the process where ***Size*** is applied to warp yarns for weaving. The purpose of size is to protect the yarn from the abrasive action of the loom. The process is carried out on a ***Slasher*** and the application procedure is called ***Sizing*** or ***Slashing.*** While technically this process is not considered as a step in preparing fabric, the materials used in this operation, to a large measure, account for the bulk of what must be removed. Because the desizing step is highly dependant on what size was used, it is deemed instructive to discuss the slashing process as well as discuss the nature of the sizing materials.

Figure 1 shows a schematic diagram of a slasher. In slashing, section beams are combined to create a loom beam and at the same time apply the appropriate size to the warp yarns. The section marked (1) is the let-off station where one or more section beams are combined and fed through the rest of the range. The warp yarns are let-off as a flat sheet and then pass through a size applicator (2) consisting of a trough containing the size formulation and squeeze rolls. The yarns pass over heated cans (3) to dry. Located at the exit end of the slasher is an arrangement of bust bars which separate each warp end from its neighbor. The individual warp ends pass through a reed which guides the yarn onto the take-up beam. Associated with the slasher is a cooking station, where the sizing material (starch or polyvinyl alcohol) is dissolved and stored. The solution is metered to the applicator as needed to replenish what has been taken up by the warp sheet. The chemical nature of the size will be discussed in a later section along with the conditions needed to effectively remove the size.

Figure 1. Schematic of a Slasher



II. FABRIC PREPARATION EQUIPMENT

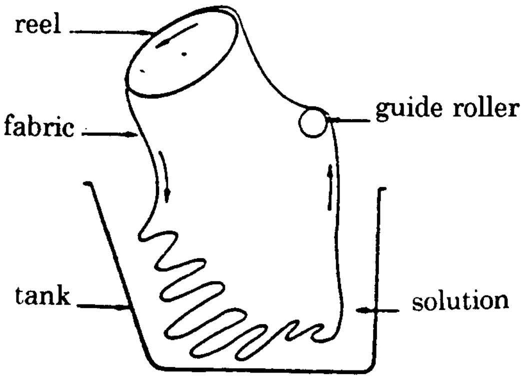
A. Batch Machines

In batch processing, machines are used where the entire load of fabric is immersed in the total amount of liquid needed for that process. These machines are primarily used to dye fabric, however, in many cases they are also used to prepare fabric prior to the dyeing cycle. The section that follows describes some of the more popular machines.

1. Becks

A beck is the simplest type of wet processing batch equipment. It is a large vat which holds the entire lot of fabric. The fabric is fed into the machine in the form of a rope and is made into a continuous loop by sewing the two ends together. The length of the loop is equal to a piece length, usually 100 to 200 yards. The fabric is agitated by the action of a lifter wheel which gently moves the fabric through the liquor by lifting and dropping the rope in and out of the liquor. Lot size is determined by the number of loop strands that can be accommodated by the machine and is a function of the front width of the machine. Commercial machine are available ranging from one strand to 16 strands. A schematic of a beck is shown in figure 2.

Figure 2. Schematic of an Atmospheric Beck

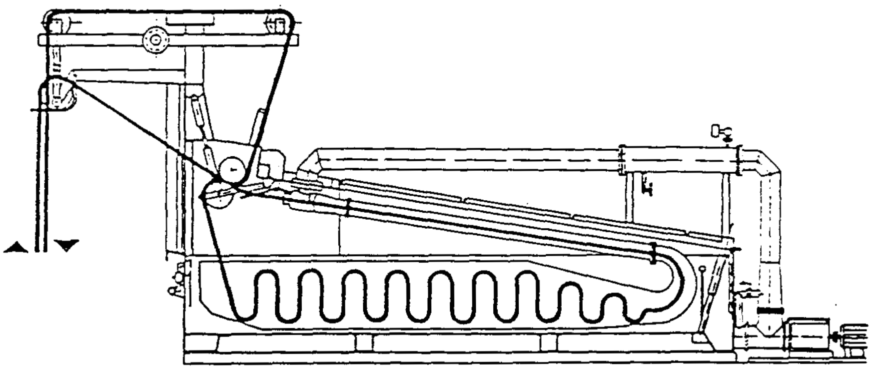


2. Jet Machines

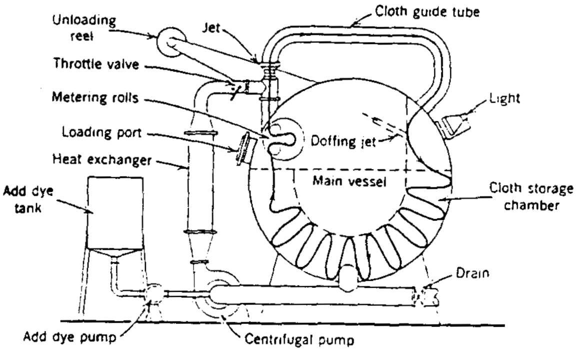
Jet machines are similar to becks in that a continuous loop of fabric circulates through the machine. They differ however in that a stream of liquor is forced through a venturi tube. This provides the force to propel the fabric through the machine. Temperatures in Jet machines that operate at atmospheric pressure cannot exceed the boiling point of water; however, higher temperatures can be obtained in those that are operated under pressure. An advantage of the jet machines is that lower liquor ratios can be used. In a beck, the liquid is stationary and the fabric moves through it. In a jet however, both the liquid and the fabric move in relation to each other. This increases the rate of interchange between the liquid and fabric and speeds up the process. The distinguishing features of jet machines are the venturi tubes which create the force to circulate fabric, and circulating pumps which cycle the bath through the venturi tubes. Figures 3 shows schematic diagrams of pressure and atmospheric jets.

Figure 3. Schematics of Jet Machines

Atmospheric Jet



Pressure Jet

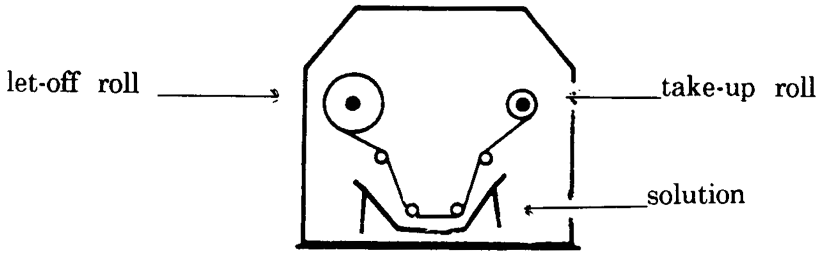


4 Schematic view of jet dyeing machine. (Courtesy of Gaston County Dyeing Machine Co., Stanley, North Carolina, U.S.A.)

3. Jig

A Jig or Jigger is a batch machine which handles fabric in open width. It is a simple machine consisting of let-off and take-up rolls, a trough containing the processing liquor and guide rolls which allow the fabric to pass from the let-off to the take-up roll. After all the fabric transfers, the driving mechanism is reversed and the fabric makes a second pass through the liquor by returning to the original let-off roll. The cycle can be repeated as many times as it takes to achieve the desired effect. Figure 4 shows a schematic of a jig.

Figure 4. Schematic of a Jig



B. Continuous Preparation. Ranges

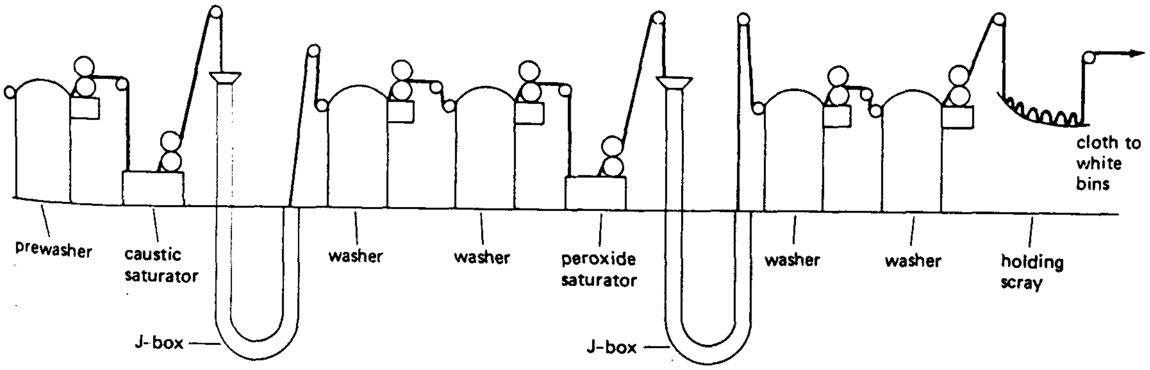
Continuous ranges are used whenever large volumes of a relative few styles of fabrics are being processed. The fabric moves continuously (at relative high rates of speed) through stages and compartments which provide the chemicals, time, temperature and rinsing needed for cleaning the fabric. Many fabrics go through a three section range where each section is dedicated to desize, to scour and to bleach. Some fabrics however, may only require one or two steps to complete the preparation process. For example knit goods are not sized so desizing is not necessary. Synthetic yarns may not need to be bleached. Some fabrics may go through one section where desizing, scouring and bleaching is accomplished in one step. The pros and cons of each of these set-ups become fabric specific and the appropriate procedure is determined by trial and error.

Each stage contains three substations: an applicator where the fabric is impregnated with appropriate chemicals, a holding station which provides reaction time and temperature and finally a washing station for flushing out the impurities. The equipment is designed for handling the fabric as a continuous rope or as an open width sheet. An open width range needs more sophisticated equipment such edge guide rollers, fabric spreaders and steam chambers to keep the fabric flat and smooth. A rope range need not be as sophisticated.

1. Continuous Rope Range

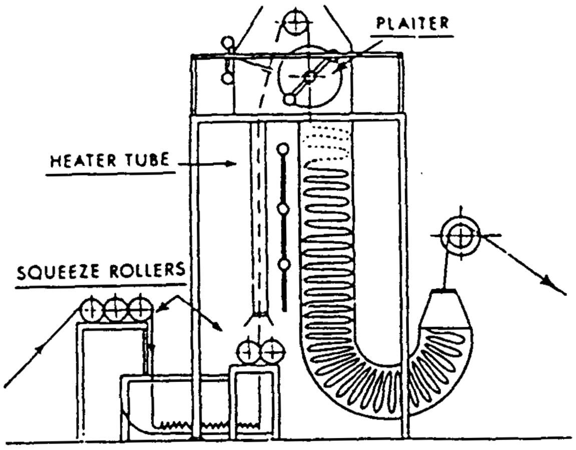
Figure 5 shows the schematic of a rope range. This drawing only include scouring and bleaching stages. Each stage contains a saturator, J-box and rope washers.

Figure 5. Schematic of a Continuous Rope Range



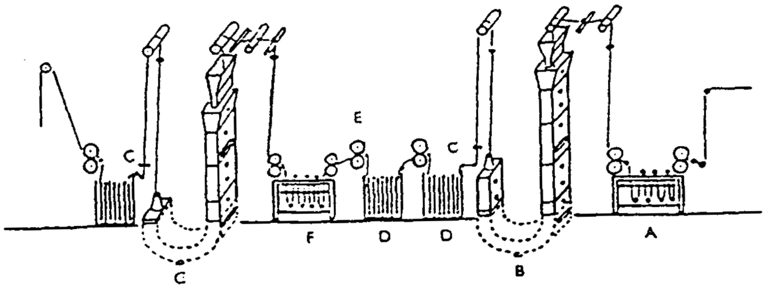
The heart of a rope range is the J-box which is detailed in figure 6. The saturated fabric is plaited into the top leg of the J and feeds by gravity out through the lower leg. The size of the J-box depends on the dwell time and the speed of the range. These boxes are usually jacketed and steam heated.

Figure 6. Schematic of a J-Box



More details of a preparation utilizing J-boxes is seen in figure 7.. The saturator is placed in front of a J-box and the washers are placed immediately after. Without pause, the fabric exits the washer and enters the next saturator. The sequence saturator g J-box g washer is repeated until all of the preparation steps are completed.

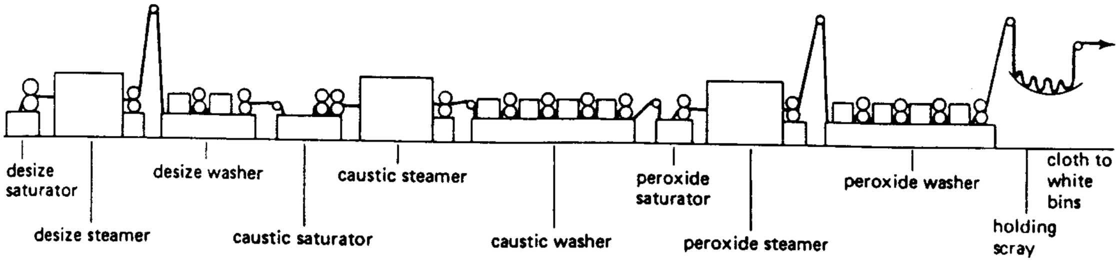
Figure 7. Details of Continuous Rope Range



2. Continuous Open Width Range

An open width range differs from a rope range only to the extent that the fabric handling equipment is different. The chemicals, temperatures and dwell times, for the most part are the same as that for a rope range. A schematic of an open width range is seen in figure 8.

Figure 8. Schematic of an Open Width Range



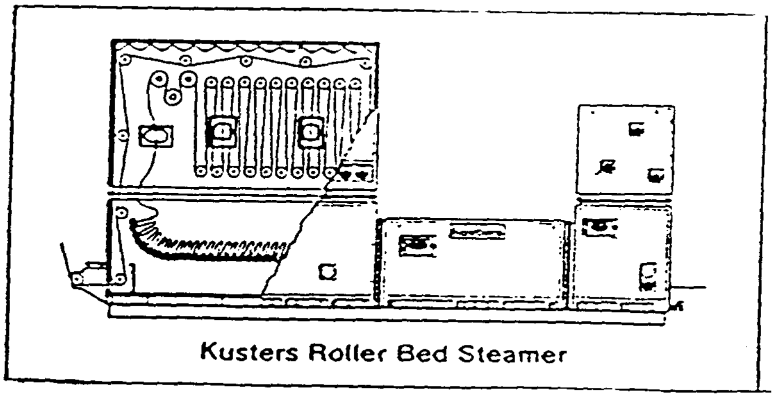
a. Applicators - Pads

Chemicals are applied by padding. Pad designs will be discussed later in the section on finishing.

b. Steamers

Steamer provides dwell time, moisture and temperature. The drawing in figure 9 shows a combination roller section - conveyer-bed steamer. The impregnated fabric enters the roller section where the fabric is exposed to heat and moisture in open sheet form. It is then plaited onto a conveyer-bed to provide reaction time for the chemicals to work before the fabric is washed. Some steamers have only the roller section. These require more floor space if the dwell time is to be equivalent. The combined roller, conveyor bed steamers are the result of new developments aimed at improving cost/performance.

Figure 9. Schematic of a Roller Bed Steamer



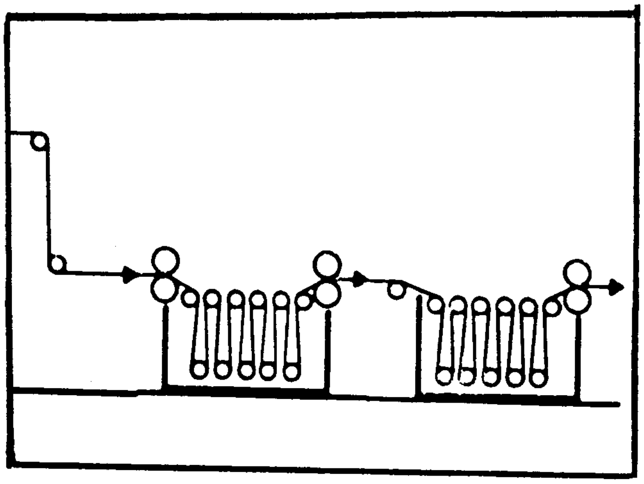
c. Open Width Washers

An open width washer can be a simple box (figure 10) containing a series of vertically stacked rollers where the lower rollers are submerged in the wash water. Fabric enters the box at one end and traverses the box by going over and under each stack. Any number of these boxes can be arranged in series to provide the appropriate amount of rinsing. More sophisticated boxes will be divided into several compartments. Squeeze rolls are placed between them to speed up the removal of impurities. Some are equipped with spray nozzles which also facilitate the flushing action.

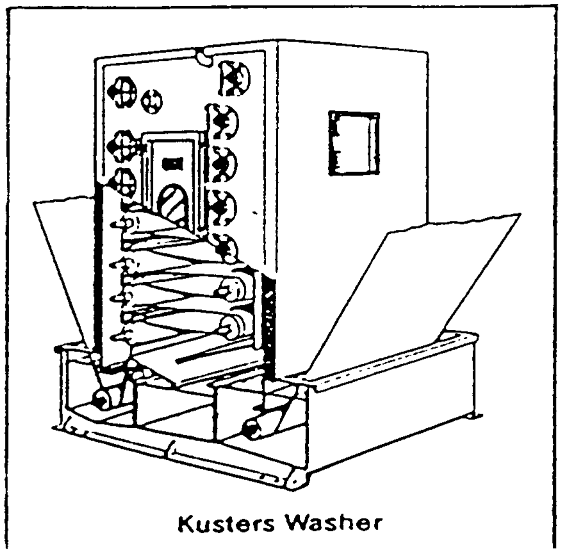
In another design, the rollers are stacked horizontally. The fabric enters through a trough at the bottom of the box. The thread-up is such that the fabric travels to the upper set of rollers and works its way down successive pairs of rollers until it reaches the bottom. There it exits through another trough. Water cascades downward through the layers so the flushing action is assisted by the physical force of the water impacting the fabric.

Figure 10. Washers

Open Box Washer



Horizontal Washer



Since hot water is an expensive raw material and environmental pollution laws regulate discharge water, it is important to reduce the amount of water consumed by these operations. One way to reduce water consumption is by ***Counterflow Washing.*** Water flow through the wash boxes counter to the flow of the fabric. Fresh water is fed to the exit compartment to insure that the fabric exits through the cleanest water. The water from the last box is pumped to the preceding wash box which in turn is pumped to the one preceding it. The water from the entry box is dumped into the drain since it is the most heavily contaminated wash water. This technique saves on water consumption since only the most heavily contaminated water is discharged, cleaner water is reused until it becomes heavily contaminated.

III. REFERENCES

CHAPTER 2

CHEMISTRY OF YARN AND FABRIC PREPARATION

I. YARN PREPARATION

A. Warp Size

In the production of woven fabrics, warp yarns are sized with a protective coating to improve weaving efficiency. Movement of the warp yarn through the heddles and mechanical actions during insertion of filling creates a great deal of abrasive stresses on these yarns. Unprotected, the warp yarns cannot withstand the rigors of weaving. They will break causing machine to stop and thus be responsible for loss of productivity. Weaving efficiencies are vastly improved when the warp is properly sized. *Size* or *Sizing* is defined as the composition of matter applied to the warp yarn for weaving protection. Size usually consists of a water soluble, film-forming macromolecule and a lubricant.

1. Requirement of a Good Size

The qualities required of a good size depends, in the main, on what type of yarn is in the warp. For example, fine count spun yarns require more protection than do plied yarns or course count spun yarns.

a. Spun Yarns

Spun yarns require that size contribute to yarn strength and that the protruding fiber ends be glued down to make it less hairy. To do this, the sizing solution must have a high viscosity to prevent penetration into the yarn. Optimum protection is afforded when most of the size remains on the yarn surface to coat the yarn and glue down the protruding hairs.

b. Continuous Filament Yarns

These yarns are strong to begin with. The main purpose of the size is to tie all of the filaments together. Stray filaments are easily broken; however, as part of a single, large bundle, the yarn is strong and abrasion resistant. Viscosity needs to be low so that the solution penetrates into the yarn bundle. Also the better the adhesion between the size and the fiber, the better is the protection.

c. General Requirements of a Good Size

- Tensile Strength
- Inexpensive
- Flexible
- Not support bacteria
- Abrasion Resistant
- Good adhesion
- Extensible
- Easily removed

II. FABRIC PREPARATION

A. Warp Size and Desizing

For woven fabrics, warp size constitutes the major impurity that must be removed in fabric preparation. This section introduces the materials often used as warp sizes and the chemistry needed to remove them.

1. Sources of Sizing Compounds

The following list summarizes the materials that can be used as warp sizes. Some of the base materials are used either alone or as additives to impart desirable properties to other bases. When designing the desizing step, it is important to know what base size was used. Each film-former has its own optimum conditions for effective removal. A knowledge of the chemistry of the film-formers will make it easier for one to grasp how to best desize specific fabrics.

- Starches
- Polyvinyl alcohol
- Gums
- Glue
- Carboxymethyl Cellulose
- Flours
- Dextrine
- Polyacrylic Acid
- Gelatins
- Synthetic Polymers and Co-polymers

Of the bases listed above, starch and polyvinyl alcohol are the polymers most often used when sizing spun yarns. Synthetic polymers work best on filament yarns. These polymers at times are blended with starch to improve starch's adhesion to synthetic fibers.

III. STARCH

Historically, starches and flours have been the film-formers of choice for textile sizing. The key difference between flours and starches is the gummy substance gluten, starches are flours which have had the gluten removed. Nature produces a wide variety of starches as a white granular substance found in seeds, roots and stem piths of growing plants. Flours or meal is leached with water (to remove the gluten) leaving the white, free-flowing granule which has limited solubility in cold water.

A. Sources of Starches Used as Textile Size

Listed below are the natural sources of starch used as textile size:

- Corn (maize)
- Tapioca (cassava)
- Wheat
- Sweet Potato
- Potato (farina)
- Sago
- Rice
- Yucca

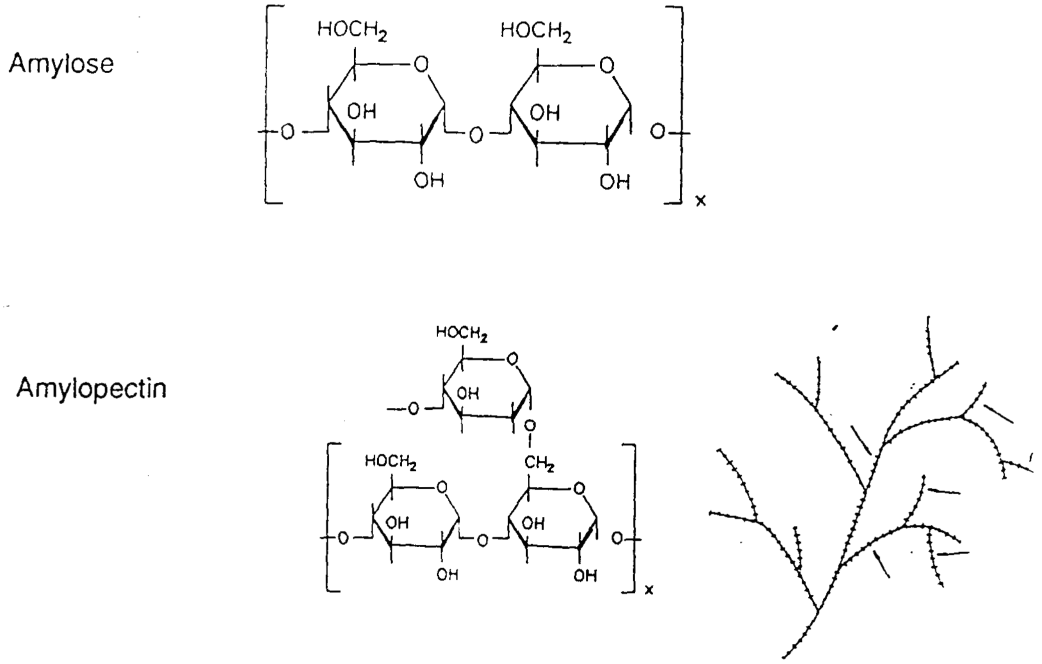
B. Chemical Constitution

Starch polymers are carbohydrates composed of repeating anhydroglucose units linked together by an alpha glucosidic linkage. The structure contains two secondary hydroxyls at the -2,3- positions and a primary hydroxyl at the -6- position. The alpha linkage is an acetal formed by the linkage of the hydroxyl at the -1- position with the -4- position of another. This gives rise to a linear polymer called ***Amylose.*** Branching can occur when an acetal linkage between the -1- position of one ring forms with the -6- position of another. Highly branched polymers are called ***Amylopectin.*** The differences between amylose and amylopectin are:

- **Amylose** is a linear polymer, molecular weight range 100,000 to 300,000, found in the interior of the starch granule and accounts for 19 to 26% of the weight. It is soluble in hot water; however, when the solution is cooled, it will form strong hydrogen bond between adjacent chains making it difficult to re-solubilize.

- **Amylopectin** is the major component of starch and comprises the outer sheath of the granule. A highly branched, high MW polymer (1.6M), less water soluble than amylose.

Figure 11. Chemical Structure of Amylose and Amylopectin



C. Starch Solutions

Natural starches are not very soluble in cold water. Cooking is necessary to get the starch granules to form a homogenous solution. Typically the starch granules are stirred in cold water and kept suspended by high speed mixing. As the temperature is raised, water penetrates through the amylopectin membrane solubilizing amylose. The granules swell as more and more water diffuses in enlarging to many time their original dimensions. The viscosity of the solution increases as the granules swell, reaching a maximum at the point where the swollen granules are crowding against each other. Prolonged heating and mechanical shearing cause the swollen granule membrane to rupture allowing the solubilized amylose to spill into the bulk of the solution. At this point the viscosity begins to fall off, finds a stabilized level and remains there. The starch solution can be considered as solubilized amylose molecules intermingled with ruptured swollen fragments of the amylopectin membrane.

1. Retrograding

The solution will remain fluid as long as it is stirred and kept hot. However if the solution becomes concentrated by evaporation of water, and/or should the solution cool, an irreversible gel is formed which will not redisperse, no matter how long it is heated or stirred. Materials that won't redissolve once they have been solubilized are said to retrograde. In the case of starch, the linear amylose molecules align themselves, and through hydrogen bonding, form 3-dimensional arrays that are difficult to break apart. This peculiarity in starch is the reason specific processing conditions are needed to economically remove it during desizing.

D. Modified Starch

The working properties of starch solutions (viscosity, retrograding point, penetration into yarns etc.) are influenced by the source of starch. The reader is referred to any of a number of well written books and reviews extolling the virtues of the various natural starches. In addition to naturally occurring variations, there are chemical modifications where some of the natural starch properties are altered to make them more useful.

1. Thin Boiling Starch

Thin boiling starches are made by adding a small amount of acid to a starch suspension that is held just below its gel point. The acid cleaves the polymer at the glucosidic linkage thereby lowering the viscosity of a solution made from it. Hydrolysis occurs within the granule without breaking the granule. Mostly corn starch is used to make thin boiling starches. Their solutions still retrograde.

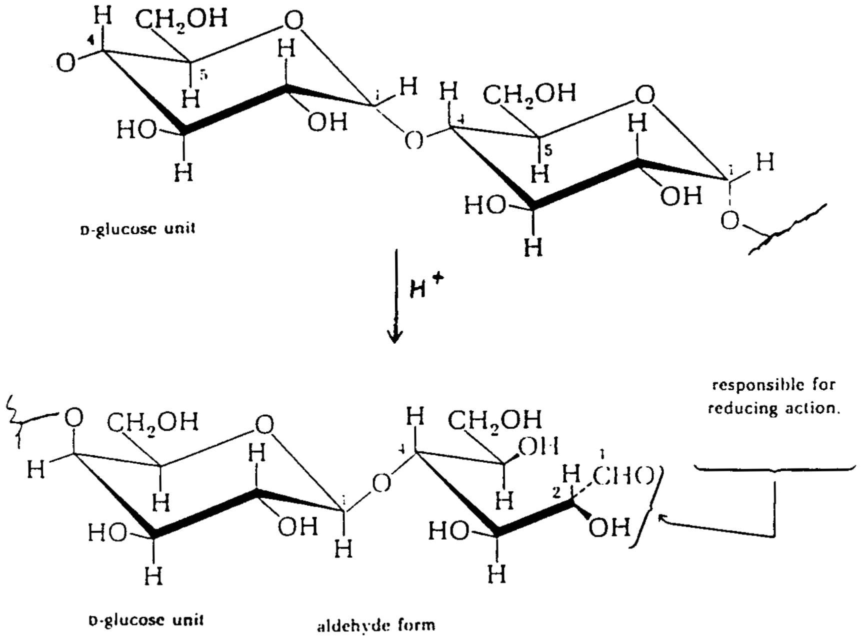
2. Dextrin

Dextrine are made by heating dry starch with a mineral acid. White dextrin is made byheating at moderate temperatures and yellow dextrine is made by heating at higher temperatures with less acid. The degree of hydrolysis is higher than for thin boiling starch so dextrine solutions have lower viscosities.

3. British Gum

British gums are made by dry heating starch granules at 180 ^{0}C without acid. Some of the 1-4 acetal linkages are broken and 1-6 are formed. A more highly branched, lower molecular weight product is formed having more reducing end groups. British gums are more water soluble and produce higher solution viscosities. They are mainly used as print paste thickeners.

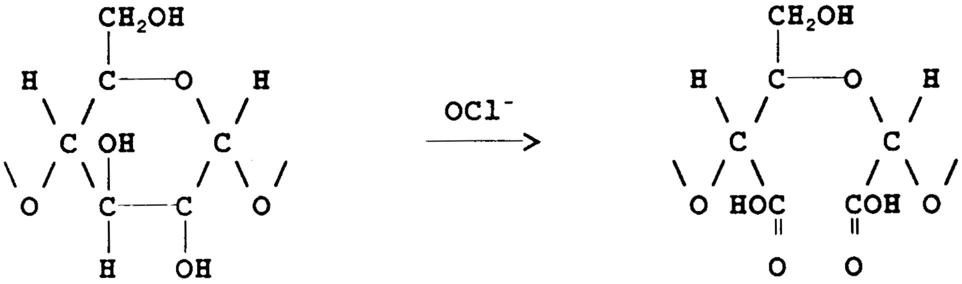
Figure 12. Hydrolysis of Starch



4. Oxidized Starch

Starch granules are oxidized with sodium hypochlorite which converts the 2-3 hydroxyl into -COOH groups breaking the ring at that point. Five to seven -COOH groups per 100 anhydroglucose are introduced. Sodium bisulfite is added to destroy excess hypochlorite. The granular structure is retained and films from oxidized starch are better than those formed from thin boiling starch.

Figure 13. Oxidation of Starch



5. Starch Ethers

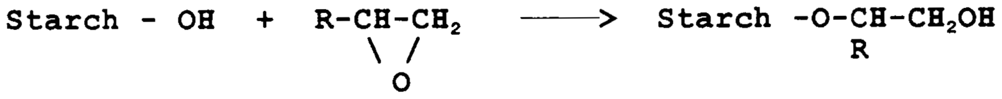
Starch ethers are made by reacting the hydroxyl groups in the anhydroglucose ring with appropriate reagents. These reactions add to the hydrophilic nature of the starch and decrease the ability to form hydrogen bonds between polymers, modifying solution and dry film properties.

Figure 14. Starch Ethers

Carboxylated Starch

$$\text{Starch} - OH + ClCH_2COOH \longrightarrow \text{Starch} - O - CH_2COOH$$

Hydroxyethyl or Hydroxypropyl Starch



$$\text{Starch} - OH + \underset{\backslash\ / \atop O}{R-CH-CH_2} \longrightarrow \text{Starch} - O - \underset{R}{CH} - CH_2OH$$

where $R = H-$ or CH_3-

E. Desizing Starch

Once a cooked starch solution dries, the resulting film will not readily re-dissolve in water; therefore, to completely remove starch from a fabric, the polymer must be chemically degraded to make it water soluble. Three chemical methods can be used to degrade starch into water soluble compounds namely, ***Enzymes, Acid Hydrolysis*** and ***Oxidation.*** Each method has its own peculiar advantages and disadvantages.

1. Enzyme Desizing

Enzyme desizing is the most widely practiced method of desizing starch. Enzymes are high molecular weight protein biocatalyst that are very specific in their action. Enzymes are named after the compound they break down, for example, ***Amylase*** breaks down amylose and amylopectin, ***Maltase*** breaks down maltose and ***Cellulase*** breaks down cellulose. For desizing starch, amylase and maltase are used. Cellulase, on the other hand, is used for finishing cotton fabrics. This will be discussed in later chapters. Amylase will degrade starch into maltose, a water soluble disaccharide and Maltase will convert maltose into glucose, a simple sugar.

a. Alpha and Beta Amylase

There are two types of amylase enzymes, ***Alpha*** and ***Beta.*** Both alpha and beta amylases hydrolyse glucosidic linkages in starch; however, the point along the polymer chain at which the reaction occurs differs between the two. ***Alpha amylase*** attacks the chain at random points. The molecular weight of the starch is rapidly reduced facilitating complete removal. ***Beta amylase,*** on the other hand, starts at a chain end removing one maltose unit at a time. The molecular weight is gradually reduced thereby taking a longer time to complete breakdown. In addition, the action of beta amylase is stopped at the 1,6 branch glucosidic linkage found in amylopectin leaving relatively high molecular fractions. Alpha amylase is the predominate enzyme used in desizing starch. A major advantage favoring enzymes is that they not damage cellulosic fibers. On the other hand, cellulase enzyme will destroy cellulose and while it is not used in desizing, it has found a specialty application in the production of stone-washed denim look.

There are three major sources for amylase enzymes. ***Malt Enzymes*** are extracted from the fermentation of barley grain which produces a mixture of alpha and beta amylase. ***Pancreatic Enzymes*** are extracted from the pancreas of slaughtered cattle which is mainly alpha amylase and ***Bacterial Enzymes*** are prepared from the bacteria "bacillus subtilin". This too is mainly alpha amylase.

b. Effect of Temperature, pH and Electrolytes on Enzymatic Desizing

Activity of enzymes increase with temperature; however, above a critical temperature, enzymes are deactivated. The effectiveness of enzymes exhibit a maximum at certain temperatures, usually 40 -75 ^{0}C. Bacterial enzymes are the most thermally stable and can be used up to 100 ^{0}C under special stabilizing conditions.

Certain salts increase the activity of specific enzymes. Pancreatic amylase is ineffective without the addition of salt. A combination of sodium chloride and calcium chloride increases the stability of bacterial amylase above 160 ^{0}F. Activity of amylase enzymes are also optimum at specific at specific pH. Table 1 summarizes the optimum conditions for the various sources of enzymes.

Table 1

Summary of Optimum Operational Conditions for Amylases

Alpha Amylase	Optimum pH	Effect of Temp.°C	Effect of NaCl	Effect of $CaCl_2$
Pancreas	6.8-7.0	40 - 55	+	+
Malt	4.6-5.2	55 - 65	-	+
Bacteria	5.0-7.0	60 - 70	O	+

2. Desizing with Acids

Mineral acids will hydrolyze starch by attacking glucosidic linkages. Acid hydrolysis lowers the molecular weight and eventually reduce starch to glucose. Hydrochloric and sulfuric acids can be used. One problem with acid desizing is that cellulose fibers are also degraded which is why the method is not used much. One advantage with using acids is that cotton fibers can be demineralized more easily. Insoluble salts are solubilized by acids making the removal of such troublesome metals such as iron more thorough.

3. Desizing with Oxidizing Agents

Sodium hypochlorite, sodium hypobromite and sodium or potassium persulfate will also degrade starch. The reaction opens anhydroglucose rings at the - 2,3-hydroxyls, converting them into carboxylic acid groups. This method is not used much either because it too degrades cellulose fibers. Hypochlorite is used for bleaching however.

4. Test for Starch

A drop of iodine solution placed on a test specimen resulting in a characteristic blue color is the universal test for identifying starch. It can be used as a qualitatively test to show whether all the starch was removed. Absence of the blue color signifies that all the starch has been removed. The intensity of the color is some what related to how much is left. Usually, if the color is faintly perceptible, the remaining starch will come out in the scouring and bleaching steps that follow.

5. Typical Procedures

Most woven fabrics are prepared on continuous ranges. For desizing and scouring, the fabric may be handled as a continuous rope or in open-width form. While the equipment is specifically designed for each set-up, the chemical requirements for both are the same.

1. Saturate fabric with a solution containing:

Bacterial Amylase	0.8 - 1.0 %
Wetting agent	0.1 - 0.2 %
Sodium Chloride	10 %

2. Hold:

<u>Open-width Range</u>: Steam 1 to 2 minutes at 200 to 212 ^{0}F.

<u>Rope Range</u>: Store in J Box for 20 to 30 minutes at 170 to 180 ^{0}F. or over night at room temperature.

3. Thoroughly rinse with hot water, 175 ^{0}F or hotter.

IV. CARBOXYMETHYL CELLULOSE (CMC)

Carboxymethyl cellulose is made by the reaction of sodium chloroacetate with cellulose. Lumbering by-products, namely stumps, limbs etc. are ground-up, soaked with alkali and made to react with sodium chloroacetate. The degree of substitution can be controlled up to a maximum of 3 carboxymethyl groups per anhydroglucose unit. For textile sizes, the DS is usually 1.5.

A. Synthesis

$$\text{Cell-OH} + \text{NaOH} \longrightarrow \text{Cell-O}^{-} \xrightarrow{\text{ClCH}_2\text{COONa}} \text{Cell-OCH}_2\text{COONa}$$

B. Advantages and Disadvantages over Starch

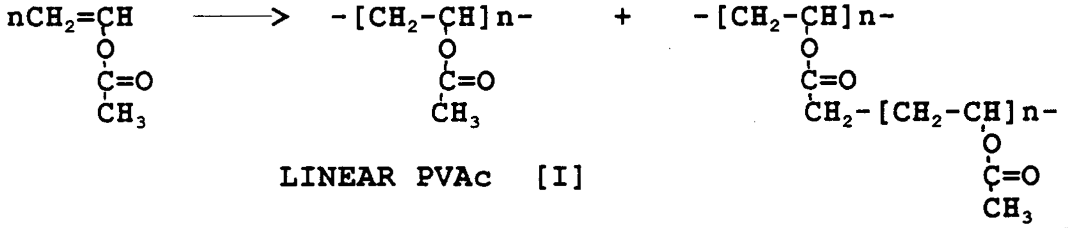
CMC is soluble in cold water and does not requiring a cooking step. Solutions remain fluid at room temperature and don't retrograde, They can be reheated and cooled repeatedly. It is easy to remove and redissolve CMC size in warm water. CMC like starch supports mildew on storage of fabrics. It is more expensive than starch.

V. POLYVINYL ALCOHOL (PVA)

Polyvinyl alcohol comes in several grades, differing in molecular weight and solution viscosity. Polyvinyl alcohol is manufactured by hydrolysing polyvinyl acetate. The reason is because vinyl alcohol does not exist as a monomer, tautomerization favors the more stable acetaldehyde. Polyvinyl acetate, however, can be hydrolysed into polyvinyl alcohol under acidic or basic conditions. Either method leaves undesirable salts that are difficult to remove. The preferred commercial method of hydrolyzing polyvinyl acetate is to use catalytic amounts of sodium methoxide in methanol. The reaction proceeds through trans-esterification where the by-product, methyl acetate, is easy to remove by distillation. The parent polyvinyl acetate forms branches during polymerization by a chain transfer mechanism at the methyl group of the ester. However, the corresponding polyvinyl alcohol is lower in molecular weight and virtually linear. The branch points are ester linkages which are broken during the hydrolysis step. The branches become linear, lower molecular weight fragments. This accounts for both lower molecular weight and the linearity of the PVA.

A. Synthesis of Polyvinyl Alcohol

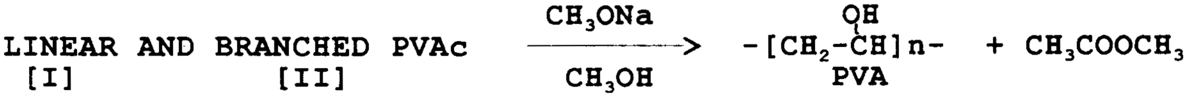
1. Polymerization of Vinyl Acetate



LINEAR PVAc [I]

BRANCHED PVAc [II]

2. Hydrolysis to Polyvinyl Alcohol



$$\text{LINEAR AND BRANCHED PVAc [I] [II]} \xrightarrow[CH_3OH]{CH_3ONa} -[CH_2-\overset{OH}{C}H]n- + CH_3COOCH_3$$

PVA

B. Commercial Method of Manufacture

Polyvinyl acetate is dissolved in methanol to form a 20% solution. Sodium methoxide is added while the solution is being stirred by a high speed mixer. The solution is poured onto a conveyor and passed through a gelling zone. Polyvinyl alcohol is not soluble in methanol so as the hydrolysis proceeds, a gel is formed. The gel, consisting of polyvinyl alcohol, methyl acetate, methanol and catalyst is choppedup, the catalyst neutralized with acetic acid, squeezed to remove the excess liquids and the solids purified by washing with more methanol. The solids are dried and pulverized into relatively pure polyvinyl alcohol.

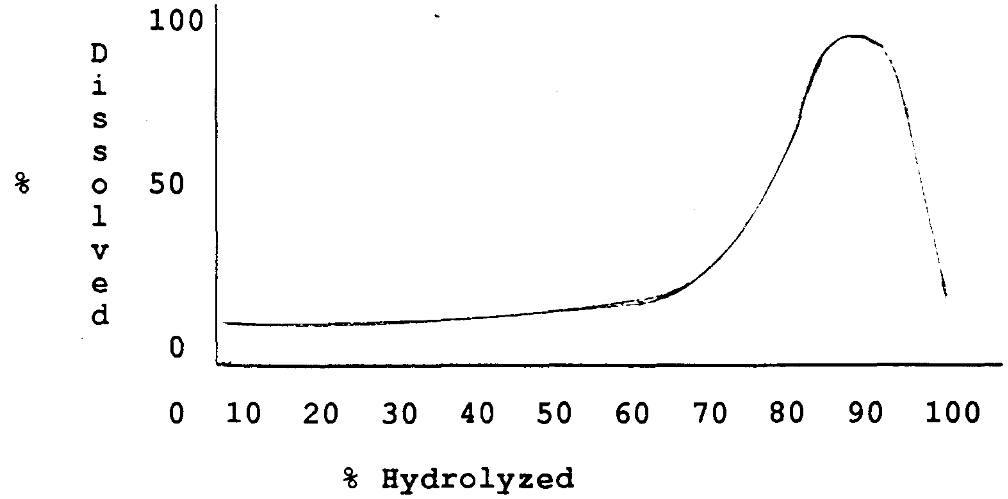
C. Solution Properties

Water solubility, solution viscosity and film properties are influenced by the molecular weight and degree of hydrolysis. As the acetate ester, the polymer does not have hydrophilic groups to assist in water solubilization. However -OH groups are able to hydrogen bond with water; therefore, as the number of acetate groups are converted to the corresponding -OH group, the hydrophilic nature of the polymer increases up to a point where 88 % of the ester groups are hydrolyzed. Beyond this, the hydrophilic nature drops off rapidly as the polymer nears the fully hydrolyzed state. Fully hydrolyzed polyvinyl alcohol (PVA) strongly hydrogen bonds with neighboring chains. Being linear, the chains can align themselves to form a tightly packed array. Higher energies are needed for water molecules to penetrate the network so fully hydrolyzed grades require very hot water to solubilize them.

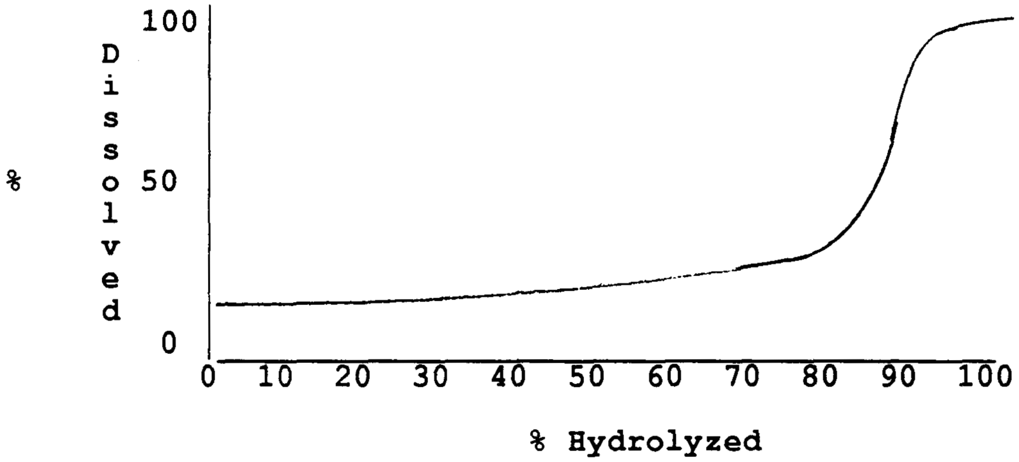
When acetate ester groups remain, the ability of the polymer chains to form H-bonds is interrupted by the pendant nature of the ester group. This allows water molecules easier access to the -OH groups and at 88 % hydrolysis, a balance between the number of hydrophilic groups and chain separation is struck for optimum water solubility. See figure 15.

Figure 15. Water Solubility

Room Temperature Solubility



Hot Water Solubility (140 °F)



D. Grades of PVA Available as Textile Size

Commercial PVA comes in grades which reflect the molecular weight and degree of hydrolysis. For textile size applications, three grades are mainly used. These are summarized in Table 2.

Table 2

	% Hydrolyzed	Solution Temperature
Fully Hydrolyzed	99	Boiling Water
Intermediate Hydrolyzed	95	160 °F
Partially Hydrolyzed	88	120 °F

Solution viscosities are mainly a function of molecular weight. Low viscosity solutions are produced with low molecular weight polymers in the 25-to-35,000 range whereas polymers in the 250-to-300,000 range give high viscosity solutions.

E. Film Properties

Dried film properties are a function of both molecular weight and the degree of hydrolysis. Super tough films are formed from high molecular weight, fully hydrolyzed polymers. As a textile size, the adhesiveness and toughness of the dried film are advantages which have been responsible for its growing usage, especially on spun yarns. Added pluses are easy handling and the ability to cool and reheat (doesn't retrograde). Because of the film properties, less add-on required to produce a good weaving warp.

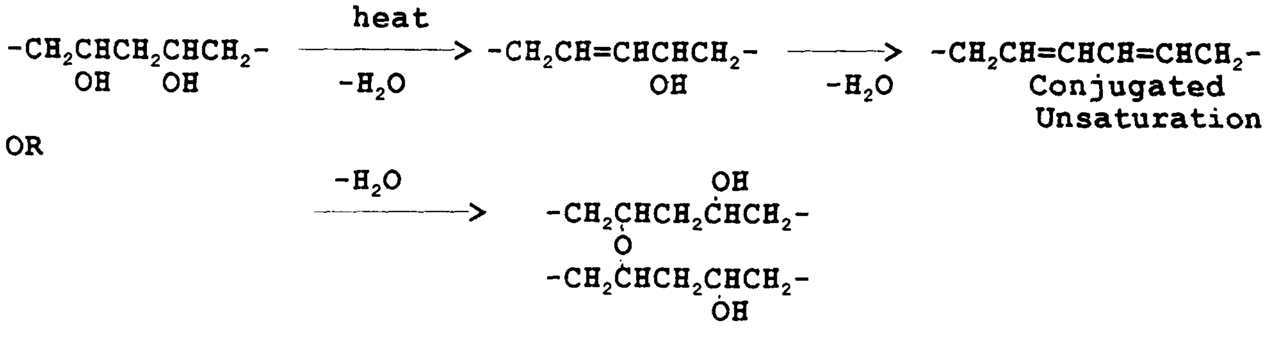
F. Desizing PVA

One of the advantages of PVA is that a dried film will redissolve in water without having to degrade it first. Fabrics sized with PVA are desized by first saturating with water containing a wetting agent (for rapid penetration) and then by heating in a steamer or J-box (to hydrate the film). The desizing step is completed by rinsing in hot water to complete the removal. The polymer is inert to most chemical reactions available for use in desizing. The optimum wash temperature is a function of the grade used to size the warp yarns. Lower molecular weight, partially hydrolyzed grades require lower temperatures than fully hydrolyzed, high molecular weight ones. Temperatures near the boil are required for the fully hydrolyzed grades.

1. Effect of Heat-Setting on Removal of PVA

Greige heat-setting fabrics with PVA size may insolubilize the size. When PVA films are heated above 120 °C, water is eliminated from the polymer backbone to form either unsaturation, or to form ether crosslinks between polymer chains. Either reaction will alter the water solubility of the polymer. Once unsaturation starts, the double bond activates the splitting out of a second mole of water to form a conjugated system. Conjugation is responsible for the darkening color of the polymer film.

a. Dehydration of PVA



$$\mathrm{-CH_2\underset{OH}{CH}CH_2\underset{OH}{CH}CH_2-} \xrightarrow[\mathrm{-H_2O}]{\text{heat}} \mathrm{-CH_2CH{=}CH\underset{OH}{CH}CH_2-} \xrightarrow[\mathrm{-H_2O}]{} \mathrm{-CH_2CH{=}CHCH{=}CHCH_2-}$$

Conjugated Unsaturation

OR

$$\xrightarrow{\mathrm{-H_2O}} \begin{array}{l} \mathrm{-CH_2CHCH_2\overset{OH}{C}HCH_2-} \\ \mathrm{\quad\;\; O} \\ \mathrm{-CH_2CHCH_2\underset{OH}{C}HCH_2-} \end{array}$$

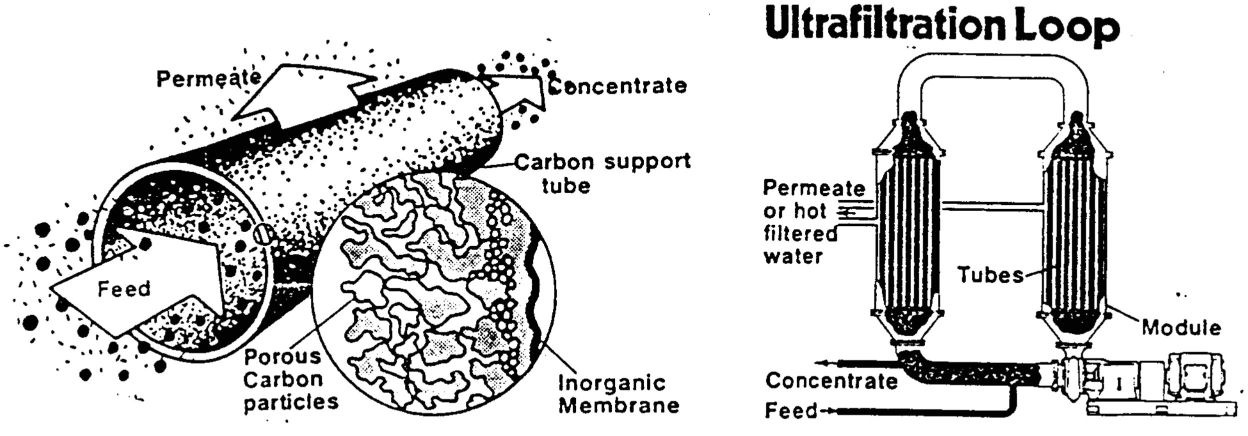
Ether Crosslink

2. Size Recovery

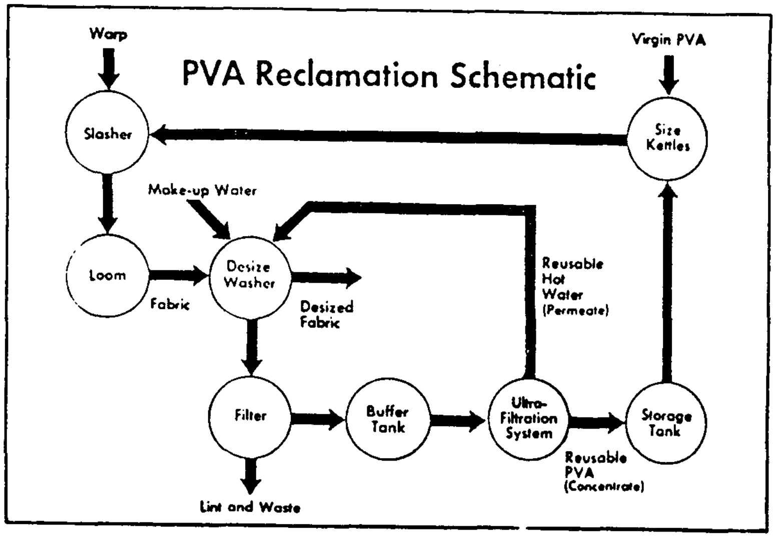
Since PVA's properties are not altered in desizing, the solids in the spent desizing liquor can be reused as warp size provided the concentration can be built back up to the level used in sizing warp yarns. This can be accomplished by passing the spent liquor through a size recovery unit. ***Ultrafiltration*** is one technique for doing this. The equipment consists of porous tubes lined with a water permeable membrane and the tubes are arranged in a high pressure unit. Dilute liquor passes through the center of the tube and clean hot water is forced through the outer part of the tube. As the interior liquor loses water, the solids build and the solution becomes more concentrated. By passing through a number of these units, the concentration can be increased to a point where it is economically practical to reuse it as a warp size. Weaving efficiencies with the reconstituted size are just as good as with virgin size. An additional plus from this operation is that the filtered water is clean and hot so it can be reused in the dyehouse. A diagram showing the unit is shown in figure 16. Ultrafiltration recovers two useful products, the polymeric size and hot water. The hot water is clean enough for reuse in the desize range. The schematic in figure 21 shows the process flow for the recovered materials. The recovery unit is usually found at the dye house so the hot water can be recycled into the normal flow of desizing. The recovered size however must be returned to the weaving mill. Seldom are weaving mills and dye houses located near each other so an added concern is transporting the concentrated size solution back to the weaving mill. Tanker trucks are used for this purpose.

Figure 16. PVA Size Recovery

Ultrafiltration Unit



PVA Reclamation Schematics

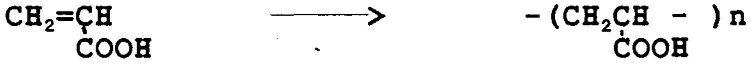


VI. ACRYLIC SIZES

A. Polyacrylic Acid

Polyacrylic acid is a water soluble polyelectrolyte that has excellent adhesion to nylon therefore it is used to size filament nylon yarns. The affinity is through hydrogen bonding of the -COOH with amide and amine end groups in the nylon polymer.

1. Synthesis of Polyacrylic Acid



$$\underset{\displaystyle COOH}{CH_2{=}CH} \longrightarrow -(CH_2\underset{\displaystyle COOH}{CH} -)n$$

Acrylic Acid Polyacrylic Acid

2. Desizing Polyacrylic Acid

By converting the -COOH to -COONa, water solubility of the polymer is increased and hydrogen bonding with the fiber is overcome. Polyacrylic can readily be desized by saturating fabric with alkali and washing out the solubilized size.

3. Acrylic Acid Co-Polymers

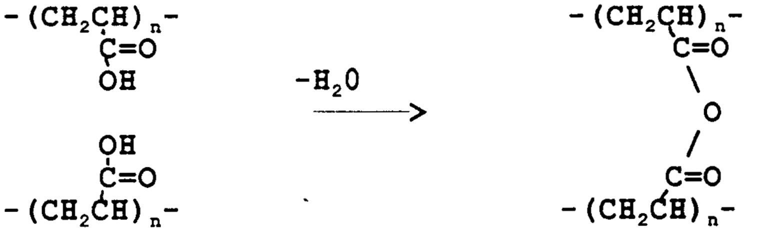
Acrylic acid can be co-polymerized with many vinyl and acrylic monomers. Usually acrylate esters (ethyl, butyl) are co-polymerized with acrylic and methacrylic acid. These co-monomers reduce water solubility and increase polymer flexibility and adhesion. As the free acid, the number of carboxyl groups in the copolymer are not sufficient to render the copolymer water soluble; however, when they are converted to the corresponding alkali salt, the copolymer becomes water soluble. These properties are put to good use in water jet weaving. The size is applied on the acid side, rendering the dried film insensitive to water. Water insensitivity is needed in water jet weaving because build-up of water sensitive sizes on heddles and other loom parts will cause loss of weaving productivity.

Desizing is accomplished by saturating the fabric with a caustic soda solution which converts -COOH to -COONa making the size water soluble. Flushing with water completes the removal of the size.

4. Effect of Heat- Setting on Removal

Like polyvinyl alcohol, acrylic sizes are sensitive to greige heat setting. The carboxyl groups can split out one mole of water between two groups on adjacent polymer chains and form an anhydride. These anhydrides densify the polymer structure, slowing down the penetration of water and alkali. With time and temperature. these anhydrides can be broken and the polymer will re-dissolve. The carboxyls are also capable of reacting with the amine end groups on the nylon surface to form amides. Once this happens, it is virtually impossible to break these bonds and the size will be permanently fixed to the fiber.

a. Anhydride Formation



POLY-ANHYDRIDE

VII. POLYESTER RESIN SIZES

Water dispersible polyester polymers can be made by incorporating solubilizing groups into the polymer backbone and controlling the molecular weight. This is done by including 5-sulfoisophthalic or trimellitic acid as one of the dicarboxylic acid monomers in the synthesis of the polymer. These polymers have particularly good adhesion to polyester fibers and make good sizes for continuous filament yarns. Desizing can be accomplished in a manner similar to acrylic sizes. Alkali, wetting agents and heat assist hydration of the size, allowing it to rinse out with water.

There are two components needed to make a polyester resin, a dibasic acid and a diol. Polyethylene terephthalate (PET) fibers are made from terephthalic acid and ethylene glycol. There are other dibasic acids and diols one can choose from when designing a water dispersible polyester resin. Some of the dibasic acid are: isophthalic acid, trimellitic acid, terephthalic acid, 5-sulfoisophthalic acid and aliphatic dibasic acids (sebacic and adipic). As for the glycols, there is ethylene glycol, polyethylene glycols, polypropylene glycols etc. By selecting the appropriate combination of monomers, one can synthesize a wide range of polyester resins with varying degree of water solubility, adhesive character, softening point etc. There are a number of these water dispersible polymers on the market designed as warp sizes and soil release agents. Each has its own unique combination of monomers to give the desired properties. The chemistry used to make polyester sizes is similar to that used for making soil release agents. More details are provided in Chapter X, on Soil Release.

VIII. OTHER ADDITIVES

The basic film-former makes up the bulk of the warp size. However other ingredients are needed to optimize weaving. **Lubricants** are added to reduce the coefficient of friction and reduce drag as the yarns run over stationary objects. A thorough discussion of these will be found in the section describing oils, fats and waxes. **Humectants** are hygroscopic compounds (glycerine, ethylene glycol, urea) which absorb moisture and reduces the brittleness of starch films. They help to reduce shedding caused by fracturing the film. **Preservatives** prevent the growth of bacteria and fungi in size mixes and on sized yarn. Cresol, phenol, salicylic acid are examples of preservatives.

IX. REFERENCES

CHAPTER 3.

SCOURING

Natural fibers contain oils, fats, waxes, minerals, leafy matter and motes 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

Motes (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

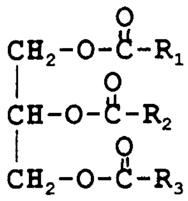
Many of the contaminates removed in scouring, both natural and man made are fats, oils or waxes. Many useful products, some used in scouring, are derived from them. This section will review some of the pertinent chemistry.

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.



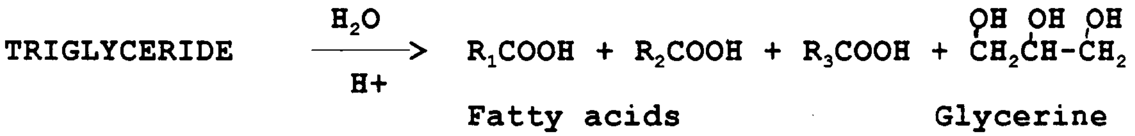
A triglyceride

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.



$$\text{TRIGLYCERIDE} \xrightarrow[H+]{H_2O} \underbrace{R_1COOH + R_2COOH + R_3COOH}_{\text{Fatty acids}} + \underbrace{\overset{OH}{CH_2}\overset{OH}{CH}-\overset{OH}{CH_2}}_{\text{Glycerine}}$$

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.

$$\text{TRIGLYCERIDE} + 3\ NaOH \longrightarrow \underset{\text{Soap}}{3\ RCOONa} + \text{GLYCERINE}$$

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	$CH_3(CH_2)_2COOH$	-4.7
Caproic	6	$CH_3(CH_2)_4COOH$	-1.5
Caprylic	8	$CH_3(CH_2)_6COOH$	16.5
Capric	10	$CH_3(CH_2)_8COOH$	31.3
Lauric	12	$CH_3(CH_2)_{10}COOH$	43.6
Myristic	14	$CH_3(CH_2)_{12}COOH$	58.0
Palmitic	16	$CH_3(CH_2)_{14}COOH$	62.9
Stearic	18	$CH_3(CH_2)_{16}COOH$	69.9
Behenic	22	$CH_3(CH_2)_{20}COOH$	80.2

Table 6

Unsaturated Fatty Acids

Acid	No. of C atoms	Formula
Palmitoleic	16	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$
Oleic	18	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
Ricinoleic	18	$CH_3(CH_2)_5CH(OH)CH_2CH{=}CH(CH_2)_7COOH$
Linoleic	18	2 -CH=CH- @ C_9 and C_{12}
Linolenic	18	3 -CH=CH- @ C_9,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 &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 C,, 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 C,, 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 (C_{12} and C_{14}) and are saturated. The laurel 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 C_{16} 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 he 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 was 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. Natures 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	$CH_3(CH_2)_{14}CH_2OH$
Oleyl alcohol	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OH$
Stearyl alcohol	$CH_3(CH_2)_{16}CH_2OH$
2-Octanol	$CH_3(CH_2)_5CH(OH)CH_3$
2-Ethylhexanol	$CH_3(CH_2)_3CH(C_2H_5)CH_2OH$

a. Sources of Fatty Alcohols

1. Reduction of fatty acids.

$$RCOOH \xrightarrow{[H_2]} RCH_2OH + H_2O$$

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 140^0 F. The melt viscosity is low.

2. Microcrystalline Wax

Microcrystalline waxes are higher melting (150^0 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 an methylethyl ketone and then allowed to crystallize.

E. Synthetic Wax

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

- **FattyAcids:** 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.

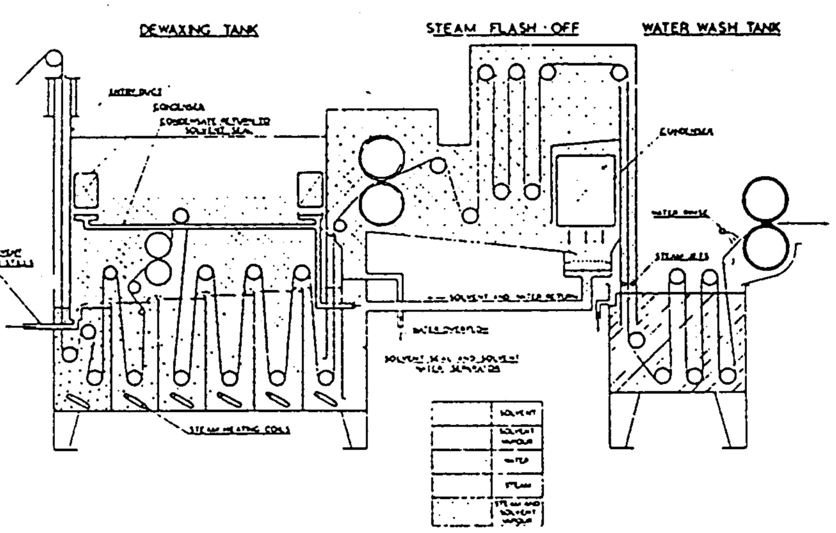
III. SOLVENT SCOURING

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 down-stream 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 elsewere. 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 motes, 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/^{0}C).
- **Latent Heat of Evaporation:** The amount of energy needed to vaporize one gram of solvent (Calories/gram).

2. Non-flammable Solvents

```
Perchloro-      Trichloro-      1,1,1-Trichloro-      1,1,2-Trichloro-
ethylene        ethylene         ethane                  1,2,2-Trifluoroethane
                                                            (Freon TF).

 Cl    Cl        Cl    Cl          Cl    H                Cl    F
  \   /           \   /             \   /                  \   /
   C=C             C=C            Cl-C-C-H               Cl-C-C-F
  /   \           /   \             /   \                  /   \
 Cl    Cl        Cl    H           Cl    H                F     Cl
```

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 212^0F 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 212^0F in J-box or steamer.

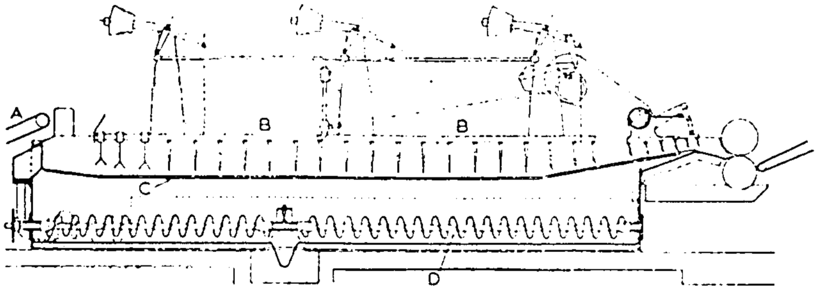
3. Rinse thoroughly at 160^0F

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 contaminates 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 becomes 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 ($Ca(OH)_2$) and sodium carbonate (Na_2CO_3) are the chemicals used.

$$Ca(HCO_3)_2 + Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow CaCO_3 + Mg(OH)_2 + H_2O$$

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

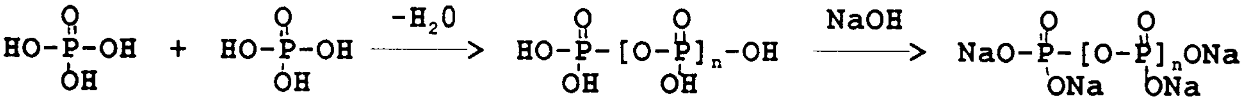
The principles behind sequestration is the formation of a water soluble complex between a sequestering agent and a polyvalent metal ion. The technique can be used for softening water; however, it is more often used as a component in many textile wet processing steps to remove metallic ions that interfere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



$$HO-\overset{O}{\underset{OH}{P}}-OH + HO-\overset{O}{\underset{OH}{P}}-OH \xrightarrow{-H_2O} HO-\overset{O}{\underset{OH}{P}}-[O-\overset{O}{\underset{OH}{P}}]_n-OH \xrightarrow{NaOH} NaO-\overset{O}{\underset{ONa}{P}}-[O-\overset{O}{\underset{ONa}{P}}]_nONa$$

2. Important Polyphosphates

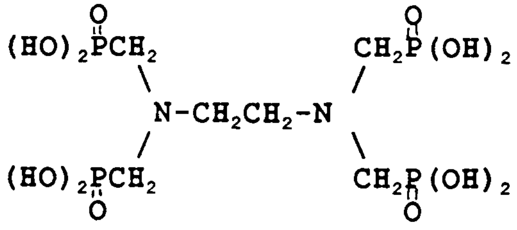
■. **Tetrasodium pyrophosphate (TSPP).**	$Na_4P_2O_7$
■ **(Tripoly)sodium phosphate (TSP).**	$Na_5P_3O_{10}$
■. **Sodiumhexameta phosphate.**	$Na_6P_6O_{18}$

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

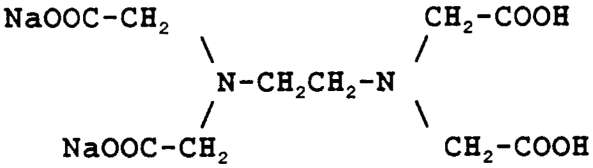


a. Advantages and Disadvantages:

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

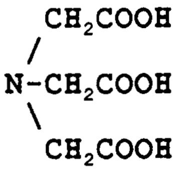
1. Disodium-Ethylenediaminetetraacetic acid (EDTA)



a. Advantages and Disadvantages:

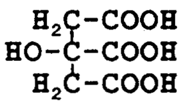
They form very stable complexes with most metal ions. They reacts stoichiometrically and can be used to quantitatively determine calcium and magnesium by titration. They do not contribute to detergency nor do they exhibit a threshold effect.

2. Nitrilotriacetic Acid (NTA)



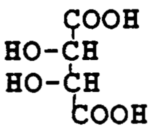
D. Hydroxycarboxylic Acids

Citric acid



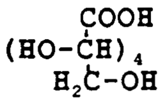
$$\begin{array}{l} H_2C\text{-}COOH \\ HO\text{-}C\text{-}COOH \\ H_2C\text{-}COOH \end{array}$$

Tartaric acid



$$\begin{array}{l} \quad COOH \\ HO\text{-}CH \\ HO\text{-}CH \\ \quad COOH \end{array}$$

Gluconic acid



$$\begin{array}{l} \quad COOH \\ (HO\text{-}CH)_4 \\ H_2C\text{-}OH \end{array}$$

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

$$M^{++} + L \longrightarrow (ML)^-$$

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	-

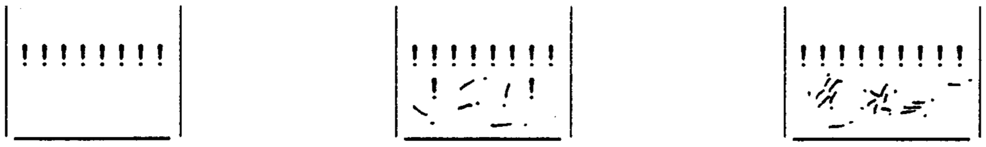
VII. SURFACTANTS

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



Packed at surface

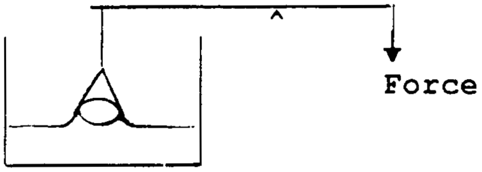
Molecules in bulk

Micelles in bulk

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.

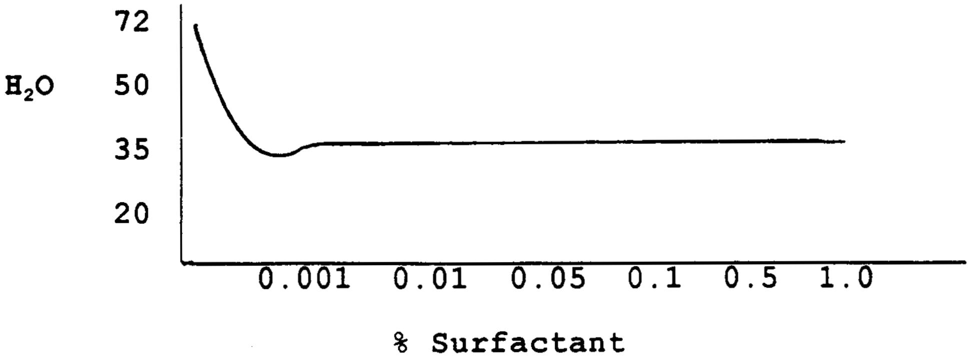
Figure 20. du Noy Tensiometer



C. Critical Micelle Concentration

A plot of soap concentration verses 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.

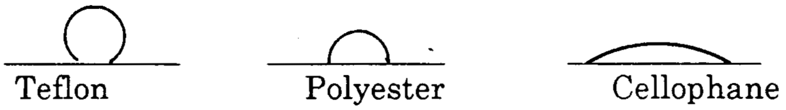
A. By Use

- **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

Pure Water



Water Plus Surfactant

- **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 keeps 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.

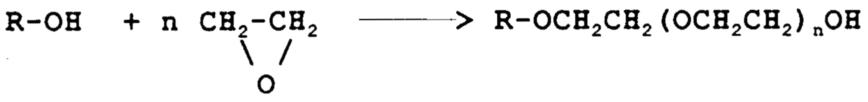
- **Amphoteric:** Those that have both a positive and negative charged group on the molecule.

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, carboxyals, amines and mercaptyl groups are active hydrogen types that can be ethoxylated. The general reaction can be written as:



$$R\text{-}OH + n\ \underset{\diagdown\ \diagup \atop O}{CH_2\text{-}CH_2} \longrightarrow R\text{-}OCH_2CH_2(OCH_2CH_2)_nOH$$

where R-OH = hydrophobe

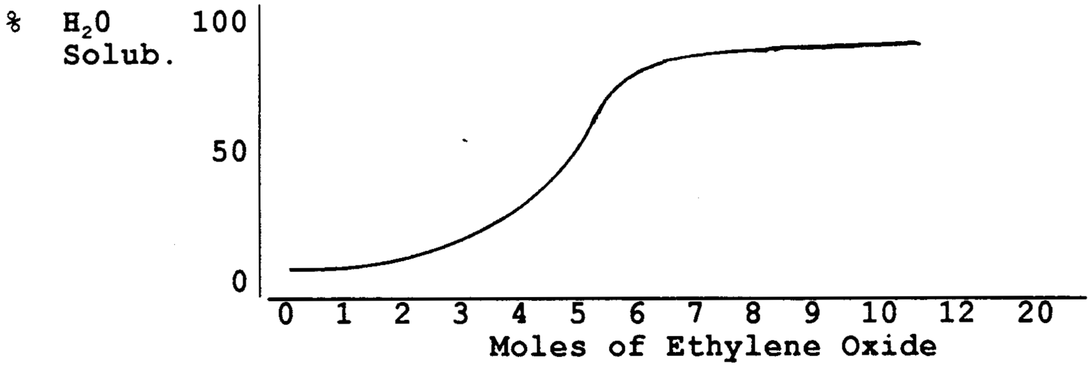
1. Typical Hydrophobes:

- 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.

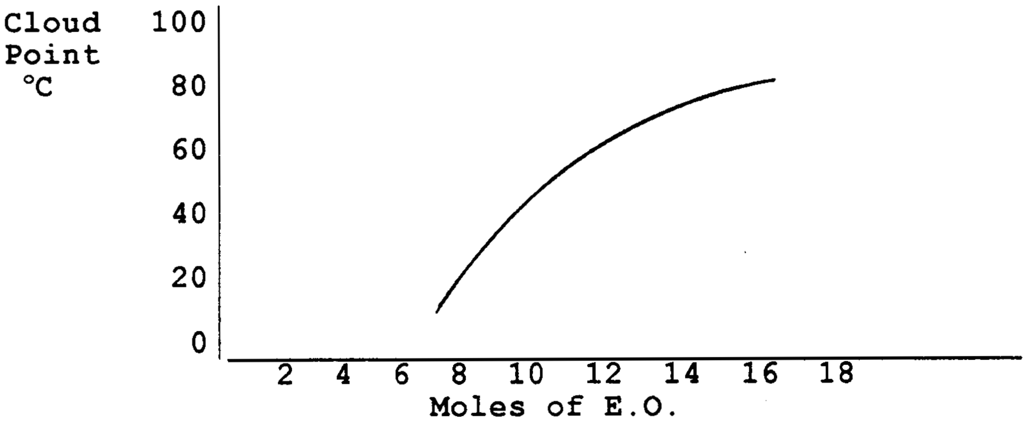
Figure 23. Solubility as a Function of Ethylene Oxide Content



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

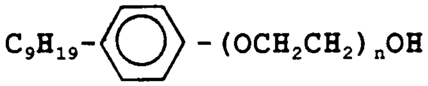


4. Hydrophilic-Lyophilic Balance (HLB)

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 verses 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.

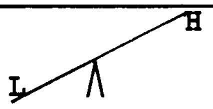
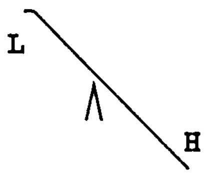
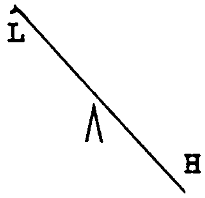
The HLB concept is illustrated in figure 25. which pictures the balance as a teeter board. For this illustration the hydrophobe is nonylphenol. One end of the board represents oil solubility while the other end represents water solubility. Figure 25 illustrates the solubility balance of the ethoxylate 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.

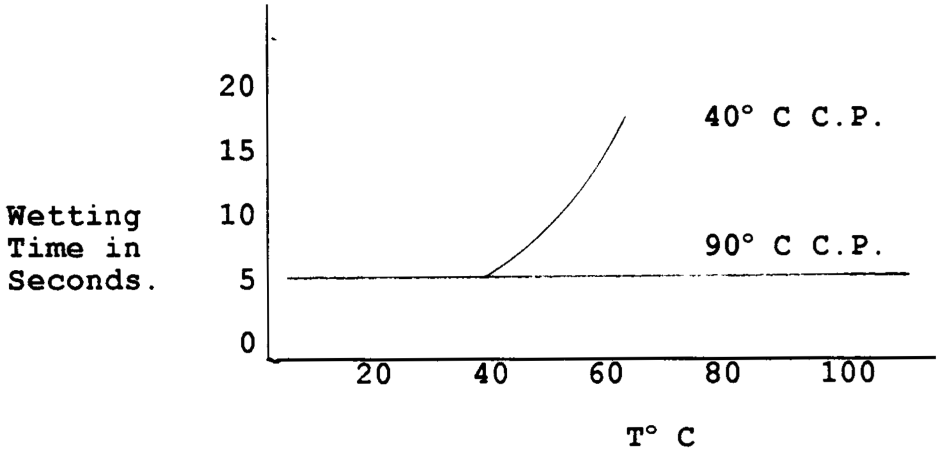
Nonionics are just the opposite. Because they are less soluble hot than cold, more micelles are formed as the temperature is raised. This unique feature gives rise to the fact that nonionics are most effective at temperatures just below their cloud point. At low temperatures, their solubility is higher 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 40^0 CP surfactant however becomes insoluble and loses its wetting-out characteristics at its cloud point. The 90^0 CP one however is still effective until it reaches boiling temperature.

a. Wetting Times

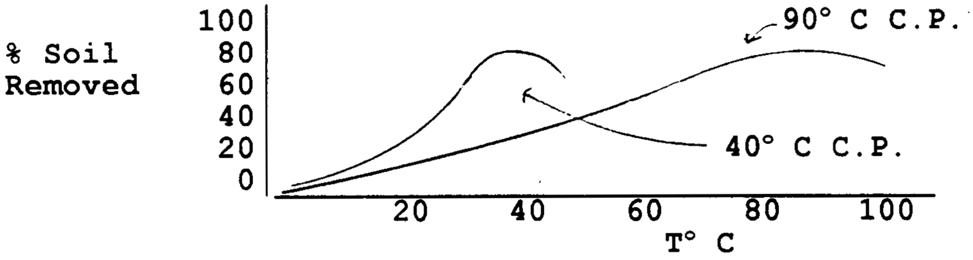
Figure 26. Wetting Times as a Function of Cloud Point



b. Detergency

Figure 26 repeats the comparison, except the surfactants were used as detergents. Again, for soil removal, the 40^0 CP surfactant was most effective at a temperature just below its cloud point. The 90^0 CP product, didn't reach its maximum efficiency until the temperature reached the boiling point. At lower temperatures, the 40^0 CP product removed more soil than the 90^0 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.

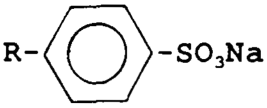
A. Chemical Classification of Anionic Surfactants

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

$C_{17}H_{33}COONa$

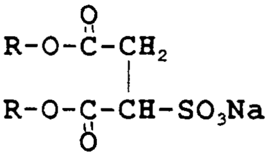
2. Sulfonates:

a. Alkylaryl Sulfonates E.g. Sodium laurelbenzene sulfonate



$R = C_{8-12}$

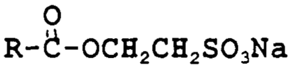
b. Sulfosuccinates E.g. Dioctylsulfosuccinate (DOSS)



$$\begin{array}{l} R-O-\overset{O}{\overset{\|}{C}}-CH_2 \\ \qquad\qquad\quad | \\ R-O-\underset{O}{\underset{\|}{C}}-CH-SO_3Na \end{array}$$

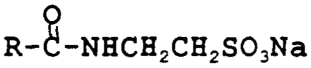
R = octyl

c. Sulfoethylesters E.g. (Igepon T)



$$R-\overset{O}{\overset{\|}{C}}-OCH_2CH_2SO_3Na$$

d. Sulfoethylamides E.g. (Igepon A)



$$R-\overset{O}{\overset{\|}{C}}-NHCH_2CH_2SO_3Na$$

3. Sulfates

a. Sulfated alcohols E.g. Sodium laurel sulfate

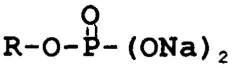
$R-CH_2OSO_3Na$

b. Sulfated ethoxylated alcohols

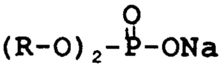
$R-CH_2(OCH_2CH_2)_nOSO_3Na$

4. Phosphate Esters

a. Monoesters and diesters



$$R-O-\overset{O}{\overset{\|}{P}}-(ONa)_2$$



$$(R-O)_2-\overset{O}{\overset{\|}{P}}-ONa$$

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

CHAPTER 4

BLEACHING

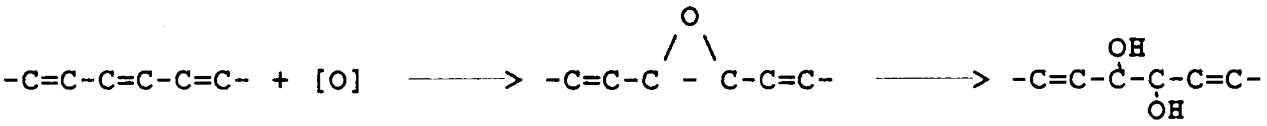
Natural fibers, i.e. cotton, wool, linen etc. are off-white in color due to color bodies present in the fiber. The degree of off-whiteness varies from batch-to-batch. Bleaching therefore can be defined as the destruction of these color bodies. White is also an important market color so the whitest white has commercial value. Yellow is a component of derived shades. For example, when yellow is mixed with blue, the shade turns green. A consistent white base fabric has real value when dyeing light to medium shades because it is much easier to reproduce shade matches on a consistent white background than on one that varies in amount of yellow.

Bleaching may be the only preparatory process or it may be used in conjunction with other treatments, e.g. desizing, scouring and mercerizing. The combination of such treatments for an individual situation will depend on the rigorousness of the preparation standard and economic factors within the various options.

Other chemicals will be used in addition to the bleaching agent. These serve various functions such as to activate the bleaching system, to stabilize or control the rate of activation, to give wetting and detergent action, or to sequester metallic impurities. This section gives consideration to the selection of bleaching agents and to the role of the various chemicals used in conjunction.

I. MAJOR BLEACHING AGENTS

The mechanism of bleaching is very complicated and not completely understood. One opinion is that the color producing agents in natural fibers are often organic compounds containing conjugated double bonds. It is known in dye chemistry that conjugation is necessary for an organic molecule to perform as a dyestuff. Decoloration can occur by breaking up the chromophore, most likely destroying one or more of the double bonds within the conjugated system. Oxidative bleaches oxidize color bodies into colorless compounds. For example, double bonds are known to be oxidize into epoxides which easily hydrolyze into diols. The major bleaching agents used in textile preparation are sodium hypochlorite, hydrogen peroxide and sodium chlorite. Other bleaching agents, of lesser importance to textile preparation but important in consumer laundry products, are perborates, percarbonates and peracetic acid. All of these are oxidative bleaches. Oxidative bleaches are also known to degrade cellulose so the objective in bleaching is to optimize whitening and minimize fiber damage.



$$-C{=}C{-}C{=}C{-}C{=}C- + [O] \longrightarrow -C{=}C{-}\overset{O}{\overbrace{C - C}}{-}C{=}C- \longrightarrow -C{=}C{-}\overset{OH}{C}{-}\underset{OH}{C}{-}C{=}C-$$

Reductive Bleaches reduce color bodies into colorless compounds. Most textile fibers are bleached with oxidizing bleaches.

II. SODIUM HYPOCHLORITE

Hypochlorite bleaching (OCl^-) is the oldest industrial method of bleaching cotton. Originally, calcium hypochlorite, $Ca(OCl)_2$ was used. Most cotton fabrics were bleached with sodium hypochlorite up until 1940. Today it accounts for only 10 % of the cotton bleaching agents in the U.S. It is however the main stay of home laundry bleaching products. Hypochlorites are excellent cidal agents for mildew and other bacteria and are used as disinfectants and to control bacteria in swimming pools. Sodium hypochlorite is the strongest oxidative bleach used in textile processing. Prior to bleaching with hypochlorite, it is necessary to thoroughly scour fabrics to remove fats, waxes and pectin impurities. These impurities will deplete the available hypochlorite, reducing its effectiveness for whitening fabric.

Sodium hypochlorite is made by bubbling chlorine into a solution of sodium hydroxide.

$$2\ NaOH + Cl_2 \longrightarrow NaOCl + NaCl$$

Conversely, when acid is added to a hypochlorite solution, chlorine gas is liberated. Product strength of hypochlorites is generally expressed as the available chlorine content. This relates to the chlorine formed on reaction with acid.

$$NaOCl + HCl \longrightarrow NaCl + Cl_2 + H_2O$$

Commercial sodium hypochlorite will have 12 to 15 % active chlorine. Household bleach is 5 % active chlorine. Calcium hypochlorite is sold as a solid material and contains 65 % active chlorine.

A. Bleaching Mechanism

Sodium hypochlorite is the salt of a moderately strong base (OCl^-) and a weak acid (HOCl). Solutions are therefore alkaline. The species present in a solution can be understood from the following:

$$NaOCl + H_2O \longrightarrow Na^+ + OCl^-$$

$$OCl^- + H_2O \longrightarrow HOCl + OH^-$$

Note: Hypochlorous acid (HOCl) is the active bleaching agent.

B. Effect of pH

pH has a profound effect on bleaching with hypochlorite. 1. If caustic is added to the solution, the equilibrium shifts to the left favoring the formation of the hypochlorite ion ($OC1^-$) at the expense of hypochlorous acid (HC1O). Under strongly alkaline conditions ($pH > 10$), little to no bleaching takes place. 2. When acid is added, the equilibrium shifts to the right and the HOCl concentration increases. At a pH between 5 and 8.5, HOCl is the major specie present so very rapid bleaching takes place. However, rapid degradation of the fiber also takes place. 3. When the pH drops below 5, chlorine gas is liberated and the solution has no bleaching effectiveness at all. 4. The optimum pH for bleaching is between 9 and 10. Although the concentration of HOCl is small, it is sufficient for controlled bleaching. As HOCl is used up, the equilibrium conditions continue to replenish it. This pH range is used to minimize damage to the fiber. Sodium carbonate is used to buffer the bleach bath to pH 9 to 10.

C. Effect of Time and Temperature

Time and temperature of bleaching are interrelated. As the temperature increases, less time is needed. Concentration is also interrelated with time and temperature. Higher concentrations require less time and temperature. In practice, one hour at 40^0 C is satisfactory for effective bleaching.

D. Effect of Metals

Copper and iron catalyze the oxidation of cellulose by sodium hypochlorite degrading the fiber. Fabric must be free of rust spots or traces of metals otherwise the bleach will damage the fabric. Stainless steel equipment is required and care must be taken that the water supply be free of metal ions and rust from pipes. Prescouring with chelating agents becomes an important step when bleaching with hypochlorites.

E. Antichlor

Fabrics bleached with hypochlorite will develop a distinctive chlorine odor. This odor can easily be removed with an aftertreatment consisting of sodium bisulfite and acetic acid.

F. Uses

Hypochlorite is used mainly to bleach cellulosic fabrics. It cannot be used on wool, polyamides (nylon), acrylics or polyurethanes (spandex). These fibers will yellow from the formation of chloramides.

Bleaching with hypochlorite is performed in batch equipment. It is not used in continuous operations because chlorine is liberated into the atmosphere. Over time, the pad bath decreases in active chlorine causing non-uniform bleaching from beginning to end of the run.

G. Typical Batch Procedure

a. Formulation:

NaOCl	2.5 %	active bleach
Na_2CO_3	1.0 %	pH buffer

b. Bleach Cycle:

1. Run one hour at 40° C.
2. Drop bath, rinse
3. Add antichlor chemicals
4. Rinse

III. HYDROGEN PEROXIDE

Hydrogen peroxide was first used to bleach cotton in the 1920's. By 1940, 65 % of all cotton fabrics were bleached with hydrogen peroxide, largely brought about by the invention of the J-box which lead to continuous processing. Today, it is estimated that 90 to 95 % of all cotton and cotton/synthetic blends are bleached with hydrogen peroxide. It is available commercially as 35, 50 and 70 % solutions. It is a corrosive, oxidizing agent which may cause combustion when allowed to dry out on oxidizable organic matter. Decomposition is accelerated by metal contamination and is accompanied by the liberation of heat and oxygen, which will support combustion and explosions in confined spaces. The material is an irritant to the skin and mucous membranes and dangerous to the eyes

A. Mechanism

Hydrogen peroxide is a weak acid and ionizes in water to form a hydrogen ion and a perhydroxyl ion. The perhydroxyl ion is the active bleaching agent.

$$H_2O_2 + H_2O \longrightarrow H^+ + HOO^-$$

Hydrogen peroxide can also decompose. This reaction is catalyzed by metal ions e.g. Cu^{++}, Fe^{+++}. This reaction is not desired in bleaching because it is an ineffective use of hydrogen peroxide and causes fiber damage.

$$H_2O_2 \longrightarrow H_2O + 1/2\ O_2$$

B. Effect of pH

Hydrogen peroxide is an extremely weak acid, Ka = 1.5×10^{12}. Since the perhydroxyl ion is the desired bleaching specie, adding caustic neutralizes the proton and shifts the reaction to the right. Therefore: 1. at pH < 10, hydrogen peroxide is the major specie so it is inactive as a bleach. 2. At pH 10 to 11, there is a moderate concentration of perhydroxyl ions. pH 10.2 to 10.7 is optimum for controlled bleaching. Sodium hydroxide is used to obtain the proper pH. 3. At pH > 11, there is a rapid generation of perhydroxyl ions. When the pH reaches 11.8, all of the hydrogen peroxide is converted to perhydroxyl ions and bleaching is out of control.

C. Effect of Time and Temperature

Stabilized hydrogen peroxide does not decompose at high temperature therefore faster and better bleaching occurs at 95 to 100 ^{0}C. This feature makes it ideal for continuous operations using insulated J-boxes or open-width steamers.

D. Stabilizers

Stabilizers must be added to the bleach solution to control the decomposition of hydrogen peroxide. Stabilizers function by providing buffering action to control the pH at the optimum level and to complex with trace metals which catalyze the degradation of the fibers. Stabilizers include sodium silicate, organic compounds and phosphates.

1. Sodium Silicates

Sodium silicates are the most commonly used and most effective hydrogen peroxide bleach stabilizers. They may be used as colloidal silicate (waterglass), ortho silicate or metasilicate. The mechanism by which silicate stabilize is not completely understood, however it is known that silicates have a natural affinity for ferrous ions and ferrous ions are naturally present in cotton. It is possible that the silicates are adsorbed onto the ferrous ions in the fiber, producing a species that catalytically enhances bleaching while reducing bleach decomposition and fiber damage. Stabilization by silicates is enhanced by the presence of magnesium ions. Magnesium serves as a pH buffer. As the concentration of OH^- rises during bleaching, magnesium hydroxide ($Mg(OH)_2$) precipitates, reducing the OH^- concentration. Bleach solutions containing only magnesium ions have good stability but the bleaching effectiveness is not as good as when silicates are included.

Silicates as stabilizers have one drawback, they tend to polymerize and form insoluble silicates. They becomes hard deposits which build-up in the machines causing the fabric to be abraded. Also some of the deposits will form in the cloth, giving it a harsh, raspy hand, a real negative for terry toweling.

2. Organic Stabilizers

Organic stabilizers avoid the problems associated with sodium silicates. These products are often referred to as silicate free or non-silicate stabilizers. They may be based on sequestering agents, protein degradation products or certain surfactants. The commercial products are of two types, those designed only to be stabilizers and those which combine stabilization with other properties such as detergency and softening. For some bleaching methods, organic stabilizers may be used alone, while in others, they are best used in combination with silicates.

3. Phosphates

Tetrasodium pyrophosphate (TSPP) and hexametaphosphates are of interest as stabilizers in alkaline bleach baths under the following conditions: 1. The alkalinity of the bleach must not be higher than pH 10 since above this, the stabilizing effect decreases rapidly. 2. Temperature of the bleach bath is limited to 60 ^{0}C. Higher temperatures reduce stabilizing properties. They should be used with ammonia, not caustic soda or soda ash.

TSPP at high pH and temperature is converted to trisodium phosphate which has little stabilizing effect. The use of TSPP is limited to bleaching wool and silk which are sensitive to high pH and high temperatures. As opposed to silicates, pyrophosphates are precipitated from solution in the presence of calcium and magnesium and therefore do not develop full stabilizing power.

E. Uses

Hydrogen peroxide is the bleach most widely used for cellulosic fibers [cotton, flax, linen, jute etc.) and well as wool, silk, nylon and acrylics. Unlike hypochlorites, peroxide bleaching does not require a full scour. Residual fats, oils, waxes and pectines do not reduce the bleaching effectiveness of hydrogen peroxide. Additionally it can be used on continuous equipment. Since it ultimately decomposes to oxygen and water, it doesn't create effluent problems.

F. Typical Bleaching Procedures

1. Batch

a. Bath Formulation

	%
Hydrogen peroxide (35 %)	3 - 5
Wetting agent	0.1 - 0.5
NaOH	0.3 - 0.8
Sodium silicate	2 - 3
Magnesium sulfate (Epsom's salt)	0.5

b. Bleach Cycle

1. Run 60 to 90 minutes at 95 to 100^0 C.
2. Drop bath
3. Rinse

2. Continuous

a. Bath Formulation

Double above formulation

b. Bleach Cycle

1. Saturate goods to 100 % wet pick up
2. Steam in J-box or steamer for one hour
3. Wash thoroughly

IV. SODIUM CHLORITE ($NaClO_2$)

Bleaching with sodium chlorite is carried out under acidic conditions which releases chlorine dioxide, a toxic and corrosive yellow-brown gas. Sodium chlorite is sold as an 80% free flowing powder. Chlorine dioxide is thought to be the active bleaching specie. It is not used much in the USA for bleaching but it is sometimes used to strip dyed goods and is often described as the bleach of last resort. One advantage of sodium chlorite bleaching is that it leaves the fabrics with a soft hand.

Because of the gaseous nature, toxicity and corrosiveness of chlorine dioxide, special attention must be paid to the equipment. It must be designed so as to not allow the gas to escape into the work place. Emissions into the atmosphere are of concern too. The gas corrodes even stainless steel so special passivating treatments must be carried out to prolong the life of the equipment.

When a solution of sodium chlorite is acidified, chlorine dioxide (ClO_2), hypochlorous acid ($HClO_2$), sodium chlorate ($NaClO_3$) and sodium chloride are formed. Chlorine dioxide and hypochlorous acid are bleaching species, sodium chlorate and sodium chloride are not. The reactions may be written:

$$NaClO_2 + H_2O \longrightarrow \underset{\text{Hypochlorous acid}}{HClO_2^-}$$

$$5\ ClO_2^{--} + 2\ H^+ \longrightarrow \underset{\text{Chlorine dioxide}}{4\ ClO_2} + Cl^- + 2\ OH^-$$

$$3\ ClO_2^- \longrightarrow \underset{\text{Chlorate}}{2\ ClO_3^-} + Cl^-$$

A. Effect of pH

Chlorine dioxide is favored at low pH - 1 to 2.5. It is a more active bleaching agent than hypochlorous acid which is favored at pH 4 to 5. However chlorine dioxide is a corrosive and toxic gas. When generated too rapidly, it escapes from the bleaching bath into the atmosphere creating an explosion and health hazard. Once the chlorine dioxide is out of solution, its effectiveness as a bleach is lost.

B. Bleaching Mechanism

Chlorine dioxide only reacts with aldehyde groups without affecting hydroxyls or glucosidic linkages. Aldehydes are converted to carboxylic acids. This is of practical importance because cellulose is very slightly damaged, even when high degree of whiteness is obtained. When strong acids are used, the low pH will damage the fiber at the glucosidic linkage so buffers like sodium dihydrogen orthophosphate are commonly used. Sodium acetate and the other sodium phosphate salts are also effective buffers. The acid is added incrementally over the bleach cycle, not all at once. This too controls the bath pH and avoids rapid evolution of chlorine dioxide.

C. Effect of Temperature

Little or no bleaching takes place at temperatures below 50^{0} C, however the bleaching rate increases considerably up to 90^{0} C. Going to the boil is not recommended because it leads to excessive loss of chlorine dioxide with the steam.

V. OTHER OXIDATIVE BLEACHES

Some other oxidative bleaches are persulfates, perborates, percarbonates and peracetic acid.

A. Persulfates

Ammonium, potassium and sodium persulfates are oxidizing agent that find use in textile processing. They are used to: 1. bleach protein fibers in combination with hydrogen peroxide, 2. activate cold bleaching of cellulosics with sodium chlorite, 3. oxidize vat and sulfur dyes, and 4. bleach fur and skins in combination with hydrogen peroxide.

B. Perborates and Percarbonates

Both perborates and percarbonates are used when full whites are not necessary such as for improving the ground color when dyeing light or pastel shades. They are often found as solid bleaches in home laundry products when fabric care require mild bleaches.

C. Peracetic Acid

Peracetic acid as a textile bleach is used mainly in bleaching nylon and acetate.

V. REDUCTIVE BLEACHES

Reductive bleaches work by reducing colored impurities into colorless forms. Reductive bleaches can be generalized as compounds which supply hydrogen for hydrogenating or reducing color bodies. For example, aldehydes are reduced to alcohols by the addition of one mole of hydrogen, double bonds are saturated by the addition of one mole of hydrogen. Both reactions can account for the decoloration of color bodies by breaking up resonance.

A. Sulfur Dioxide

In the early days (prior to 1940), sulfur dioxide was used to bleach wool. Moistened fabrics were hung on poles in a sealed chamber (called a stove). A pot of sulfur was ignited and the goods exposed overnight to the sulfur dioxide vapors. The bleached goods were rinsed in water containing sodium sulfite which removed the retained sulfur dioxide by forming sodium bisulfite. A disadvantage of this method of bleaching wool was that the white was not permanent when exposed to sun and air.

B. Sodium Dithionate (Sodium Hydrosulfite)

Sodium hydrosulfite, better known as "***hydro***" finds major usage as a reducing agent in textile processing. One of its main use is to reduce vat and sulfur dyes into the water soluble leuco form. As such it can be used to strip dyed goods, ergo bleach dyed goods. In water and with heat, hydro is oxidized into sodium bisulfite, liberating hydrogen · the reducing agent.

$$Na_2S_2O_4 \quad + \quad 4\ H_2O \quad \longrightarrow \quad 2\ Na_2HSO_4 + 3\ H_2$$

Hydro can also be used to bleach wool. It's not used much because it tends to impart a harsh handle. Reducing agents also are known to break cystine crosslinks in protein fibers. When the crosslinks are reformed by oxidation (oxygen in air or hydrogen peroxide) the protein fiber can be given a "permanent set". This has been used as a finishing treatment to impart durable creases to wool fabrics and to impart permanent waves to human hair.

VII. TEST FOR DEGREE OF BLEACHING

AATCC Test Method 82, Fluidity of Dispersions of Cellulose from Bleached Cotton Cloth and AATCC Test Method 110, Reflectance, Blue and Whiteness of Bleached Fabrics are the main tests used to determine the effectiveness of bleaching.

1. Whiteness

Since yellow impurities adsorb blue light, AATCC Test Method 110 measures the amount of blue light reflected by the goods, against a white standard (usually a ceramic tile). This gives a measure of how well the yellow impurities were removed by bleaching. Whiteness is measured by reflectance of green light and by the removal of yellow impurities. The equation below is used to calculate whiteness. The standard ceramic tile is measured and set to equal 100. The other specimen are rated against this standard. Unbleached fabrics will give values in the 50 to 60 range. Well breached fabrics will rank 95 or better.

Where: W = whiteness
B = blue reflectance
G = green reflectance

B. Fluidity

The theory behind fluidity measurements is that damaged cellulose has a lower molecular weight than undamaged cellulose. Solutions from undamaged fibers are less fluid than those from damaged fibers. Fluidity is measured by dissolving cotton in cupriethylene diamine and determining the solutions's viscosity. Viscosity of polymer solutions is directly related to the polymer's molecular weight so a fluidity measurement, in reality, is a viscosity measurement. The difference between viscosity and fluidity is the units used to express the results. Viscosity measurements use water as the reference standard, setting it equal to 1 centipoise. Therefore the higher the polymer molecular weight, the higher the viscosity number. The fluidity scale (Rhes) is just the opposite of the viscosity scale. Low numbers are used to describe high viscosity solutions while high numbers describe low viscosity (more fluid) ones. Undamaged cellulose will have low fluidity numbers and damaged cellulose will have high ones.

Table 10

Typical Fluidities

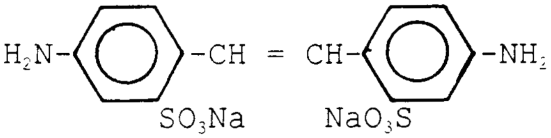
Cloth	Fluidity (Rhes)
Greige (unbleached)	0.2 - 0.4
Mild bleach	0.3 - 0.7
Average bleach	0.9 - 3.3
Over bleached	5.5 - 15.5

VIII. OPTICAL BRIGHTENERS

Certain organic compounds possess the property of fluorescence which means that they can absorb shorter wave-length light and re-emit it at longer wave-lengths. A substance can adsorb invisible ultra-violet rays and re-emit them within the visible spectrum. Therefore a surface containing a fluorescent compound can emit more than the total amount of daylight that falls on it, giving an intensely brilliant white. Compounds that possess these properties are called ***Optical Brighteners or OBA's.*** The effect is only operative when the incident light has a significant proportion of ultraviolet rays such as sunlight. When OBA's are exposed to UV fluorescing light bulbs, "black light", the objects glow in the dark, a sure fire way of identifying fibers that are treated with optical brighteners.

There are several classes of chemical compounds whose structure serve the purpose. These structures have dye-like properties and in essence are colorless dyes, they can exhaust onto various fibers. Anionic OBA's will exhaust onto cotton, wool and silk. Cationic ones exhaust onto acrylics and certain polyesters. Nonionic ones exhaust onto all synthetics.

1. Stilbene Type OBA



Disodium-4,4′-diamino-2,2′-stilbene disulfonate

OBA,s are not a substitute for bleaching. They are used to obtain brilliant market whites. These "white" whites can be obtained without over bleaching and damaging the fiber. On cellulose, they have poor wash fastness but most commercial laundry detergents contain OBA's so they are constantly replenished. Some OBAs have poor washfastness - some nonionics types have excellent light fastness. Fiber producers can include OBA,s in their spinning process. These can have excellent durability to both light and washing.

IX. REFERENCES

CHAPTER 5

OTHER PROCESSES

I. MERCERIZING

Both Mercerizing and causticizing require cotton to be treated with concentrated solutions of sodium hydroxide (caustic soda). Mercerization requires higher concentrations of caustic soda (19 to 26 % solutions) whereas causticizing is done with concentrations ranging between 10 to 16 %. Both procedures are effective in completing the removal of motes that may have escaped the scouring and bleaching steps. One major difference between the two is that causticizing improves the dyeing uniformity and dye affinity of cotton without improving luster. Caustic soda solution swells cotton fibers breaking hydrogen bonds and weak van der Waal forces between cellulose chains. The expanded, freed chains rearrange and re-orient and when the caustic soda is removed, the chains form new bonds in the reorganized state. When done tensionless, the cotton fiber swells, the cross section becomes thicker and the length is shortened. Because of fiber thickening, the fabric becomes denser, stronger and more elastic. Held under tension, the coiled shape of the fiber is straightened and the characteristic lumen almost disappears. The fibers become permanently round and rod like in cross section and the fiber surface is smoother. Decrease in surface area reduces light scattering, adding to fiber luster. Tension increases alignment of cellulose chains which results in more uniform reflection of light. The strength of the fiber is increased about 35 %. The fiber also becomes more absorbent. The cellulose crystal unit cell changes from cellulose I to cellulose II and the amorphous area becomes more open, therefore more accessible to water, dyes and chemicals. Mercerized cotton will absorb more dye than unmercerized cotton and in addition, yields an increase in color value a given quantity of dye.

The amount of fiber shrinkage is a measure of the effectiveness of caustic soda's ability to swell cotton. Table 11 summarizes the correlation between time, temperature and caustic concentration with fiber shrinkage. The data shows that maximum shrinkage occurs with the 24% solution and that most of the shrinkage occurs in the first minute of dwell time. Higher temperatures result in less shrinkage because lower temperatures favor swelling.

Table 11

Effect of Time, Temperature, and Caustic Concentration on Yarn Shrinkage

% Yarn Shrinkage

Conc. NaOH

	10%			19%			24%			29%		
Time (min.)	1	10	30	1	10	30	1	10	30	1	10	30
64° F	12	15	17	19	20	21	23	23	23	23	23	23
86° F	5	5	6	19	20	20	20	20	20	21	21	20

A. Chain Mercerizing

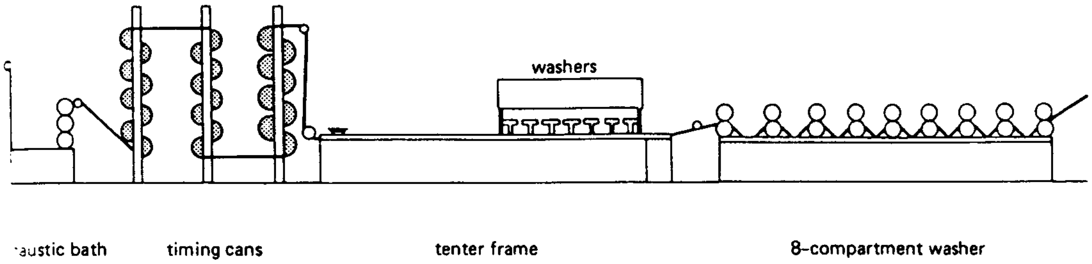
Chain mercerizing is done on a range equipped with tenter chains for tension control. The range consists of a pad mangle followed by a set of timing cans and then a clip tenter frame. Fresh water cascades onto the fabric to remove the caustic soda as it is held tensioned in the tenter frame, . The length of the frame must match the range speed and assure that the caustic level is reduced below 3% before tensions are released. The tenter frame is followed by a series of open-width wash boxes which further reduces the caustic level. Acetic acid is in one of the last boxes to complete the neutralization of caustic.

1. Procedure

1. Apply 22 to 25 % (48 - 54" Tw) caustic at the pad mangle at 100 wet pickup. 2. Pass fabric over timing cans. The number of cans must correspond to the range speed and provide at least one minute dwell time. 3. Clip fabric onto tenter chains and stretch filling-wise while maintaining warp tension. 4. Run fabric under cascade washers to remove caustic. Keep under tension until caustic level is less than 3% otherwise fabric will shrink in filling direction. This width loss is impossible to recover later. 5. Release tension and continue washing in open-width wash boxes, to further reduce the caustic. 6. Neutralize with acetic acid in the next to last wash box and rinse with fresh water in the last. It is important to control these steps because

it is important, in down-stream processing, that the alkalinity remain consistent throughout all production.

Figure 29. Chain Mercerizing Range



2. Points of Concern and Control

For best results, goods should be dry entering the liquid caustic impregnation unit. Need to get uniform and even caustic pick-up through out the fabric. Wet pick-up must be at least 100 %. A certain amount of liquid caustic must surround each fiber to provide proper lubrication so that the fibers can be deformed. For piece goods, a caustic concentration between 48 - 54^0 Tw should be maintained. Caustic stronger than 54^0 Tw does not add to Mercerized properties whereas below 48^0 Tw, the Mercerized fabric will have poor luster and appearance. Caustic solution and impregnated fabric temperatures should be controlled between 70 - 100^0 F. Above 110^0 F, there is a noticeable decrease in luster of the Mercerized goods. Below 70^0 F, there is no noticeable improvement. Proper framing during the washing step is crucial. The goods must be maintained at greige width to one inch over greige for maximum luster. The tensioned width must be maintained through out the caustic removal operations otherwise the fabric shrinks and luster is lost. If optimum washing is obtained. there will be only a slight loss in width as the goods come off the tenter clips.

B. Caustic Concentration Units

Caustic concentrations, expressed as percentages, are ratios calculated as weight caustic/weight solution. However the specific gravity or density of the solution (weight/volume) is directly related to the concentration. Calibrated hydrometers are used to determine specific gravity. The calibration scales most often used on caustic solutions are Twaddle (“Tw) and Baume’ (“Be’). The relationships between concentration and hydrometer readings are:

- °Tw equals 2.15 x [conc. %]

- °Be′ approximates [conc. %]

The relationship between the Baume’ scale and concentration is not linear, the values get closer at higher concentrations. The reader is referred to various handbooks and manuals that have conversion tables.

C. Test for Mercerization

1. Barium Number

AATCC Test Method 89 is a common test used for quantifying the degree of Mercerization. It is based on the fabric‘s ability to absorb barium hydroxide. A two gram swatch of fabric is placed in a flask containing 30 ml of a standardized 0.25 N barium hydroxide solution. The fabric is stirred for two hours (to allow the barium hydroxide to be absorbed by the fabric). A 10 ml aliquot is withdrawn and titrated with 0.1 N hydrochloric acid to a phenolphthalein end point. The difference between the starting concentration and the remaining concentration of barium hydroxide is the amount absorbed by the fabric. The procedure is carried out on the fabric both before and after Mercerizing and the barium number is calculated as shown below.

$$\text{Ba No.} = \frac{\text{Amt. absorbed by Mercerized}}{\text{Amt. absorbed by unmercerized}} \quad \text{X } 100$$

Unmercerized fabric will give a barium number of 100 to 105. Completely mercerized fabric will give a barium number of 150. Commercially treated fabrics fall in a range between 115 to 130.

D. Mercerizing Fiber Blends

Color yield, ease of dyeing and uniformity of dyed fabric will offset cost of Mercerizing. This holds true even for yarn blends with low levels of cotton. The temptation to Mercerize must tempered with thoughts about how caustic affects the blending fiber. The following section discusses these issues.

1. Polyester/Cotton

These can be handled under the same conditions as 100 % cotton. Even though polyester fibers are sensitive to caustic, the temperature and time the fibers are in contact with Mercerizing strength caustic are insufficient to cause fiber damage. One problem with polyester/cotton blends it that they may not be as absorbent as 100 % cotton fabrics coming to the caustic saturator. This is because they have not been given the same thorough scouring and bleaching as 100 % cotton. In this case, special penetrating agents are needed to help the caustic solution wet out the fabric.

2. Cotton/Rayon

Rayon blends pose a number of special problems. Ordinary and high wet modulus viscose rayons are sensitive to caustic solutions. The degree of sensitivity is a function of fiber type and caustic concentration. For example, high wet modulus rayon can withstand caustic better than conventional rayon. Conventional rayon can be dissolved by caustic solutions. High strength caustic solution are less damaging to the high wet modulus rayon than lower strength solutions. Causticizing strength solution will cause the rayon to swell, become stiff and brittle and lose tensile strength. These conditions should be avoided. Fortunately, the higher strengths caustic solution are less damaging so conditions for Mercerizing 100 % cotton can be used. Special penetrants are also helpful in speeding up the wetting-out process to keep the time rayon is exposed to caustic to a minimum. If conditions are not correct, the damage may be so severe'that the rayon is dissolved.

E. Yarn Mercerizing

Yarns are Mercerized as continuous sheets in a fashion similar to woven fabrics. Greige yarns enter the caustic saturator and are held so they do not shrink until the caustic has been washed out. Afterwards, the yarns are dried continuously and wound onto bobbins or spools. These conditions will develop satisfactory luster, elasticity and dyeing properties; however, if higher luster and strength is desired, the yarns should be stretched beyond the greige length during the process. Increase stretch, however, reduces dye affinity and elasticity. The reasons for mercerizing yarns are: 1. To produce lustrous, strong 100 % cotton sewing thread. 2. To produce yarns for constructions that are difficult to mercerize. 3. To produce yarns for special construction effects. 4. To produce yarns for blends containing fibers too sensitive for mercerizing. 4. To provide more complete mercerization for luster and strength.

F. Chainless Mercerizing

Chainless mercerizing is practiced on a range where the cloth is maintained in contact with rotating drums virtually throughout the entire process. The tension on the fabric depends on the friction between the cloth and the surface of the drum.

This results in good control of length but limited control of width. Bowed rollers are sometimes used to stretch the width but they are much less effective when compared with the clips of the chain Mercerizer. Chainless Mercerizing is used on fabrics that cannot be handled on a clip frame such as knits. Specialized equipment has been developed for Mercerizing tubular knit goods. One arrangement is based on a spreader mechanism that resembles a floating cigar. In the USA, very little if any knit goods Mercerization is in evidence. There are some knit goods made from mercerized yarns, however.

II. SINGEING

The object of singeing is to remove projecting fibers from the surface of the fabric so as to give it a smoother, cleaner appearance. The most common singer is a row of gas burners arranged so that the material passes rapidly through the open flame. The speed of the cloth travel is adjusted to burn away the hairs without scorching the fabric. In a normal sequence of operations, the singed fabric passes directly into a quench bath that contain the desizing chemicals to douse any fuzz ball that might have been ignited. Most singers are arranged so the fabric is routed around a steel roller at the point where the flame impinges on it. This opens up the fabric to make the projecting hairs more accessible to the flame. The steel roller absorbs heat from the flame and eventually becomes hot enough to melt most thermoplastic fibers. Modern singers are designed so that chilled water passes through the rolls to keep them cool. While singeing is a simple process, care must be taken to not damage the fabric.

A. Points of Control

The fabric must move rapidly through the flame to prevent the base fabric from being heat damaged. Extremely hairy fabric may require multiple passes through the burners to remove the hairs without damaging the fabric. All the gas burners must produce a uniform flame. Clogged burners will leave a un-singed streak that will become highly visible when the fabric is dyed. The singer must be provided with a mechanism that either turns off the flame or mechanically displaces the burners away from the fabric when the line speed is decreased for any reason. If not, the fabric will scorch or burn in half. Fabrics containing thermoplastic fibers such as polyester can form hard melt balls as the fiber melts and recedes away from the heat source, These melt balls will cause the fabric to have a rough raspy hand. The fabric may require a subsequent processing step to remove the melt balls.

III. CARBONIZING OF WOOL

The purpose of carbonizing wool is to complete the removal of cellulosic impurities which is imbedded in the sheep's fleece from the animal contact with burrs, leaves and plant stems. Some of this matter will end up in the fabric having persisted through raw stock scouring and mechanical cleaning. The cellulosic matter will not dye with wool dyes so dyed fabric will have undyed specks throughout. Complete removal of this plant matter can only be effected by carbonization which is based on cellulose being degraded by strong acids at high temperatures into brittle hydrocellulose with partial conversion to dark decomposition products (carbon). Wool is not fazed by these conditions. The process involves soaking fabric in 5 -7 % sulfuric acid for 2 to 3 hours, extracting the excess acid solution, drying and baking the fabric for one hour at 100° C. The carbonized fabric is passed between fluted rollers which crush the embrittled vegetable matter and then through a machine which shakes the crushed matter out of the fabric. Finally the fabric is neutralized with soda ash and washed to remove all vestiges of acid.

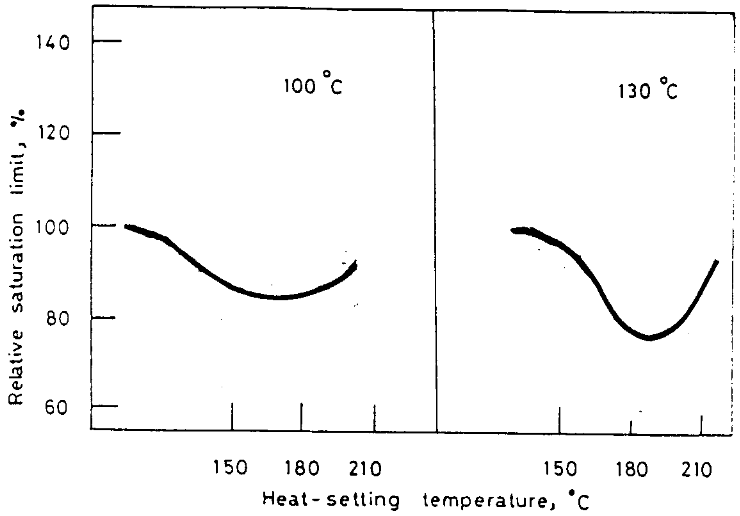
IV. HEATSETTING

The purpose of heat setting is to dimensionally stabilize fabrics containing thermoplastic fibers. Polyester and nylon are the principal fibers involved. Blended polyester/cotton fabrics are produced in large quantities. These fabrics may shrink, or otherwise become distorted either during wet processing or in the consumer's hands. Heat setting is a way of reducing or eliminating these undesirable properties. The process is relatively simple - pass the fabric through a heating zone for a time and at a temperature that resets the thermoplastic fiber's morphology memory. The new memory relieves the stresses and strains imparted to the fiber by the yarn-making and weaving processes, and makes stable the configuration it finds itself in flat smooth fabric. This newly imparted memory allows the fiber to resist fabric distorting forces and provides a way to recover from them. The time and temperature needed for the heat treatment depend on fabric density and previous heat history of the polyester. Time and temperature must exceed that imparted by previous heat treatments. Usually 15 - 90 seconds at temperatures of 385 - 415° F. will suffice. The heat setting equipment can be hot air in a tenter frame, or surface contact heat from hot cans. While the process is simple, careful control is required.

A. Points of Concern

Heat setting reduces polyester's dye up take. Heat-set goods dye lighter and slower than non heat-set good. For uniform shades, side to center, front to back and beginning to end exposure to heat must be controlled and uniform, otherwise these differences will show up in the dyed cloth. Heat-setting can be done either at the end of wet processing or at the beginning. At either point, the goods must be free of wrinkles and other distortions otherwise the distortions will be permanently set. Care must be taken when heat-setting greige goods sized with polyvinyl alcohol. At high temperatures, PVA will dehydrate, becoming discolored and insoluble in water. While greige heat-setting may be particularly beneficial when preparing easily distorted fabrics, one may have to settle for less than the full heat-setting benefit in order to still remove the size. For these cases, alternate mechanical handling preparation equipment may be the answer. Heat-setting harshen the hand and stiffens the fabric. The condition is more prone to happen when contact heat is used. The fabric may become flatter and develop an unwanted gloss or sheen.

Figure 30. Effect of Heat-setting on Dye Uptake



V. REFERENCES

PART II

FABRIC FINISHING

Finishing is the last manufacturing step in the production of textile fabrics. As an integral part of wet processing, *Finishing* is the operation where the final fabric properties are developed. Finishing is not restricted to wet processing alone since any operation for improving the appearance or usefulness of a fabric after it leaves the loom or knitting machine can be considered a finishing step. ***Finish*** can be either chemicals that change the fabric's aesthetic and/or physical properties or changes in texture or surface characteristics brought about by physically manipulating the fabric with mechanical devices. It can also be a combination of the two.

Finishing is commonly divided into two categories, ***Chemical and Mechanical.*** In chemical finishing, water is used as the medium for applying the chemicals. Heat is used to drive off the water and to activate the chemicals. Mechanical finishing is considered a dry operation even though moisture and chemicals are often needed to successfully process the fabric. Mechanical devices are used in both categories - the major distinction between the two is what caused the desired fabric change, the chemical or the machine?

Today's finisher deals with many points of concerns since he is responsible for the ultimate quality of the fabric. Among the points of concerns are those that deal with chemistry, i.e. reactions with the fabric, safe handling of bulk quantities of hazardous chemicals, worker safety and environmental issues involving air and water discharges. Another point of concern deals with the machines used to process the fabric and controlling them to produce first quality goods. Still another point of concern deals with economic factors, i.e. chemical and process costs, output, certification of quality and timely delivery of products to customers.

The chapters that follow will review both the chemical and mechanical aspects of fabric finishing. All of the points of concerns will be considered in this section. The material will be divided into Chemical Finishing and Mechanical Finishing.

CHAPTER 6

MECHANICAL ASPECTS OF CHEMICAL FINISHING

When chemicals are used to change fabric properties, they must be applied uniformly throughout the fabric and fibers. Chemical finishing steps involve applying a chemical solution with a suitable applicator, removing water (drying) and heating the fabric to a temperature that activates the chemical (curing). The process is often referred to as pad-dry-cure. Each part of the process can influence the outcome of the treatment. This chapter will focus on the equipment used in chemical finishing.

I. FINISH APPLICATORS

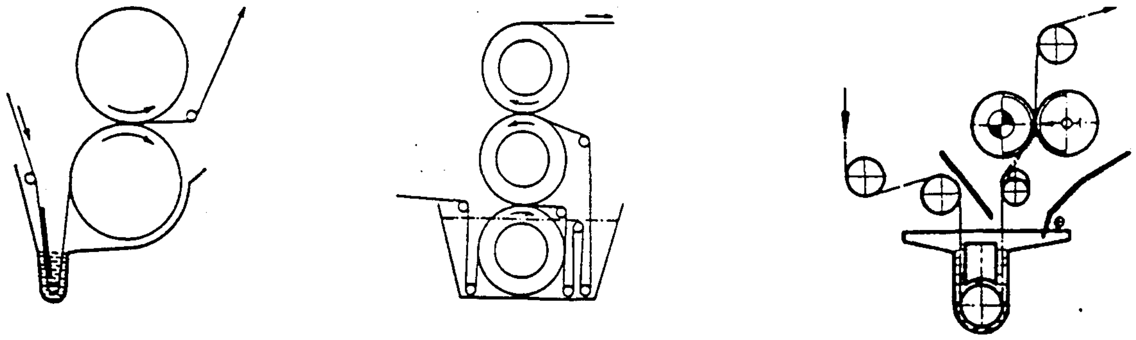
Traditionally, padders have been used to apply chemical finishes. More recently, the cost of energy as it relates to the cost of finishing fabric has escalated interest in low wet pick-up techniques. This section introduces some of the more common apparatus found in a finishing plant.

A. Padder

A padder consists of a trough and a pair of squeeze rolls (mangle). The fabric passes under a submerged roll in the trough filled with the treatment bath and then through squeeze rolls. The process is called padding. Figure 1. shows several types of padders. Diagram (A) is the simplest arrangement, a single dip followed by a single nip. Only two squeeze rolls are used as the mangle. In diagram (B), three rolls are used and the fabric is impregnated twice, double dipped - double nipped. This insures better wet-out and penetration of the finish. Diagram (C) shows a horizontal arrangement of the squeeze rolls.

Three factors control the amount of solution remaining on the fabric, squeeze pressure (which is influenced by the composition of the rolls), fabric construction (the solution resides in the capillary spaces between yarns and fibers), and the absorptive nature of the fiber. All fabrics have upper and lower wet pick-up limits. Within these limits, adjustments in wet pick-up can be made by increasing or decreasing the squeeze pressure. If the squeeze pressure is too low, puddles of solution will remain on the surface of the fabric. When this is dried, excess chemical will deposit in the overly wet areas resulting in non-uniform treatment.

Figure 31. Padders



(A). Single Dip-
Single Nip

(B) Double Dip-
Double Nip

(C) Horizontal
Configuration

1. Location of Padded Liquid

When textile fibers are wetted with a liquid, the liquid can either penetrate into the fiber cross section or remain on the surface. The hydrophilic nature of the fiber will determine where this liquid will be. Cellulose and wool fibers will absorb water; therefore, a certain portion of the wet pick-up will be inside the fiber - the rest will be on the fiber's surface. The amount of surface liquid will be influenced by the yarn's interstitial spaces and the spaces between yarns in fabrics. Polyester fibers, being hydrophobic, do not absorb water so the entire wet pick-up will be located in the capillary spaces within the yarns and fabrics. Wet pick-ups in the range of 75 to 100% are common by padding. Usually the baths contain 10% active chemical and the rest is water. The bulk of what is applied must be removed by drying. It takes 980 BTU'S of heat to evaporate one pound of water so the more water that is on the fabric, the more it will cost to dry. It follows then that if the solution has a higher concentration of active ingredients, the same quantity of chemical can be delivered by lowering the wet pick-up. Less energy is needed to dry the fabric because there is less water to evaporate. With less water to evaporate, the range can be run faster increasing the amount of fabric produced in a given unit of time. Production cost are significantly lowered - lower energy cost and higher through put.

There are several techniques that can be used to apply more concentrated solutions at wet pick-ups lower than can be achieved by padding. The major concern with low wet pick-up applicators is uniformity of deposition. These **Low Water Applicators** are:

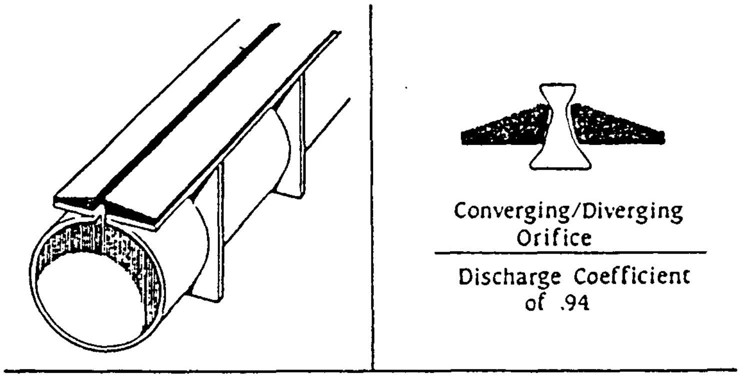
B. Vacuum Slots

Water in capillaries and spaces between fibers and yarns is not bound as strongly as water in the interior of the fiber. The amount in the pores and spaces can be reduced by passing the fabric over a vacuum slot. Figure 2 shows the cross-section of a vacuum slot. It consists of a hollow tube with a slot orifice running the length of the tube. A vacuum pump is connected to the end of the tube and fabric passes over the orifice. The orifice is designed to get the greatest pressure drop through the fabric. An automatic slot seal covers the portion of the slot left uncovered by the fabric and insures maximum vacuum efficiency through the fabric.

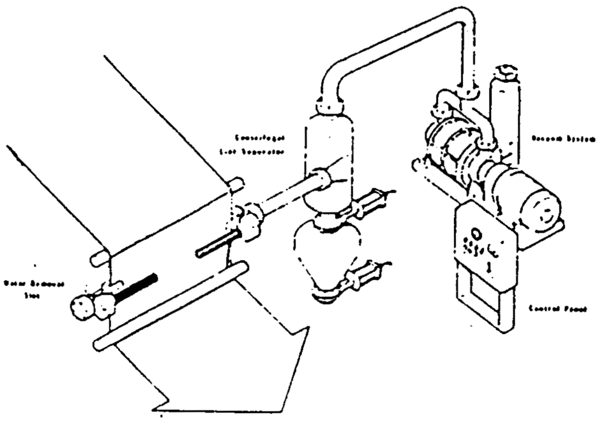
If a vacuum slot is added in line with a padder, the vacuum will extract the liquid residing in the fabric capillaries and open spaces reducing wet pick-up. Most of the solution that remains will be located where it will do the most good, in the interior of the fiber. Finish location and how it influences fabric properties will be discussed in a later section. The finish can be recycled back to the pad for reuse - usually it passes through a filter first to remove lint coming from the fabric.

Figure 32. Vacuum Extractors

Vacuum Tube and Orifice



In Line Slot, Lint Filter and Vacuum System



1. Advantages of Vacuum Slots

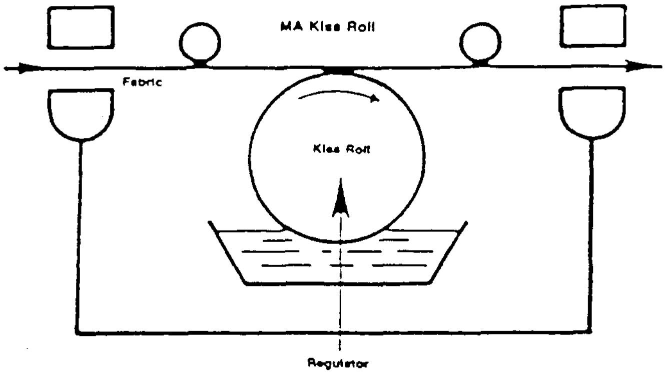
1.They are relative simple devices and are easily fitted onto existing finishing ranges. 2. The extracted solution can be saved and fed back to the pad after the lint has been filtered out. Most fabrics will have short fibers (lint) that come out with the extracted solution. 3. The entire fabric is exposed to the treating solution, therefore the solution is uniform throughout the fabric cross section. Face-to-back uniformity is good. 4. Units have been designed that have movable slot openings to accommodate the need to process fabrics of different widths.

C. Kiss Rolls

A kiss roll applicator consists of a drum rotating in a trough containing the finish. A layer of liquid is picked up by the drum surface. This liquid is transferred onto a fabric "kissing" the exposed section of the drum. Kiss roll applicators are relatively simple devices. Within certain ranges, the wet pick-up can be adjusted to meet whatever is desired by controlling the variables stated above. However, uncontrolled variations in fabric speeds or drum rpm will cause unwanted variations in fabric properties. Figure 3 shows the schematic of the Tritex MA kiss roll applicator. The guts of the unit is a kiss roll rotating in the finish reservoir. Guide rolls position the fabric to contact the wetted surface. This system has beta gauge moisture sensors ahead of and behind the kiss roll to monitor and control wet pick-up. The sensors are connected with speed controllers that adjust either the fabric or the roll speed accordingly.

Figure 33. Kiss Roll Applicator with Moisture Monitors

Triatex MA Kiss Roll



1. Factors Affecting Wet Pick-Up

1. The speed of the fabric travelling over the drum, the faster the fabric travel, the lower the wet pickup, 2. The number of drum revolutions per minute, the greater the number of revolutions per minute, the higher the wet pickup, 3. The viscosity of the liquid controls the thickness of the film on the drum surface. More liquid will be delivered from a viscous liquid than from a less viscous one.

D. Engraved Roll Applicator

Engraved rolls similar to ones used for rotogravure printing can be utilized as low-water finish applicators. In this technique, an etched metal roll revolves in a trough of finish. A "doctor" blade wipes off the surface leaving liquid only in the engraved depressions. The liquid in the engravings wick into the fabric as the fabric passes between the engraved roll and a pressurized backing roll. Engraved roll applicators have advantages over kiss rolls because wet pick-up is not influenced by changing fabric speeds, the depth of the engravings are responsible for metering the liquid. One disadvantage is that the roll must be changed, causing machine down-time, when one wants to change wet pick-up.

Figure 34. Engraved Roll Applicator

E. Foam Applicators

Foam, a collection of bubbles, is created when air is whipped into a liquid. Since a bubble is a sphere of air entrapped by a thin layer of liquid, a volume of foam can be considered a quantity of liquid diluted by air. The volume of foam produced by an amount of liquid is called the ***Blow Ratio.*** Blow ratio is a way of describing foam density since collections of large bubbles result in low density foams whereas small bubbles yield higher density foams. Not all liquids foam when whipped with air. Pure water alone will not foam, a surfactant must be added to lower the surface tension before it will foam.

A volume of foam will eventually break and revert to the original amount of liquid. The time it takes for a foam to revert back to liquid is called ***Persistence*** and the foam's persistence depends on the strength of the bubble's liquid wall. For example, if water drains easily, the bubble's wall become thinner and breaks. However, drainage is influenced by the liquid's viscosity. Water soluble macromolecules, (thickeners) increase viscosity and therefore prolong the time it takes for the cell wall to drain. This will increase the life of the foam and therefore these foams are said to be more persistent.

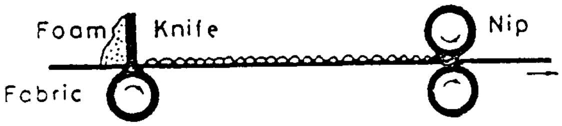
Many textile finish formulations can be foamed by incorporating a foaming agents into the bath. A foaming agent is a surfactant that lowers the surface tension of the bath. The foam's persistence can be controlled by adding water soluble macromolecules. These foams can be metered onto fabrics and represent another low-water application technique. Foamed formulations that break quickly are called ***Metastable Foams*** and those that last are called ***Persistent Foam.*** Each type can be metered onto fabric however, different types of applicators are required. Persistent foams can be applied with knife-coating equipment, while metastable foams require equipment where the foam is generated and applied at the same time.

1. Knife Coaters

A knife-coater is a metering device that continuously spreads viscous liquids onto fabric. This type of equipment is commonly used in the coated fabrics industry. It consists of a stationary knife blade positioned over a fabric support. The material applied to the fabric is fed to one side of the knife blade as the fabric moves continuously under the spreader. The amount deposited on the fabric is controlled by the gap formed between the blade and the fabric. An example of a knife-coater is seen in figure 35. There are several ways the fabric can be supported while moving under the applicator. The fabric can pass between the knife blade and either a table or roll placed directly underneath. These applicators are called knife-over-table and knife-over-roll. Another arrangement has the fabric supported between two horizontal rollers and the knife blade positioned between them, floating on top of the fabric. This arrangement is called a floating knife coater.

Persistent foams of controlled density lend themselves to knife coating. The add-on is controlled by the gap setting and the density of the foam. After the foam has been metered, the fabric either passes between squeeze rolls or a vacuum slot to break the bubbles and to allow the liquid to penetrate the fabric.

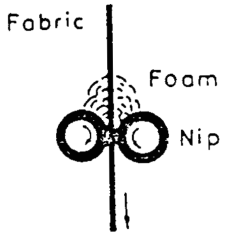
Figure 35. Knife Foam Coater



2. Horizontal Pad

A horizontal pad with a controlled gap between the rollers is a variation of knife coating. Banks of foam can be placed in the crevice between the rollers and the fabric so when the fabric passes downward, the roller will act as the knife allowing a measured amount of foam to pass through. This method applies foam to both sides of the fabric at the same time. Figure 6 illustrates this type of applicator.

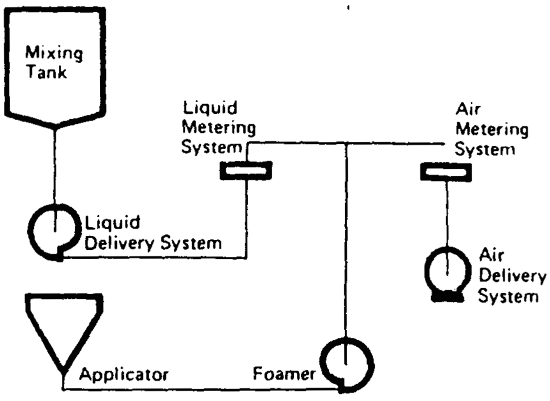
Figure 36. Horizontal Pad Foam Applicator



3. FFT Applicator

Union Carbide and Gaston County developed a low-water finish applicator based on metastable foams. The finish bath and air are continuously metered into a foam generator and the foam is routed through distributing heads directly onto the fabric. Being metastable, the foam immediately breaks on contact with the fabric and the fabric becomes wet with finish solution. Figure 37 shows a schematic of the FFT system. The wet pick-up is regulated by controlling the ratio of liquid feed rate into the foam generator with the cloth speed. By holding the solution feed rate constant, speeding-up or slowing down the cloth speed decreases or increases wet pick-up respectively. Foam density is not a factor affecting wet pick-up by this system. Applicators are designed with two distributing heads so the finish can be applied either to one or both sides of the fabric.

Figure 37. Schematic of FFT System



F. Location of One-sided Applied Finishes

The penetration of a solution from face to back in a one-sided application will depend on several factors. Liquid moves through a fabric by capillary action. The capillaries are the spaces between adjacent fibers in a yarn. If a fabric contains absorptive fibers such as cotton or rayon, a certain amount of liquid will be absorbed within the fiber cross section. This liquid is not available to be transported by the capillaries. The distribution of finish from face to back will be highly dependent on the wet pick-up. For cellulose fabrics, it takes in excess of 40% to get even distribution from front to back. Lower wet pick-ups will cause more of the finish to be located at the face side. This can be an advantage or a disadvantage. For most finishes, it is desirable to have the finish penetrate all of the fibers uniformly throughout the fabric cross-section; however, there are cases where concentrating the finish on one side is advantageous.

If the same amount of liquid is deposited on the face of a polyester fabric as on a cellulosic fabric, more liquid will be found on the back of the polyester fabric than the corresponding cellulosic fabric. The reason for this is that in the polyester fabric, all of the solution resides in the yarn capillaries, all of it can move as capillary liquid; however, in the cellulosic fabric, a certain portion will soak into the interior of the fiber, therefore less is available to migrate as capillary liquid.

II. DRYING AND CURING

Drying is defined as the step where the liquid portion of the solution is evaporated from the fabric. While the concept of drying is simple, in practice it can be the source of unsuspected problems. For drying to take place, the liquid must be converted to vapor and the vapor must be moved away from the surface. The amount of liquid water that evaporates from a given source largely depends on the relative humidity of the air and the volume of air passing over it. Air with low relative humidity has a greater capacity for water vapor than air with a high relative humidity. When the relative humidity nears the saturation value, liquid water is in equilibrium with water vapor and so evaporation is slowed. The absolute amount of water vapor in a volume of air is a function of temperature. For example, at any given relative humidity, the actual amount of water vapor is much greater at high temperatures than at low temperatures.

The rate at which water evaporates from fabric depends on the temperature of the fabric and the volume of air that passes through it. Evaporation of water occurs rapidly at its boiling point. When wet fabric is heated with hot air, (regardless of the air's temperature), the temperature of the fabric will not rise above water's boiling point until all the liquid water is gone. This is true regardless of the fabric's heat source. As water evaporates, the fabric is cooled by evaporative cooling. Some people lose sight of this fact and hold the misconception that wet fabric will be as hot as the air temperature. Some of the factors affecting drying rate are air temperature, relative humidity of drying air and volume of air passing over fabric (air flow).

A. Migration

Chemicals dissolved or suspended in water will move to the point where liquid is converted to vapor. Liquid held in the capillaries is responsible for the phenomenon called migration. If a fabric is heated from one side, the dissolved or suspended chemicals will concentrate at that side. The movement will continue until the moisture level in the fabric is reduced below that required to sustain the filled capillaries. For cellulosic fabrics, this level is about 30 to 40%. To prevent migration, dryers must be designed to evenly remove water from both sides of the fabric. Once the level of moisture is below a critical point, the source of heat becomes less critical.

III. DRYERS AND OVENS

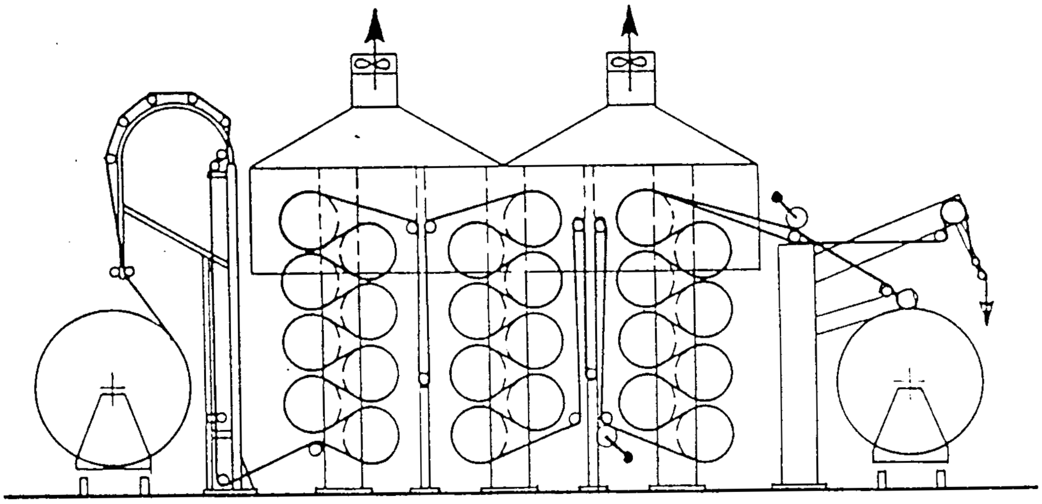
Generally speaking, the same equipment used to dry fabric is also used for curing, provided the equipment is capable of reaching curing temperatures. In many finishing procedures, drying and curing will be divided into two steps. Each step will have its own individual specified conditions. Sometimes however, no delineation between the two is made. Wet fabric enters the oven and cured fabric exits. It is well to remember that fabric temperature will not approach air temperature until all the moisture is gone. In many chemical finishing procedures, the actual fabrics time/temperature relationship is critical in order to activate the chemical reactions. Therefore in one-step drying and curing operations, it is important to know when the fabric is dry so the curing time/temperature relationship is met.

The type of dryer used will affect fabric properties. For example, some fabrics will develop a surface sheen when in contact with heated surfaces, some will shrink unless the fabric is restrained and tension can cause the fabric to become stiff. Additionally tensions can distort fragile fabrics. Choosing the right equipment to handle the fabric is an important matter when one is trying to create specific fabric properties.

A. Dry Cans

The simplest way to dry fabrics is by contacting the fabric with heated surfaces. Fabrics can be dried by continuously running them over a series of large diameter, heated cylinders (cans). By vertically stacking the cans, a lot of heated area can be created with little floor space. Steam, hot oil, electricity and gas flames can be the source of heat for these cans. Most often the cans are heated with high pressure steam. Fabrics dried this way will be under tension in the warp direction. Little warp shrinkage occurs during drying. The fabrics are also somewhat restrained in the filling direction giving some measure of width control.

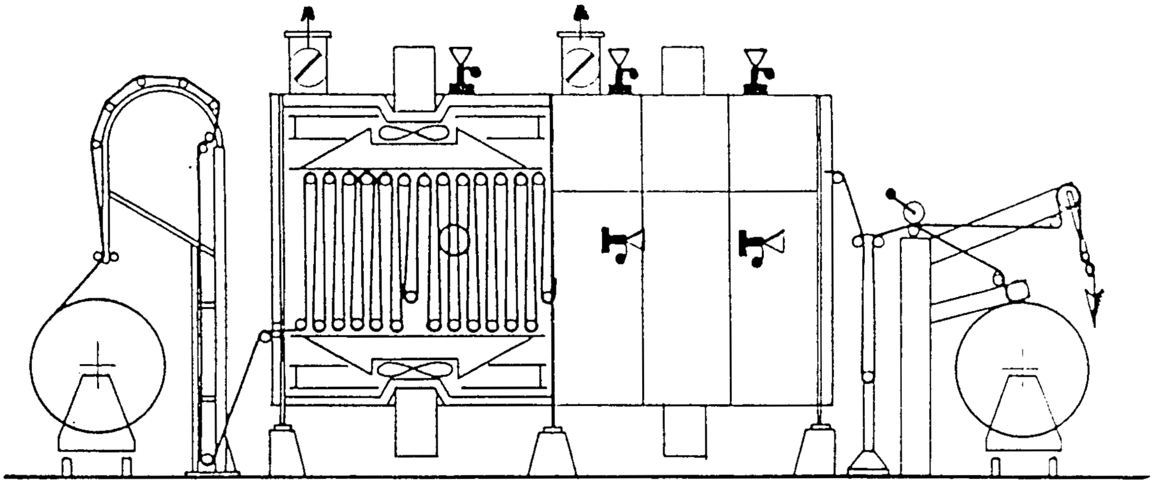
Figure 38. Stacked Drying Cans



B. Roller.Ovens

Roller ovens consist of a series of stationary rollers stacked vertically in a chamber. Fabric enters at one end and passes from the upper roller to the lower roller, threading its way through the chamber to exit out the other end. Air is circulated past the open sheets formed by the alternating pair of upper and lower roller. This allows the fabric to be dried from both sides at the same time. The tensions on the fabric are similar to dry cans, the major difference is that fabric-to-metal surface contact is minimal and water can evaporate from both sides of the fabric simultaneously. Figure 10 shows a two section hot flue, roller oven. Each section can be heated to different temperatures so this arrangement would allow for lower temperature drying zone followed by a higher temperature curing zone.

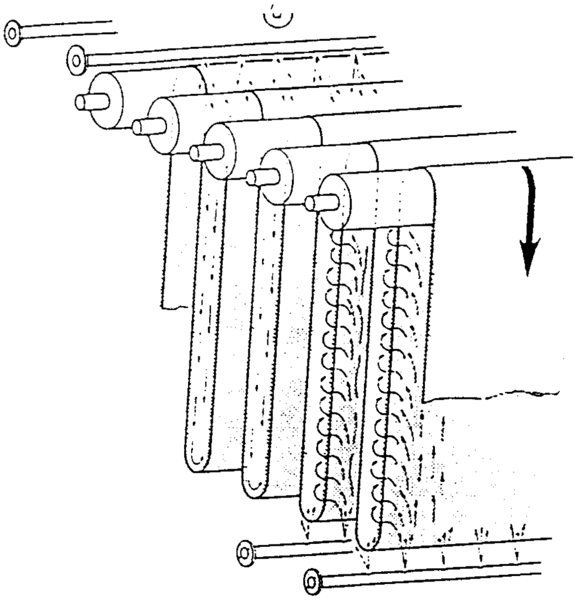
Figure 10. Two Section Roller Oven



C. Loop Ovens

Loop ovens differ from roller ovens in that the rollers move horizontally from the entry side of the chamber to the exit side carrying a loop of fabric along the way. The loop is formed by forcing the fabric between adjacent rollers (sometimes called sticks). The ends of the sticks are attached to a rotating mechanism that constantly propels them through the chamber. Individual loops are continuously being formed at the fabric entry end and removed at the exit end. Hot air circulates through the chamber and the loops are free to flap around as they dry (see figure 11).Fabrics dry in a relaxed state. The fabric is free to shrink so residual shrinkage is lower. Flexing action in the loop oven keeps the fabric from becoming stiff.

Figure 40. Loop Formation over "Sticks"

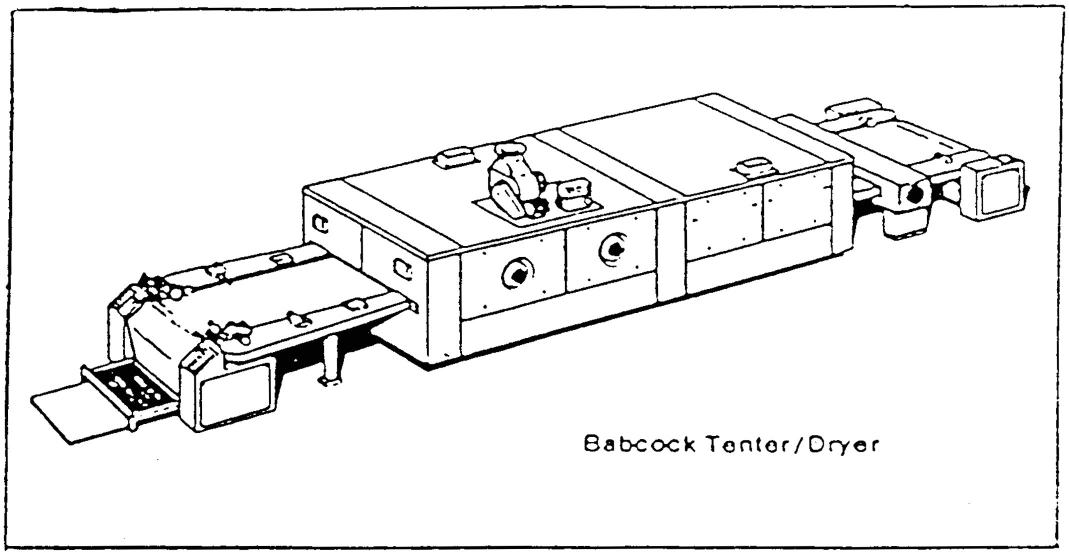


D. TENTER FRAMES

A tenter is a fabric transport device that simultaneously grasps fabric at both selvages and continuously carries it from one point to another. Two endless chains equipped with either clips or pins grasp the selvages and move in synchrony, carrying the fabric between them. The width between the two chains can be automatically adjusted by means of a motor driven screw. The entry end is equipped with edge sensors which signals the screw to move the chains in or out to assure that the edges have been engaged. The width along the length of the chain can be varied by additional independently driven screws located downstream. Sections of the chain can be set to different widths. For example, the width may start out narrow and be pulled out at a subsequent section to make it wider, or it may be set narrower and allowed to shrink. A tenter is the best method of handling fabrics that require precise width control. The tenter also has provision for length control. The fabric either can be stretched or overfed as it enters onto the pins or clips. Many fabrics are sold by the linear yard so as long as the shrinkage requirements are met, stretching is a method of increasing yardage yield. Pin tenters allows for just the opposite to be done; wet fabric can be overfed onto the pins by a separate drive mechanism. The fabric will shrink when it enters in the heated zones. The net effect is to impart low d residual shrinkage at the expense of reduced yardage yield. Overfeeding is a mechanical method imparting low residual shrinkage.

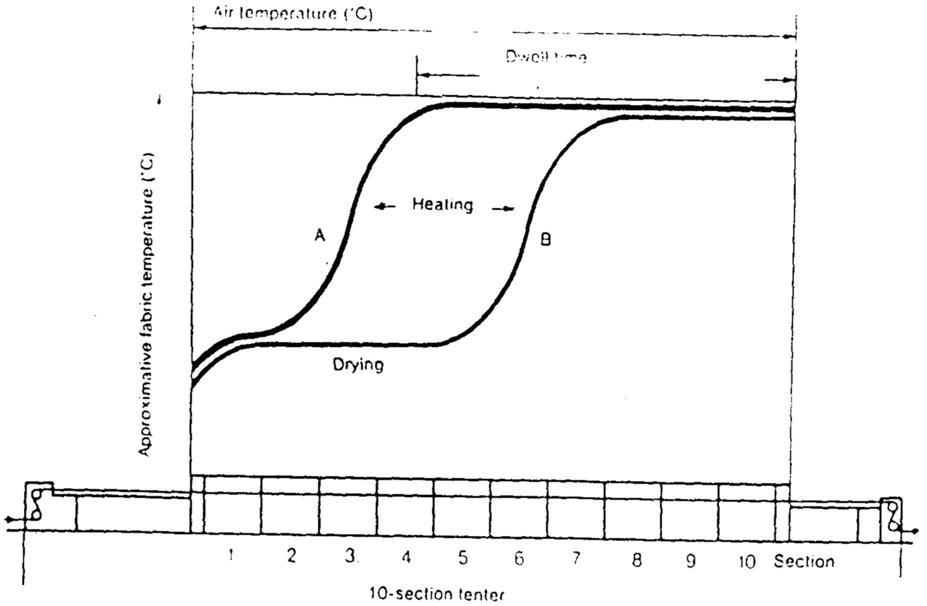
Heating of the fabric occurs when the fabric enters the heated zones. Most tenters are equipped with hot air distribution heads that blow directly onto the top and bottom of the fabric. Either slots or tubes direct the air onto the fabric. Air is directly heated by a gas flame and some of the air is recirculated through the burner while some is exhausted out the stacks. Figure 41 shows a diagram of a typical tenter frame.

Figure 12. Tenter Frame



The heating section of a tenter frame also can be broken down into heating zones. The temperature in each zone can be independently set to profile any drying and curing conditions desired. Figure 42 illustrates the fabric temperature profiles when wet fabrics travel through a ten section tenter frame. Curve A is the profile seen by a fabric when the frame is run at slow speed. Water evaporates quickly after the wet fabric enters the first section. As soon as all the water is gone, fabric temperature reaches the temperature of the heated air. The time it takes to travel from this point to the exit end is the actual time the fabric is exposed to the higher temperature. Curve B represents the temperature profile when the frame is speeded up. Note that it took longer to dry the fabric so the time the fabric was exposed to the higher temperature was less. In both cases, the air temperatures in each section was unchanged, only the fabric speed changed. The implication of this is that knowledge of the fabric temperature profile is a must if time of cure influences the properties of finished fabrics (which it does for many finishes). All older frames have air temperature indicators located along the inside of the frame. However this alone will not insure proper control of the drying and curing process. Some modern frames are equipped with fabric temperature sensors located along the length of the frame as a better way of controlling the process. By knowing the point within the frame when the fabric is dry, the frame could be programmed to give the time necessary for curing to take place. For a light weight fabric, the frame could be speeded up and the chances of overcuring eliminated. Conversely the frame should be slowed down for a heavy fabric that takes longer to dry otherwise the time of cure will be much less.

Figure 42. Effect of Range Speed on Fabric Temperature Profile



E. OTHER DRYERS

There are other types of dryers, each designed for a specific purpose. For example,

- Drum and conveyer dryers for knit goods. These accommodate the need to not put excessive tensions in either direction of the fabric.
- Tumble dryers - used to develop fabric texture.
- Combination heated cylinder/forced hot air dryers - designed for faster heat up of woven goods.

A detailed description of all types of dryers is beyond the scope of this manuscript.

IV. REFERENCES

CHAPTER 7

DURABLE PRESS FINISHES

Durable press finishes can be defined as those chemicals used to improve the properties and performance of washable fabrics. Apparel fabrics, from a historically perspective were made from natural fibers, namely wool, silk and cotton. Of these, cotton was the one best suited for washable fabrics because wool and silk would not stand up to the rigors of washing. Before 1960, 100% cotton yarns dominated the washable fabric market. Garments made from 100% cotton fibers are comfortable because they absorb perspiration. Even today cotton garments are preferred by many consumers because of the comfort factor. Unfortunately, garments made from cotton become badly wrinkled during wear, they don't retain the nice smooth "just ironed" look. After they have been washed and dried, they must be ironed otherwise they will look very rumpled. Garments also shrink in the washer. Most of these shortcomings can be improved by properly applying durable press finishes.

I. WHY FABRICS WRINKLE

Why do some fabrics wrinkle and others don't? Close examination of this question reveals a relationship between moisture absorption and wrinkling. Wool and cotton fabrics wrinkle, both fibers absorb water. Polyester and nylon fabrics are more resistive to wrinkling, they absorb much less than the other two.

To understand wrinkling of cellulose fibers, consider the stress and strain forces within a smooth rod as it bent - see figure 43. The stretching stresses at the outer reaches of the bend provide lateral forces to adjacent polymer chains which can cause them to move. The inner polymer chains are under compressive stresses - also providing lateral forces. A large diameter rod, because the radius of curvature is bigger, will exhibit greater strains than a thinner rod.

Under stress, the hydrogen bonds between adjacent cellulose chains can break allowing the chains to slip past each other. New H-bonds can form as the hydroxyl groups re-associate with different partners. Having done so, there are no forces to pull the neighboring chains back to their former position. The stressed shape of the fiber is just as stable now as was the original shape.

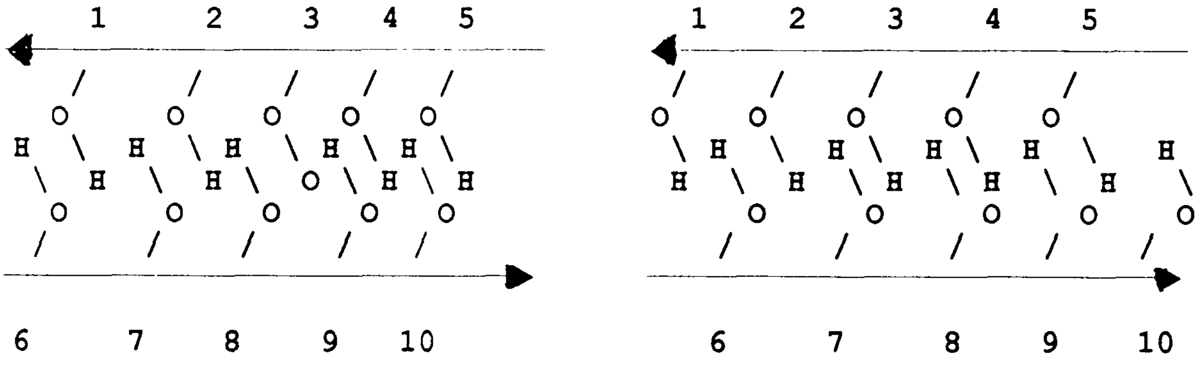
Figure 43. Bending Stresses in Fibers

Bending Forces in a Thin Rod

Bending forces in a Thick Rod

Water will facilitate the disruption of these bonds by forming H-bonds between the water molecule and the cellulose hydroxyls. Now the hydrated polymer chains can slide past each other more easily so the strain level to deform the fiber is even lower than before. Water acts as a lubricant allowing the chains to slide past one another easily. Illustrative of this point is ironing wrinkles out of a cotton garment. It is impossible to iron out wrinkles from a dry garment. However, when the garment is dampened first or if a steam-iron is used, the wrinkles will iron out and the fabric becomes flat and smooth.

Figure 15. Lateral Forces Between Cellulose Chains



Before Stress **After Stress**

A. Factors Affecting Wrinkling

For wrinkles to set in, the forces distorting the fabric must be transmitted to the individual fibers. The forces must then place a strain on the individual fibers and distort them. Some of the physical factors that come into to play are summarized below.

1. Fiber Factors

Fabrics made from fine cotton fibers do not wrinkle as badly as fabrics from course fibers. The explanation for this observation is that the bending radius of curvature is greater for a thick fiber than for a thin one. The greater the radius, the greater is the stress on the polymer chains. Fabrics made from fine Egyptian cotton wrinkle less than those made 'from course fibers

2. Yarn Factors

Fabrics made from high twist yarns wrinkle worse than those made from low twist yarns. For low twist yarns, the distortion stresses are dissipated by the physical rearrangement that takes place as adjacent fibers slip by each other. The stress is dissipated before it can affect the individual fibers.

3. Fabric Factors

Tightly woven fabrics wrinkle worse than loosely constructed fabrics. In a loosely constructed fabric, the yarns can move as they respond to the wrinkling forces. The individual fiber is spared. Woven fabrics wrinkle worse than knits. The knit loops allow an even greater freedom of yarn movement again sparing the individual fiber.

II. THEORY OF CREASE RECOVERY

In polymer chemistry, it is well known that certain types of polymers must be cross-linked before they develop elastic properties. Elastomers are materials that readily recover from deformation stresses. Since the case has been made that chain slippage under moist conditions is responsible for wrinkling, it is logical to reason that cross-linking adjacent cellulose chains should be a way of improving crease recovery. Time has shown that this theory does indeed work so the mechanism for improving cotton's resilience is to cross-link cellulose chains with appropriate reactants.

A. Crosslinking Cellulose

The hydroxyl groups on the anhydroglucose units of the cellulose polymer backbone are functional groups that can undergo typical reactions involving alcohols. Organic acids, isocyanates, epoxy and aldehydes all react with hydroxyl groups to form their corresponding reaction products. Over the years nearly all known reactions involving alcohols have been investigated as possible cellulose crosslinkers. Formaldehyde and formaldehyde derivatives were among the earliest ones discovered and have stood the test of time in terms of effectiveness and cost. They are still the mainstay of today's chemistry.

B. History of Crease Recovery

In the mid 1920's, the managing director of Tootal, Broadhurst and Lee challenged his research chemists to make cotton fabric as wrinkle resistant as silk. It was know that formaldehyde would react with cellulose, however formaldehyde is not a pleasant material to work with as it irritates mucus membranes, causes runny noses and watery eyes. The chemists discovered that phenol/formaldehyde condensates would also cross link cotton and at the same time reduce the formaldehyde risks. Unfortunately the phenol/formaldehyde resins caused the cotton fabrics to become severely discolored and excessively boardy. Soon thereafter, they discovered that urea/formaldehyde resins also improved crease recovery and did so without discoloring the fabric. While not completely free of formaldehyde odor, these resins could be handled on commercial equipment. From the 1930's until 1961, cotton fabrics were crosslinked with a number of N-methylol compounds to give fabrics that were classified as ***Wash & Wear*** or ***Easy Care*** fabrics. Several other names were associated with these fabrics e.g. ***Crease Resistant, No Iron, CRF*** etc. The performance of these fabrics were pretty good. As will be made more clear in ensuing discussions, the best balance of improved ease of care properties to fabric strength loss was struck. All of the fabrics were treated at the mill in the flat state.

In 1961, The Koret Company marketed garments with permanent creases. This was revolutionary at that time because the activation of the cross-links was delayed until after the garment was made and the creases pressed in. What Koret did was to impregnate the fabric with the chemicals, carefully dry without activating the cross-links, make, press and then hang the garments in an oven to activate the cross-links. The consumer's reaction to these garments was double edged. They complained about the fact that the cuffs fell off and holes appeared in the sharp creased areas when the garments were worn and laundered, yet turned around and wanted more. The consumer had been freed from the tedious task of ironing their garments. signalling the birth of the *Permanent Press* era. From the chemist's point of view, the lack of abrasion resistance and weakened fabric was expected since the original garments were made from 100 % cotton. It was well understood at that time that creases set into the fabric prior to curing would be permanent and that excessive chemicals, curing times and temperatures would severely weaken the fabric and drastically reduce abrasion resistance. Nonetheless the industry, sensing a new marketable product, immediately launched into development programs to overcome the deficiencies and still maintain the permanent press qualities. The solution came about quickly. Serviceable garments were made from nylon blended with cotton. Soon thereafter, polyester blended with cotton also provided serviceable garments. At that point in history, polyester was relatively new, expensive and not a truly commercial item. Yarn spinners found that polyester was easier to blend with cotton than nylon, so it became the preferred fiber for permanent press fabrics. The original blend was 35 % polyester, 65 cotton. This amount of polyester provided the strength without interfering with cotton's contribution to shape retention.

It can be said that the commercial success of Permanent Press (Durable Press) is largely ,responsible for today's position enjoyed by polyester manufacturers. It provided the initial need for volume production which lead to the polymer's more competitive pricing structures, opening up more and more markets.

C. Definitions

- **Muss Resistance (Wrinkle Resistance).** The fabric must not wrinkle when a garment is worn. Wrinkling performance can be expressed in *Crease Recovery* terms. *Crease Recovery Angle (CRA)* are used to measure crease resistance or crease recovery.

- **So-Iron (DP Rating).** Fabric must have a smooth appearance after it is laundered dried (line dried or tumble dried). Fabric smoothness is referred to as *Durable Press Rating (DP Rating)* and is judged on a 1 to 5 scale. A 5 DP rating is the highest (most smooth) and a 1 is the most wrinkled. A 3.5 rating is considered commercially acceptable.

- **Low Residual Shrinkage.** Fabric must shrink less than 2 % when laundered.

- **Permanent Press.** Garment shape is maintained during wearing and washing. Creases must be sharp, flat areas must be smooth. Creases are rated on a 1 to 5 scale. A 5 rating is perfect.

- **Delay Cure.** **A** process where the curing step is delayed until the garment has been made and pressed.

- **Precure.** **A** process where the curing is done at the finishing plant in the flat state.

- **CRA.** Crease recovery angles. AATCC Test Method 66-1984

- **CRF.** Crease resistant finish.

III. CELLULOSE CROSSLINKERS

Cellulose crosslinkers can be divided into two categories, those that predominately crosslink cellulose, also known as cellulose reactants, and those that self-polymerize as well as crosslink cellulose (aminoplasts). Both types involve the reaction chemistry of formaldehyde so a review of pertinent formaldehyde chemistry will help in understanding how these auxiliaries work.

A. Reactions of Formaldehyde

Formaldehyde is capable of reacting with many active hydrogen compounds, e.g -OH, -NH and activated -CH.

1. Formation of Hydroxymethyl Derivatives

a. With Alcohols

$$R{-}O{-}H + HCHO \longrightarrow R{-}OCH_2OH$$

Hemiacetal

b. With Amides

$$R\overset{O}{\overset{\|}{C}}{-}N{-}H + HCHO \longrightarrow R\overset{O}{\overset{\|}{C}}{-}NCH_2OH$$

N-Methylol

c. Activated C-H

$$-C-H + HCHO \longrightarrow -C-CH_2OH$$

Hydroxymethyl

The hydroxymethyl group formed in the first reaction is also capable of undergoing a second reaction. The second reactions also involve activated hydrogens described above and result in the formation of a methylene link ($-CH_2-$) between the reacting species. Usually this reaction requires an acid catalyst and heat.

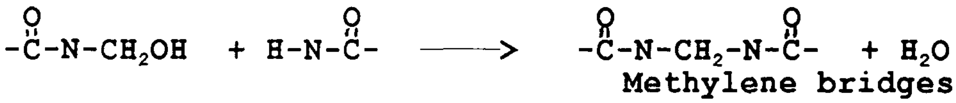
2. Reactions of Hydroxymethyl

a. With Alcohols

$$R-OCH_2OH + R-OH \xrightarrow{H^+} R-O-CH_2-O-R + H_2O$$

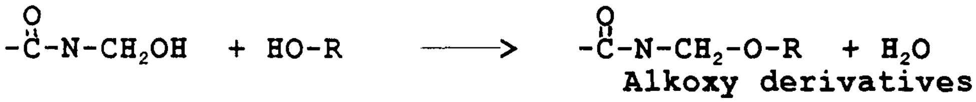
Acetal

b. With N-Methylol



$$-\overset{\overset{O}{\|}}{C}-N-CH_2OH + H-N-\overset{\overset{O}{\|}}{C}- \longrightarrow -\overset{\overset{O}{\|}}{C}-N-CH_2-N-\overset{\overset{O}{\|}}{C}- + H_2O$$

Methylene bridges



$$-\overset{\overset{O}{\|}}{C}-N-CH_2OH + HO-R \longrightarrow -\overset{\overset{O}{\|}}{C}-N-CH_2-O-R + H_2O$$

Alkoxy derivatives

B. Resin Formers (Aminoplasts)

There are two major types of formaldehyde condensates that fall into the resin former category, urea/formaldehyde and melamine/formaldehyde. These condensates are capable of self-crosslinking to form resinous, three-dimensional polymers as well as crosslinking cellulose. They find non-textile applications as plastics, adhesives and are also used to modify other polymeric systems. Because of the tendency to self-condense, the two mentioned above are often called ***Aminoplasts.*** The tendency to self-crosslink adds stiffness to fabrics. While stiffness may be undesirable on some fabrics it can be an asset as for example when ***Handbuilders*** are needed to enhance fabric properties.

1. Urea/Formaldehyde (U/F)

The reaction of an amide -N-H with HCHO to form a $-NCH_2OH$ is often termed ***Methylolation*** because the reaction product is called an N-methylol group. Accordingly urea can be metholylated with up to 4 moles of formaldehyde and the reaction products used as crease resistant finishes. When 2 moles of HCHO is reacted with one mole of urea, dimethylol urea is formed. Being difunctional, it is capable of serving as a crosslinking agent.

a. Synthesis of Dimethylol Urea

$$NH_2-\overset{O}{\overset{\|}{C}}-NH_2 + 2\ CH_2O \longrightarrow HOCH_2NH-\overset{O}{\overset{\|}{C}}-NHCH_2OH$$

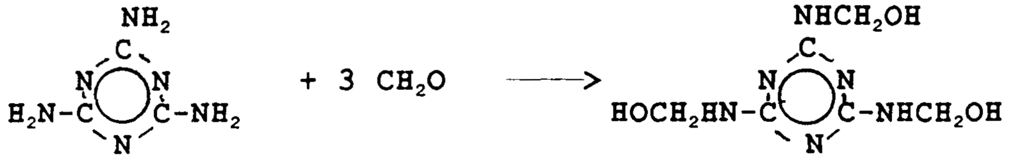
b. Important Features

1. The condensate has an extremely short shelf life. It must be used within a few days after its been made. When formulated with catalyst, the finish bath must be used within a few hours. The solution has high free formaldehyde and will readily liberate formaldehyde into the work place. 2. It is easy to cure on fabrics and imparts outstanding crease recovery. Fabric hand becomes stiffer which is usually undesirable for many cotton fabrics. Most rayon fabrics are very limp compared to cotton so the added firmness is desirable. 3. Finished fabrics have poor durability to repeated laundry. Crease recovery is lost because the crosslinks have poor stability to hydrolysis. 4. The finish adversely affect the light fastness of direct and fiber reactive dyes. 5. The finish reacts with hypochlorite bleaches to form a reaction product which decomposes with heat to form HCl. Acid degradation of the cellulose scorches the fabric and causes it to become very much weaker (tender). 6. Finished fabric is prone to liberate formaldehyde odor. Released formaldehyde is high. Overcured fabrics also develop an unpleasant fish odor.

2. Melamine/Formaldehyde

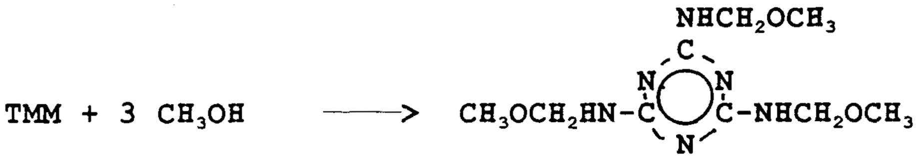
Melamine can react with up to 6 moles of formaldehyde to form a variety of products. Commercially, trimethylol and hexamethylol melamine are the more important condensates. In storage, the hydroxymethyl (N-methylol) groups tend to polymerize and liberate formaldehyde. By converting them to the methoxymethyl derivative, the shelf life is much improved. Most of the commercial products are methylated.

a. Synthesis of Trimethylol Melamine



Melamine Trimethylol Melamine

b. Synthesis of Trimethoxy Melamine



Trimethoxymethyl Melamine

c. Synthesis of Hexamethoxymethyl Melamine

The corresponding hexamethylol- and hexamethoxymethyl condensates are made by increasing the formaldehyde/melamine mole ratio to 6:l.

d. Important Features

1. The tri- products produce firmer hands than the hexa derivatives and are extensively used as hand builders for fabrics other than cotton (Acrylic, nylon, polyester). 2. Durability to repeated laundering is much better than U/F. This feature is a plus for permanent hand builders. 3. Chlorine bleaches cause the fabrics to yellow; however, the reaction product does not decompose with heat to liberate HCl and tender the fabric. 4. They are used in combination with phosphorus flame retardants as a source of nitrogen. Nitrogen synergism enhances phosphorus flame retardants and melamine is an excellent source of nitrogen. 5. They are used as finishes for reducing wool shrinkage.

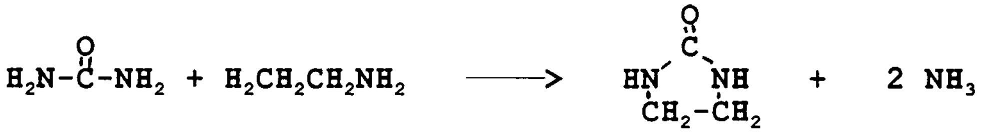
C. Reactants

Reactant N-methylol compounds differ from aminoplasts in that reactants do not form three-dimensional polymers by self-condensation. When applied to cellulose, they mainly crosslink adjacent polymer molecules. The commercially important ones are derived from ethylene urea, 4,5-dihydroxy- ethylene urea and hydroxyethyl carbamate. There is a wealth of literature published about these and related compounds - the reader is urged to consult these reference for greater depth.

1. Dimethylolethylene Urea (DMEU)

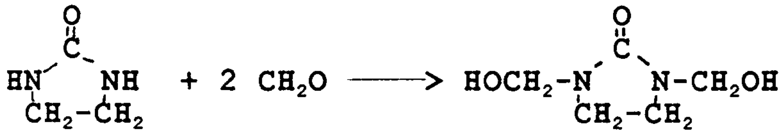
The starting material for making dimethylolethylene urea (DMEU) is ethylene urea. a 5 membered heterocyclic, nitrogen compound (imidazolidone-2). It is made by reacting ethylene diamine with urea. Ethylene urea contains 2 N-H groups capable of reacting with formaldehyde and forms a difunctional product. Since there are no other active hydrogen sites, the N-methylolated product cannot self-condense.

a. Synthesis & Monomer



Ethylene urea

b. Methylolation Reaction



DMEU

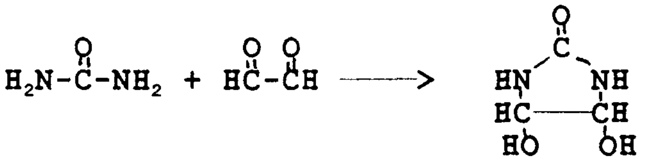
c. Important Features

1. It was widely used prior to 1961 as a wash and wear finish. 2. The product has moderately good shelf life, much better than the aminoplasts. Even with catalyst mixed in, the bath life is more than adequate for most commercial applications. 3. DMEU is easily cured. It will begin to cure at 90 to 100° C. 4. It is highly efficient and gives good wrinkle recovery with nominal losses in fabric strength. 5. The product does affect lightfastness of certain direct and fiber reactive dyes. 6. Chlorine resistance is poor even though there are no remaining N-H groups. 7. Hydrolysis resistance is poor. Crosslinks are not durable to laundering, especially industrial laundering conditions.

2. Dimethylol-4,5-Dihydroxyethylene Urea (DMDHEU)

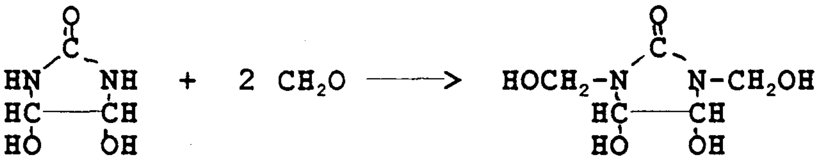
DMDHEU is the workhorse durable press finish. It and some of its modified versions account for over 85% of all crease resistant chemicals consumed today. DMDHEU achieved this prominent role in 1961 when delay cure processing came into being. In the trade, DMDHEU is often referred to as the ***Glyoxal*** resin. This jargon came as a way to distinguish it from DMEU, in that glyoxal was used to make the starting monomer. The starting heterocycle is made by reacting stoichiometric amounts of urea and glyoxal. The reaction is straightforward and can be carried out in regular laboratory glassware. The methylolation step is also straightforward. While the synthesis is shown in two steps, commercially **DMDHEU** is made directly in one step. Urea, formaldehyde and glyoxal are all combined together and heated. The extent of reaction is followed by monitoring the free formaldehyde content. The product is sold as a 46% solution.

a. Synthesis of 4,5 - Dihydroxyethylene Urea



4,5-Dihydroxyethylene Urea

b. Methylolation



DMDHEU

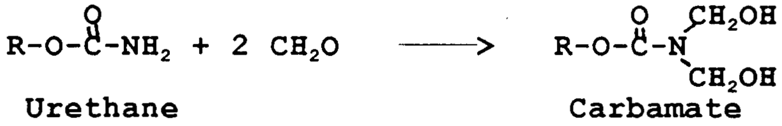
c. Important Features

The commercial product has low free formaldehyde which makes it easy to handle in a finishing plant. It does not liberate formaldehyde from the reverse reaction as rapidly as do other reagents. The product has extremely good shelf life and even finish baths with catalyst present are stable for prolong periods of time. Fabric temperatures exceeding 130^0 C are needed before the cross-linking reaction takes place. This feature is responsible for why it has become the dominate DP finish. The reactant does not crosslink on storage so fabrics can be left in a sensitized state (uncured) for over six months before post curing. Hydrolysis resistance of the cellulose crosslinks are much better than DMEU so durability to laundering is very acceptable. Resistance to chlorine bleach is also acceptable. While this finish reduces the light fastness of direct and fiber reactive dyes, it is better than DMEU.

3. Carbamates

Carbamates are a family of related compounds that also react with formaldehyde to form N-methylol derivatives. A general structure of the starting compound is shown in the box below. This structure is also called a urethane so carbamates are simple urethanes. The alkyl group (R-) can be methyl, ethyl, propyl or hydroxyethyl. The methyl and ethyl carbamates are carcinogenic and no longer used. The propyl and hydroxyethyl are safe and are used today. Carbamates react with formaldehyde to form N-methylol derivatives. They can react with up to two moles as shown below. The reaction is difficult to drive to completion and the equilibrium is such that the best that can be done is 1.7 to 1.8/1. This leads to products that have high free formaldehyde.

a. Synthesis



$$R{-}O{-}\overset{O}{\overset{\|}{C}}{-}NH_2 + 2\ CH_2O \longrightarrow R{-}O{-}\overset{O}{\overset{\|}{C}}{-}N(CH_2OH)_2$$

b. Important Features

Carbamate finished fabrics have good DP properties. These products are harder to cure and require stronger catalyst and/or higher curing conditions. This leads to greater losses in strength and abrasion resistance. The crosslinks are extremely stable to alkaline hydrolysis and stand up well to the rigors of commercial laundries. Fabrics treated with carbamates are well suited for industrial laundry applications such as rental uniforms and hospital linens. Chlorine resistance is good. The commercial products have high free formaldehyde leading to fabric with high formaldehyde release.

IV. CONTROLLING FORMALDEHYDE EXPOSURE

A. Atmospheric Formaldehyde

Strict exposure limits to formaldehyde vapor in the work place have been imposed on all industries using formaldehyde products. OSHA has lowered worker exposure to airborne formaldehyde to 0.75 ppm over an 8 hour time weighted period. Worker training, medical surveillance, removal of those sensitive to its exposure are other requirements of the new regulations. Worker exposures in the dyeing and finishing plant and in garment sewing plants are the issues. Better ventilation in those areas where formaldehyde is prone to be present has been particularly effective in meeting the limits. Another area of concern is the formaldehyde emanating from DP finished fabrics. If the amount coming from a roll of fabric is high, it would soon fill the air space around it and exceed the control limits. This is a particularly bad problem in cut-and-sew industries which manufacture consumer products. Newer reactants containing lower free formaldehyde have been developed to combat this problem. Towards this end, a lot of effort has been spent to reduce the formaldehyde released from a DP finished fabric and still maintain the desirable DP performance. The discussions that follow describe efforts in modifying reagents to reduce the formaldehyde release.

B. Formaldehyde in Fabrics

1. Free Formaldehyde

Free formaldehyde is defined as the uncombined monomeric formaldehyde that exist in finish solutions. Usually, its sources are stoichiometric excesses that may have been included in the resin manufacturing step to drive the reaction and/or the amount arising from the equilibrium established by the particular reactants. Free formaldehyde is determined by suitable analytical titration procedures.

2. Formaldehyde Release

Formaldehyde release, not to be confused with free formaldehyde, is the amount of formaldehyde that escapes from a fabric into the atmosphere. It is determined by the mason jar method, AATCC Test Method 112. The method calls for suspending 1 gram of fabric in a sealed quart mason jar containing distilled water in the bottom. The jar is incubated for 20 hours at 49° C. The formaldehyde that collects in the water is analyzed and the results are reported in ppm or µg/g fabric. There are other fabric test methods used for determining formaldehyde in fabric. For example the Japanese method calls for titrating the free formaldehyde in the fabric by a cold procedure. The box below shows a comparison of the results obtained on the same piece of fabric tested by the different analytical procedures. The results obtained by the mason jar method are much higher than the Japanese method so the reader is cautioned to be sure of the details of what is being reported before jumping to conclusions.

TABLE 11

HCHO TEST METHOD COMPARISON

Method	HCHO (ppm)
Cold Sodium Sulfite	57
MITI	250
Japanese Law	454
AATCC 112-1983	818

The analytical procedures for the jar test usually call for the use of a colorimetric method using Nash Reagent. This procedure is not very reproducible for low levels of HCHO without extreme care. Methods using chromotropic acid to develop the color are more accurate. Recently, even more accurate methods utilizing HPLC techniques have been introduced.

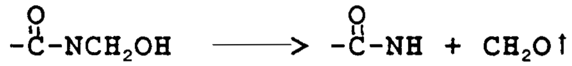
3. Linkages Responsible for HCHO Release

There are three major types of formaldehyde linkages that are responsible for released formaldehyde. The most labile linkage is cellulose hemiformal. Cellulose readily picks up formaldehyde from the atmosphere and give a positive reading by the jar test. Free formaldehyde in solutions and formaldehyde made available from the N-methylol equilibrium are also sources. A second linkage that can be a source of gaseous formaldehyde is uncured resin or pendant N-methylol groups. These linkages are rather labile and easily revert back to their starting materials. It is difficult to cure 100% of the resin that is applied and make sure there are no pendant N-methylol groups left. Therefore, all fabrics will have some, and the amount will depend on how well the fabric was cured. The third source of released formaldehyde is the crosslink itself. The finish will decompose under the jar test conditions and liberate CH_2O.

a. Cellulose Hemiacetal

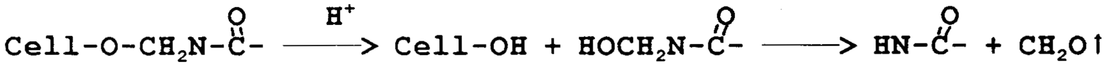
$$Cell-OCH_2OH \longrightarrow Cell-OH + CH_2O\uparrow$$

b. Pendent N-Methylols



$$-\overset{\overset{O}{\|}}{C}-NCH_2OH \longrightarrow -\overset{\overset{O}{\|}}{C}-NH + CH_2O\uparrow$$

c.-Cellulose Crosslinks

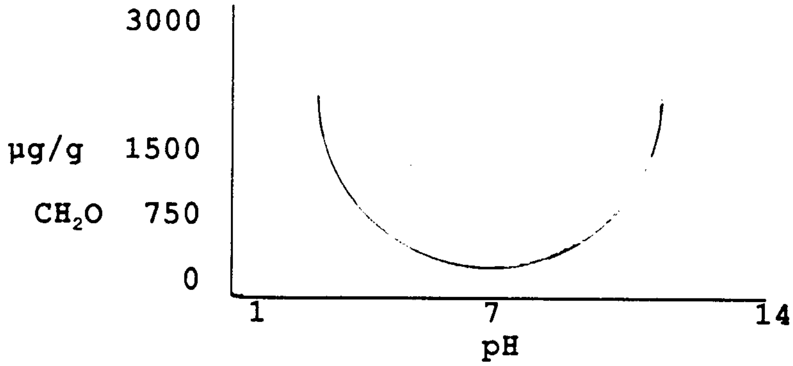


$$Cell-O-CH_2N-\overset{\overset{O}{\|}}{C}- \xrightarrow{H^+} Cell-OH + HOCH_2N-\overset{\overset{O}{\|}}{C}- \longrightarrow HN-\overset{\overset{O}{\|}}{C}- + CH_2O\uparrow$$

4. Fabric pH and Formaldehyde Release

Fabric pH has a great influence on the mason jar test results. As seen in figure 20, a pH of 7 will result in the lowest release values. However if the pH is alkaline or acidic, all else being equal, the test will show much higher values. If the same swatch is resubjected to the jar test?additional formaldehyde will be released and test values will be in the same ballpark as the first run. The swatch will continue to give positive release values until all the crosslinks have been broken. The shape of this curve can be explained by an understanding of the three linkages that are responsible for HCHO release.

Figure 45. Effect of pH on CH_2O Release.



The cellulose hemiacetals are the ones that most easily revert back to HCHO monomer. They are the ones that are released at neutral pH. The pendent N-methylols are unstable at alkaline pH. Fabric tested under alkaline pH would liberate both the hemiacetals and the pendent N-methylols. Under acidic conditions, cross links are broken so all three linkages would contribute to the total amount emitted.

V. METHODS OF REDUCING FORMALDEHYDE RELEASE

A number of approaches have been tried to reduce HCHO release. These approaches range from afterwashing the cured fabric to developing non-formaldehyde reactants. The section that follows will review some of the more important developments.

A. Scavengers

Scavengers are defined as materials capable of reacting with monomeric formaldehyde and tying it up. Scavengers are added to the finish formulation and can be grouped into two categories, nitrogenous compounds and alcohols. The two groups control HCHO by different mechanisms. The nitrogenous additives not only react with HCHO to form N-methylols, but also react with the pendent N-methylols to form methylene bridges. Essentially they compete with the cellulose and when enough additive is present to lower HCHO release, cellulose cross links are reduced resulting in lower DP performance. Additional N-H groups are in the fabric further affecting chlorine damage and reduced lightfastness. Effective nitrogenous scavengers are urea, ethylene urea and carbohydrazide.

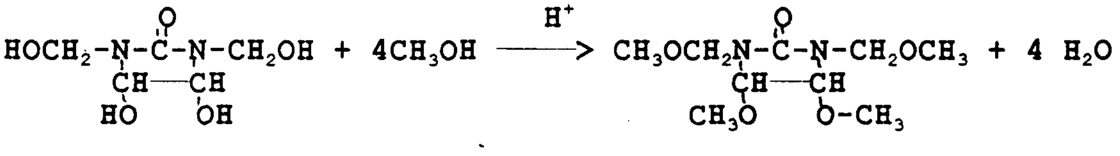
High boiling alcohols also act as scavengers and lower HCHO release. Their mechanism involves capping pendent N-methylol groups. The capped end-groups are more stable than the hydroxymethyl so the equilibrium of the reverse reactions is shifted. These additives also compete with crosslinking so DP ratings are somewhat diminished. Not having N-H groups, however, mitigates against chlorine resistance and lightfastness problems. Effective alcohol scavengers are nitroalcohols, ethylene glycol, diethylene glycol and sorbitol.

B. Modified DMDHEU

Modifying DMDHEU has been the most successful approach for reducing HCHO release. Among the first modified versions were those made from purer starting materials and rigidly controlling the stoichiometry. Later versions led to alkylated DMDHEU and two types have become commercially important products, methylated and glycolated DMDHEU.

1. Methylated DMDHEU

DMDHEU has 4 reactive hydroxyls. The 4,5-ring hydroxyls are as reactive to alkylation as are the pendant N-methylols. Alkylating with methanol can replace anywhere from 1 to 4 -OH groups with -OCH_3. Partially methylated DMDHEU refers to products where an average of two methoxy groups are attached. Fully methylated refers to products where all four have been reacted. To accomplish the latter, the reaction must be driven to completion by removing water of reaction. This involves a distillation step making the fully methylated product more expensive.

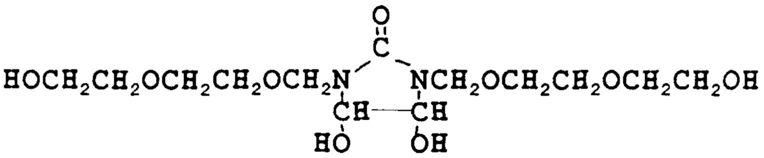


$$HOCH_2-\underset{\underset{HO}{CH}}{N}-\overset{O}{C}-\underset{\underset{OH}{CH}}{N}-CH_2OH + 4CH_3OH \xrightarrow{H^+} CH_3OCH_2\underset{\underset{CH_3O}{CH}}{N}-\overset{O}{C}-\underset{\underset{O-CH_3}{CH}}{N}-CH_2OCH_3 + 4\ H_2O$$

When CH_3- = 4, Product is Fully Methylated
When CH_3- = 2, Product is Partially Methylated

2. Diethyleneglycolated DMDHEU (ULF)

Glycolated DMDHEU is made by reacting 2 moles of diethylene glycol, (DEG), with 1 mole of DMDHEU. It is often referred to as a ***ULF*** (ultra low formaldehyde) reactant. This product evolved from the successful experiences noted when DEG was added to the finish formulation. Precapping before it is applied insures that there are no pendent N-methylol groups so the HCHO release is even lower. The DEG still functions as a leaving group during cure so crosslinking with cellulose is not severely impaired.



C. Important Features of Alkylated DMDHEU

Both fully and partially methylated DMDHEUs are harder to cure than their un-methylated counterpart. Stronger catalyst are needed to cure these products. DP properties of the methylated varieties are not quite as good as their un-methylated counterpart. Lowering of formaldehyde release is accomplished at the expense of DP performance. The ULFs produce fabrics with the lowest formaldehyde release of all. Surprisingly, the DP performance of the ULFs is still as good as the un-alkylated products. Unmodified DMDHEU when properly applied to fabrics will give values in the 750-1000 µg/g range. If the fabric is undercured or if the fabric has an acidic pH (catalyst dependent), the values will be higher. Methylated DMDHEU are better, with the partially methylated ones being 300 to 500 range and the fully methylated at 300 µg/g. DMDHEU modified with diethylene glycol will give fabrics at 50 or below.

Table 12

Formaldehyde Release

Comparison of Modified DMDHEU

	HCHO Release µg/g	DP Ratings
Unmodified DMDHEU	750 - 1000	4
Partially Methylated	300 - 500	3.0
Fully Methylated	< 300	3.0
Glycolated (ULF)	< 50	3.25

NOTE: DP performance is somewhat lower for the low release types: Where 3.5 or higher ratings were once marketplace requirements, acceptable standards have been lowered to 3 in order to meet low formaldehyde release.

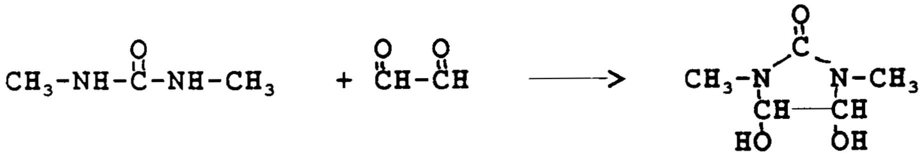
VI. NON-FORMALDEHYDE DP FINISHES

Impending OSHA regulations and several state regulations require that products manufactured with formaldehyde containing components be labeled with a warning label. Even though the use of formaldehyde will not be completely banned, compliance with the safety aspect requires a lot of effort and expense, e.g. work place monitoring and worker medical surveillance. Industry management would prefer to manufacture their products without HCHO rather than put up with the hassle of dealing with the regulations.. Several countries such as Japan and Germany have even more stringent HCHO requirements than the USA. Because of this, there has been and continues to be interest in non-formaldehyde DP finishes. The section that follows describes two products that fit the description "non-formaldehyde" finishes.

A. Dimethyl-4,5, Dihydroxyethylene UREA (DMeDHEU)

DMeEU is the reaction product of dimethyl urea and glyoxal. The -4,5- ring hydroxyls are reactive with cellulose and form the same ether links as do the N-methylol groups. Even though the electronic configuration around the ring hydroxyls are the same as the pendant N-methylol groups, the reaction is much more sluggish because of steric hindrance and therefor require harder cures and more and stronger catalyst. Even with all this, the DP results are not near as good as the more conventional reactants. The product is more expensive; however, the fabric can truthfully be labeled as formaldehyde-free.

1. Synthesis



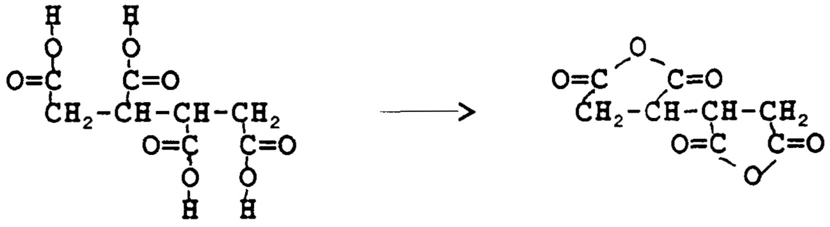
2. Important Features

This product can be absolutely classified as a non-formaldehyde finish. It is much harder to cure and the DP properties are poor. It is more expensive than DMDHEU.

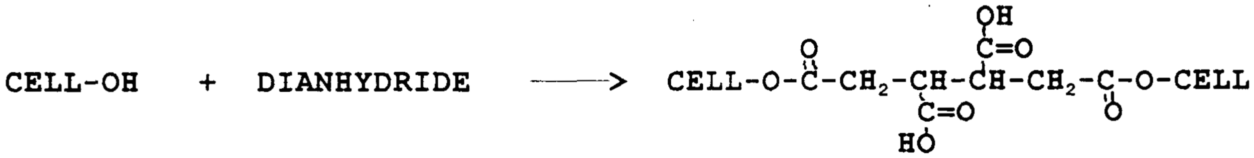
B. Butanetetracarboxylic Acid (BTCA)

BTCA reacts with cellulose hydroxyls to form ester cross-links. The reactions of carboxylic acids with cellulose is rather old knowledge and has been practiced commercially for many years to make a variety of fibers and plastics from wood pulp. Using dibasic acids to cross-link cotton is also old technology. Problems with this in the past were excessive strength loss, poorer DP performance and poor durability to laundering. Recently, workers at USDA's Southern Regional laboratories reported some unexpected and useful DP properties obtained with several specific polycarboxylic acids, BTCA being one of the better ones. They also reported that certain phosphorous based salts were effective catalyst for the reaction. Because this too is classified as non-formaldehyde, there was a great deal of interest in this approach. The exact mechanism of the reaction is not know, nor is it known why the crosslinked product are so much more resistant to hydrolysis than are other cellulose esters. The following rational has been suggested as a possible mechanism.

1.



BTCA BTCA Anhydride



$$\text{CELL-OH} + \text{DIANHYDRIDE} \longrightarrow \text{CELL-O-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-CH}_2\text{-}\underset{\text{HO}}{\underset{|}{\underset{\text{C=O}}{\underset{|}{\text{CH}}}}}\text{-}\overset{\text{OH}}{\overset{|}{\overset{\text{C=O}}{\overset{|}{\text{CH}}}}}\text{-CH}_2\text{-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-O-CELL}$$

1. Catalyst

a. Sodium Hypophosphite

The most effective catalyst for promoting Durable Press properties. DP rating and shrinkage control equivalent to DMDHEU have been obtained. Catalyst is expensive higher than normal amounts are needed. The hypophosphite is a reducing agent. This is beneficial for maintaining white fabrics, however, it discolors certain dyes especially sulfurs.

b. Sodium Phosphate

Not as effective in promoting DP ratings. Requires higher temperature cure. Much less expensive than hypophosphite. Discolors whites at higher temperatures. Does not affect dye shade.

C. Reactive Silicones

Elastomeric, amino functional and epoxy functional silicones will give a modest boost to DP performance. The elastomeric silicones add resiliency to the fabric improving wrinkle recovery. The amino and epoxy functional improve fiber and yarn slippage, reducing the transmission of the wrinkling force to the fiber. Also wrinkles will fall out easier. These products are often included with conventional resins to boost performance.

D. Liquid Ammonia

Ammonia (NH_3) is a liquid at -18^0 C. It will cause cellulosic fibers to swell and bring about some of the changes associated with Mercerizing. As a fabric treatment, it will remove stresses and strains and stabilize the fabric. When done properly, cotton fabrics will have somewhat improved DP ratings and improved residual shrinkage. Although the performance does not rival conventional resin treatment, a process using anhydrous liquid ammonia (Sanforset) has been commercialized for stabilizing Denim fabrics. Smooth drying ratings and reduced residual shrinkage were improved without losses in strength and abrasion resistance. The improvement was not to the level one would expect of durable press but enough to warrant the expense. A variation of this process has also seen commercial usage. Cotton shirting fabric was passed through the liquid ammonia process and then topped with a low level of DMDHEU. The DP performance was higher than if the resin had been used alone. The losses in strength and abrasion were minimized by the low level resin treatment.

The liquid ammonia process involves passing the cotton fabric containing a controlled, low level of moisture into a pad bath of liquid ammonia. The ammoniated fabric is put through a Palmer unit and removing the ammonia while the fabric is pressed flat against the drum. A Palmer unit is a large heated cylinder with an endless rubber belt pressing against it.

VII. DURABLE PRESS CATALYST

The reaction of $N\text{-}CH_2OH$ with cellulose is acid catalyzed. The stronger the acid. the faster the reaction. Selecting the proper catalyst becomes important because acids also damage cellulose fibers. Here too the stronger the acid, the greater the damage. Since some reactants are less reactive than others, there are times when stronger catalysts are needed to achieve proper curing. Maximizing crosslinking while keeping acid hydrolysis to a minimum is tricky. It requires a good understanding of acid/base chemistry and of buffers. With this in mind, a quick review of acids is appropriate. There are three types of compounds that create acidity. 1. Compounds that ionize to liberate protons (hydrogen ions). These are further divides into strong and weak acids, depending on their ionization constant and are called Bronsted acids. 2. Neutral salts of strong acids and weak bases that decompose under certain conditions to liberate protons (latent acids). 3. Metal ion with vacant orbitals capable of accepting a pair of electrons. These are called Lewis acids.

A. Bronsted Acids

Compounds that ionize in water to form protons (H^+) are called Bronsted acids. Strong acids are those that completely ionize, e.g. hydrochloric, sulfuric, and formic, Weak acids are those that partially ionize in water, e.g. acetic, boric and citric acids. The ionization constant of acids can be expressed by the equilibrium shown in the box below. The equilibrium established between the ionized and un-ionized species is a steady source of controlled amounts of hydrogen ions. Strong acids provide an immediate source of protons. The number of protons depend solely on the initial concentration of acid. For weak acids, the hydrogen ion concentration depends not only on the initial concentration of acid, but also on its ionization constant.

a. Ionization Constant

The ionization constant is determined by the expression:

$$HA \longrightarrow H^+ + A^-$$

$$Ki = \frac{[H^+][A^-]}{[HA]}$$

b. Hydrogen Ion Concentration

The hydrogen ion concentration is a function of the ionization constant and 'can be calculated by rearranging the above expression.

$$[H^+] = Ki \frac{[HA]}{[A^-]}$$

Another factor to considered when selecting an acid as a catalyst is its volatility. For example, acetic acid does not function as a catalyst. Citric acid, on the other hand does. The major reason for this is that acetic acid is volatile and will be driven off the fabric before curing temperatures are reached. Citric acid is non-volatile at curing temperatures therefore it stays where it is needed to function as a crosslinking catalyst. Acetic acid's volatility is an asset when it come to adjusting fabric and bath pH, the acid is gone before temperature becomes high enough to damage cellulose fibers.

1. Latent Acids

Neutral salts of weak bases (amines) and strong acids will dissociate under certain conditions to become sources of protons. The ease with which these compounds dissociate is related to the ionization constant (K_b) of the base. The weaker the base, the easier it is to liberate the conjugate acid. Amine hydrochlorides are particularly useful neutral salts that function as latent catalyst in DP finishing. They will dissociate to liberate hydrochloric acid under curing conditions. Ammonium salts also function as latent catalyst. Ammonium chloride, ammonium sulfate, ammonium phosphate are sources of ammonium ions in water. Under certain conditions, the ammonium ion will dissociate into ammonia and a proton. Under curing condition, some of the ammonia is lost into the atmosphere and the system become acidic. Another mechanism involved with ammonium salts becoming acidic is their ability to react with formaldehyde to form trimethyl amine hydrochloride and formic acid. The reaction intermediate in this transition is methyleneimine hydrochloride. Both the methyleneimine and trimethylamine are weak bases so the dissociation of their respective hydrochlorides occurs easily. The reaction with formaldehyde can be followed with a pH meter. Solutions of ammonium chloride are neutral and remain so even after boiling for several hours. However if formaldehyde is present, the pH will begin to drop. With time the solution becomes highly acidic. The reactions schemes are shown in the box below.

a. Dissociation & Amine Hydrochlorides

$$R\text{-}NH^+_3Cl^- \longrightarrow R\text{-}NH_2 + HCl$$

b. Dissociation of Ammonium Chloride

$$NH_4Cl \xrightarrow{H_2O} NH_4^+ + Cl^- \longrightarrow NH_3 + H^+$$

c. Reaction of Ammonia with Formaldehyde

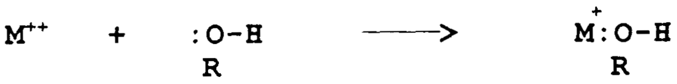
$$NH_4Cl + CH_2O \longrightarrow HOCH_2NH_2 \cdot HCl \longrightarrow HOCH_2NH_2 + HCl$$

$$HOCH_2NH_2 \cdot HCl + CH_2O \longrightarrow CH_3NH_2 \cdot HCl + HCOOH$$

B. Lewis Acids

Metal ions that have unfilled orbitals capable of accepting a pair of electrons function as Lewis acids. Mg^{++}, Zn^{++}, Al^{+++} and Fe^{+++} are examples of metal ions that can function as Lewis acids. True Lewis acid maintain a neutral pH when in solution, however, some metal ions form soluble hydrates with water. When these hydrates polymerize to form an insoluble oxide, they leave protons behind (Bronsted acid). For example, when aluminum chloride is dissolved in water, the solution will develop a measurable acidity on standing. This comes about because aluminum ions form partial covalent bonds with water to form aluminum hydroxide. At this point all of the ionic species are in equilibrium so the solution's pH is neutral. Aluminum hydroxide, in time, will precipitate as aluminum oxide. When this happens, the neutral balance of all the ionic species is disrupted because the hydroxyl ions supplied by the water molecules have been consumed, leaving behind their corresponding protons.

1. True Lewis Acids



$$M^{++} \quad + \quad :\underset{R}{O}-H \quad \longrightarrow \quad \overset{+}{M}:\underset{R}{O}-H$$

2. Metal Hydrates

$$AlCl_3 \longrightarrow Al^{+++} + 3\ Cl^-$$

$$Al^{+++} + 3\ H_2O \longrightarrow Al(OH)_3 + 3\ H^+$$

$$2\ Al(OH)_3 \longrightarrow Al_2O_3\downarrow + 3\ H_2O + 3\ H^+$$

3. Important Considerations

Solutions of magnesium chloride do not develop measurable acidity on standing. Magnesium chloride therefore acts like a classical Lewis acid. The reason for this is that magnesium does not form partial covalent bonds with hydroxyl ions unless the pH is very high. Aluminum, ferric and chromic salts are the most acidic. They are much stronger catalyst and are prone to degrade cellulose as well. Zinc salts are in between aluminum and magnesium. Zinc salts are good curing catalyst. Unfortunately the discharge of Zn in waste water is frowned upon. Magnesium is considered the mildest of the effective Lewis acids.

C. Specific Catalyst and their Use

1. Free Acids

Mineral acids, citric, tartaric are used when faster cures are wanted. They are also effective on hard to cure reactants or when curing at lower temperature. Disadvantages are reduced bath stability, damage to the fiber and increased formaldehyde release.

2. Latent Acids

Ammonium chloride, amine hydrochloride are used to cure U / F and M/F resins when fast, low temperature curing is wanted. Disadvantages are fabric pH is acidic. Ammonium salts give rise to trimethyl amine, fish odor.

3. Metal Salts

Magnesium chloride is a mild catalyst that can be used at high temperatures. It is non-corrosive and presents the fewest side reaction problems, e.g. shade change, fiber damage etc. Zinc nitrate and zinc chloride are more reactive than magnesium chloride. Zinc presents effluent disposal problems. Zinc nitrate cause dye shade changes.

4. Hot Catalyst

Usually a mixture of magnesium chloride and a source of proton such as citric acid, aluminum chloride, aluminum sulfate or ammonium chloride. These are used when stronger catalyst are needed.

D. Buffers and Alkalinity

1. Buffers

Buffers are salts of weak acids or bases that maintains a solution's pH at a constant level. Spurious amounts of H^+ or OH^- ions are neutralized, and a constant level of each is maintained by the equilibrium established by ionization constants of the buffering agents. The net effect is that buffers will neutralize equivalent amounts of catalyst. Some commercial DMDHEU solutions will have buffers added to them. This is done to overcome certain problems that may exist on specific fabrics i.e. shade changes, poor lightfastness, yellowing etc. When buffered resins are used in place of unbuffered resins, the catalyst ratio must be increased to compensate for the amount that will be consumed by the buffer.

2. Alkalinity

Alkalinity is defined as salts that consume acids. They are the salts formed when a strong base is neutralized by a weak acid e.g sodium acetate. Fabric preparation is a source of problems associated with alkalinity. Mercerized, causticized and caustic scoured fabrics are neutralized with acetic acid to control the final fabric pH. If the amount of NaOH left on the cloth varies when it reaches the acetic acid bath, the amount of sodium acetate formed by the neutralization reaction will also vary even though the fabric pH appears to be consistant. Alkalinity and buffers consume acid catalyst, therefore both must be consistently controlled to give consistently performing finished fabric. Fabric alkalinity can be determined analytically. If this value is inconsistent throughout the fabric, one can expect inconsistent performance of the finish.

VIII. CHEMICAL MECHANISMS

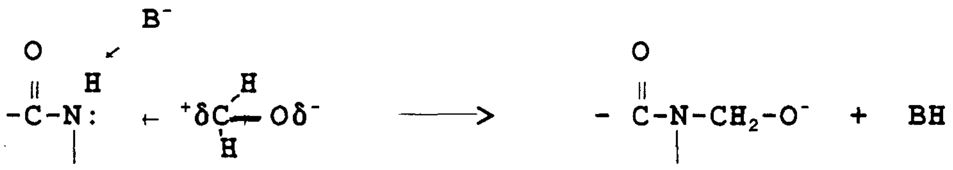
The chemistry associated with durable press finishing can be broken into three separate steps. 1. Reaction of amido compounds with HCHO to form N-methylol compounds. 2. Alkylation of N-methylol compounds. 3. Stability of the alkylated linkage. One can considers the cellulose crosslink to be identical in nature to the lower alcohol alkylates. The performance of the various products that make up this family of finishes can be summarized and explained by examining the underlying reaction mechanisms. This section is devoted to understanding the mechanisms.

A. Methylolation

The reaction of amido compounds with HCHO can be catalyzed with acids or base. When base is used, the reaction terminates at the N-CH_2OH, however, with acids the reaction can continue and form crosslinked polymers reducing the usefulness of the reactant.

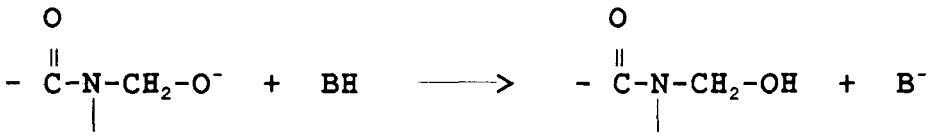
1. Base Catalyzed Methylolation

1.



$$-\overset{O}{\overset{\|}{C}}-\underset{|}{\overset{H}{N}}:\ \overset{B^-}{\swarrow}\ \leftarrow {}^{+\delta}\underset{H}{\overset{H}{C}} \leftarrow O^{\delta-} \longrightarrow -\overset{O}{\overset{\|}{C}}-\underset{|}{N}-CH_2-O^- + BH$$

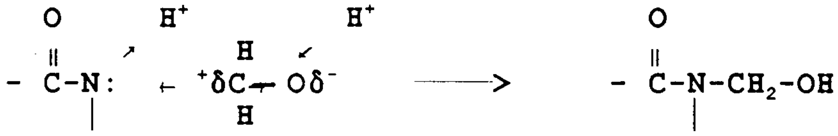
2.



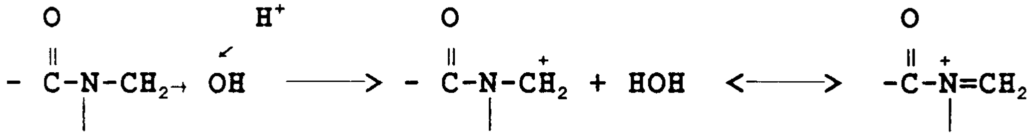
$$-\overset{O}{\overset{\|}{C}}-\underset{|}{N}-CH_2-O^- + BH \longrightarrow -\overset{O}{\overset{\|}{C}}-\underset{|}{N}-CH_2-OH + B^-$$

Equation 1 shows the base catalyst attacking the N-H group as the carbonyl group in HCHO approaches the unshared electrons on the nitrogen atom. In equation 2, the transition state abstracts a hydrogen from the BH group regenerating the base ion. In so doing, the formation of the N-methylol is completed. The only other reactions going on are the equilibriums involved in each phase.

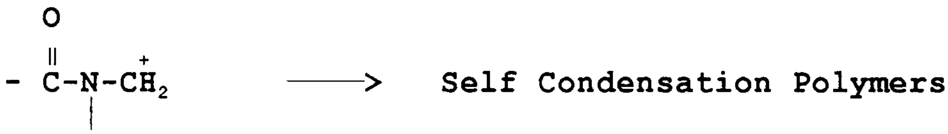
2. Acid Catalyzed Methylolation

1. 

$$-\overset{\overset{O}{\|}}{C}-\underset{|}{N}:\ \overset{H^{+}\nearrow}{\leftarrow}\ {}^{+}\delta\overset{H}{\underset{H}{C}}\rightarrow O\delta^{-}\overset{H^{+}\swarrow}{} \longrightarrow -\overset{\overset{O}{\|}}{C}-\underset{|}{N}-CH_2-OH$$

2. 

$$-\overset{\overset{O}{\|}}{C}-\underset{|}{N}-CH_2\rightarrow \overset{H^{+}\swarrow}{OH} \longrightarrow -\overset{\overset{O}{\|}}{C}-\underset{|}{N}-\overset{+}{C}H_2 + HOH \longleftrightarrow -\overset{\overset{O}{\|}}{C}-\underset{|}{\overset{+}{N}}=CH_2$$

3. 

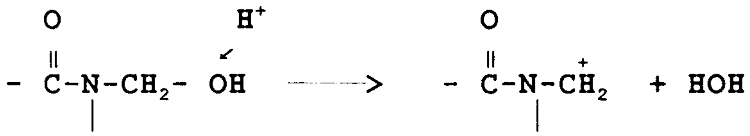
$$-\overset{\overset{O}{\|}}{C}-\underset{|}{N}-\overset{+}{C}H_2 \longrightarrow \text{Self Condensation Polymers}$$

Equation 1 shows the catalyst protonating the carbonyl oxygen in HCHO. As the protonated molecule approaches nitrogen's unshared electrons, the N-H bond breaks, regenerating a proton. This completes the formation of the N-methylol group. Equation 2 shows that protons can initiate a second reaction. A molecule of water is split off creating a carbo-cation which is stabilized by resonance structures shown in the transition equilibrium. Equation 3 indicates that the carbo-cation is capable of undergoing self condensation and creates polymers linked by methylene bridges.

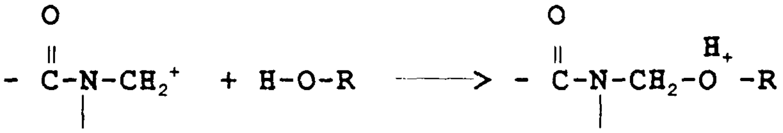
B. Alkylation of N-Methylol Compounds

The alkylation reactions of N-methylol compounds are continuations of the reactions described in the acid catalyzed methylolation mechanism. The carbo-cation is capable of reacting with alcohols as well as self-condensing with N-H groups. When the alcohols are lower alcohols such as methanol or diethylene glycol, alkoxylated modified reactants are created. If the alcohol is a cellulose hydroxyl, cross links are formed. Both protons and Lewis acids promote the reaction.

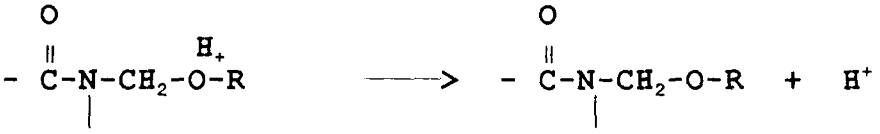
1. Proton Activated Alkylation

1. 

$$-\overset{\overset{O}{\|}}{C}-\underset{|}{N}-CH_2-\overset{H^{+}\swarrow}{OH} \longrightarrow -\overset{\overset{O}{\|}}{C}-\underset{|}{N}-\overset{+}{C}H_2 + HOH$$

2.


$$-\overset{\overset{O}{\|}}{C}-\underset{|}{N}-CH_2^+ + H-O-R \longrightarrow -\overset{\overset{O}{\|}}{C}-\underset{|}{N}-CH_2-\overset{H_+}{O}-R$$

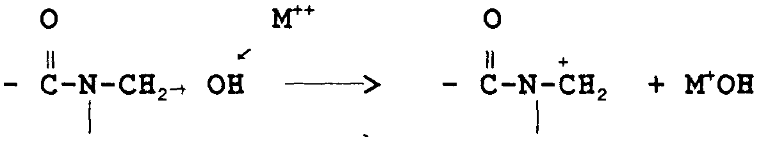
3.


$$-\overset{\overset{O}{\|}}{C}-\underset{|}{N}-CH_2-\overset{H_+}{O}-R \longrightarrow -\overset{\overset{O}{\|}}{C}-\underset{|}{N}-CH_2-O-R + H^+$$

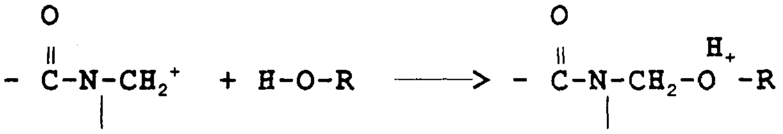
In equation 1, the -OH group on the N-methylol is protonated to form the transition state which splits water to become a carbo-cation. Equation 2 shows the carbo-cation attacking a R-OH group to form a transition state In equation 3, a proton is ejected and the alkylated reaction product is formed. The original amount of acid is still present at the end of the reaction. This acidity is responsible for side reactions, e.g. tendering the fiber and promoting hydrolysis of the cross-link.

Lewis acids can also promote alkylation, however, higher temperatures needed to drive the reaction. For this reason, these catalyst are only used for crosslinking cellulose. There is one other difference that should be noted. The Lewis acids are neutral to start with and leave the fabric neutral after the reaction is completed. This minimized side reactions such as fiber tendering and hydrolysis of the crosslink, making them the preferred catalyst for DP finishes.

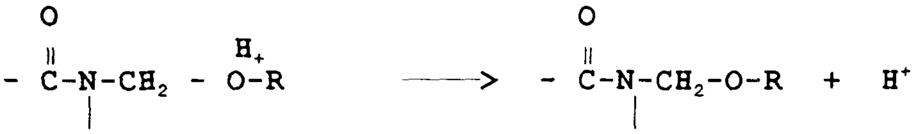
2. Cellulose Crosslinking with Lewis Acids

1.


$$-\overset{\overset{O}{\|}}{C}-\underset{|}{N}-CH_2\rightarrow \overset{M^{++}}{OH} \longrightarrow -\overset{\overset{O}{\|}}{C}-\underset{|}{N}-\overset{+}{CH_2} + M^+OH$$

2.


$$-\overset{\overset{O}{\|}}{C}-\underset{|}{N}-CH_2^+ + H-O-R \longrightarrow -\overset{\overset{O}{\|}}{C}-\underset{|}{N}-CH_2-\overset{H_+}{O}-R$$

3.


$$-\overset{\overset{O}{\|}}{C}-\underset{|}{N}-CH_2-\overset{H_+}{O}-R \longrightarrow -\overset{\overset{O}{\|}}{C}-\underset{|}{N}-CH_2-O-R + H^+$$

4. $M^+OH + H^+ \longrightarrow M^{++} + H_2O$

Equation 1 shows formation of a transition state metal complex where the metal ion attaches to the pair of electrons on the oxygen atom of the -OH group splitting out metal hydroxide and forming the carbo-cation. In equations 2 and 3, the reaction follows the same path as was postulated for proton catalysis. Equation 3 shows a proton being liberated from the crosslinking reaction. This proton is now available to function as an active catalyst in a manner identical to the mechanism depicted for proton catalysis. Both Lewis acid and protons are available to catalyze crosslinking. The activity of the proton is moderated (buffered) by neutralization with the metal hydroxide that was formed in equation 1. The stoichiometry is such that one equivalent of base is formed for each proton so the fabric should remain neutral after curing. Since it takes elevated temperatures to activate Lewis acid catalysis, nothing really happens until curing conditions are reached. When the fabric cools down, the remaining protons are neutralized and the fabric pH remains neutral, minimizing any side reactions.

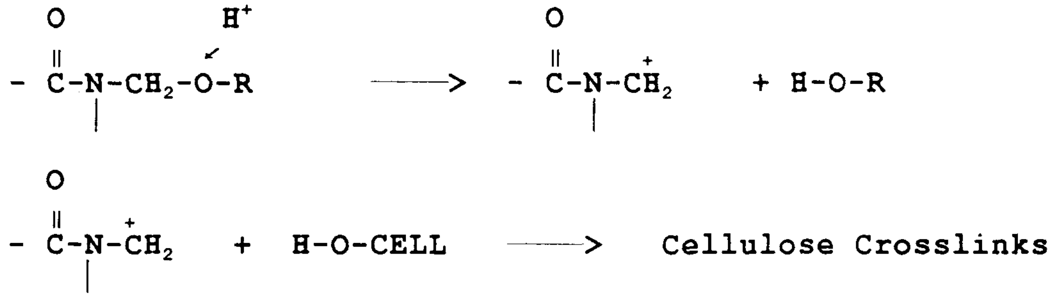
From the mechanisms shown, it is readily apparent why most finishers prefer to use Lewis acid catalysts. Magnesium chloride has become the preferred catalyst for the following reasons: 1. Alone, magnesium chloride is the least damaging to cotton. It does not affect fabric strength as much as other catalysts. 2. It does not affect dye shade or lightfastness of direct and fiber reactive dyes. 3. It is not a particularly active catalyst and may have to be supplemented with additional time or temperature of cure. 4. It can be made more active by blending in a small amount of a "hot catalyst". Citric acid, ammonium chloride and aluminum salts are added to magnesium chloride to make a class called ***"Hot Mug Chloride".***

C. Reaction of Alkoxylated Products

Alkoxylated derivatives of N-methylol compounds can be viewed either as those derived from the lower alcohols or the cellulose crosslink itself. Both alkoxylates are capable of undergoing acid catalyzed reactions. For the lower alcohols, the reactions are similar to the N-methylol and lead to the same cellulose crosslinks. The value of using the lower alcohol alkoxylates is textile fabrics with lower HCHO release. For the crosslink, the reactions lead to de-crosslinking and loss of DP properties. The latter is responsible for laundry durability and is referred to as hydrolysis stability. The crosslinks eventually revert back to the original starting materials.

Not all alkoxy groups have the same rate of reaction. For example isopropyl groups are good leaving groups so the rate of reaction of isopropoxy N-methylol are very close to that of the hydroxymethyl. On the other hand, methyl and diethylene glycol are poor leaving groups meaning that they are more stable. Because of this, they require more stringent curing conditions, e.g. stronger catalyst /higher temperature cures. Also because they are more stable, the pendent groups remaining after cure are less prone to decompose back and contribute to HCHO release.

1. Crosslinking with Alkoxykated N-Methylol Compounds



1. $$-\overset{O}{\overset{\|}{C}}-\underset{|}{N}-CH_2-\overset{H^+\swarrow}{O}-R \longrightarrow -\overset{O}{\overset{\|}{C}}-\underset{|}{N}-\overset{+}{C}H_2 + H-O-R$$

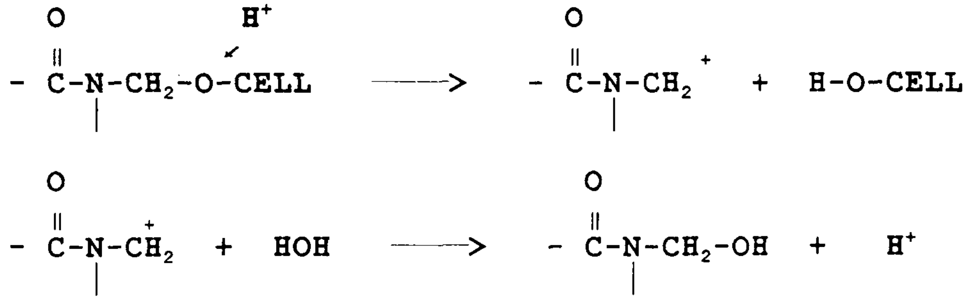
2. $$-\overset{O}{\overset{\|}{C}}-\underset{|}{N}-\overset{+}{C}H_2 + H-O-CELL \longrightarrow \text{Cellulose Crosslinks}$$

Equation 1 shows catalyst complexing with the oxygen atom, splitting off alcohol to form a carbo-cation. Since this is done under the influence of temperature, the lower alcohol is volatilized favoring the formation of the carbo-cation. In equation 2, the carbo-cation partakes of the reactions leading to cellulose linkages. The rate of reaction is influenced by the alcohol leaving group. Methyl and diethylene glycol are poor leaving groups requiring stronger catalyst and curing conditions. Because of this, pendant groups that have not entered into a cellulose crosslink are more stable and therefore less prone to contribute to HCHO release.

D. Stability of Crosslink to Laundering

The stability of the crosslinks to repeated laundering can also be considered a manifestation of alkoxy reactivity. In this case the alkoxy linkage is hydrolyzed with water. the hydrolysis reaction proceeds much faster under acidic conditions and at higher laundry temperatures. These conditions are met when goods are laundered under commercial laundry procedures. Another factor to consider is the chemical nature of the reactant. Carbamates and DMDHEU crosslinks are much more durable than DMEU and U/F crosslinks. The ability/inability of the structure to delocalize the electrons on the amido nitrogen influences this relationship. As is seen below, after the cellulose linkage is broken, the reaction can continue in the reverse direction eventually reverting back to starting materials.

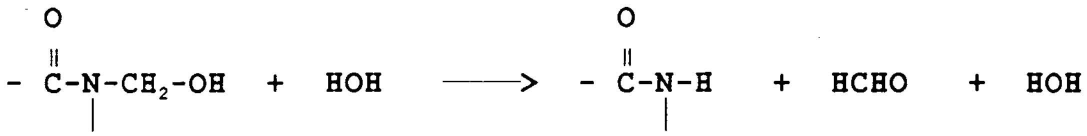
1. Hydrolysis of Cellulose Crosslinks



1. $$-\overset{O}{\overset{\|}{C}}-\underset{|}{N}-CH_2-\overset{H^+\swarrow}{O}-CELL \longrightarrow -\overset{O}{\overset{\|}{C}}-\underset{|}{N}-CH_2^{\,+} + H-O-CELL$$

2. $$-\overset{O}{\overset{\|}{C}}-\underset{|}{N}-\overset{+}{C}H_2 + HOH \longrightarrow -\overset{O}{\overset{\|}{C}}-\underset{|}{N}-CH_2-OH + H^+$$

3.



$$-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{|}{N}-CH_2-OH + HOH \longrightarrow -\overset{\overset{\displaystyle O}{\|}}{C}-\underset{|}{N}-H + HCHO + HOH$$

IX. FABRIC PROPERTIES

Changes in fabric properties are related to the number of crosslinks imparted to the fiber. Improvements in wrinkle recovery and DP ratings, and reduction in residual shrinkage are proportional to the number of crosslinks. Losses in strength and abrasion resistance are also related to the number of crosslinks and to the degree of cellulose damage by the acid catalyst. The number of cross-links is influenced by the add-on, (the amount of reagent deposited on the fabric) and the degree of curing (percentage of the amount applied that become actual cross-links). The degree of curing is influenced by the chemical structure of the reagent, the type of catalyst, the ratio of catalyst to resin, the presence of buffers and the time and temperature of cure.

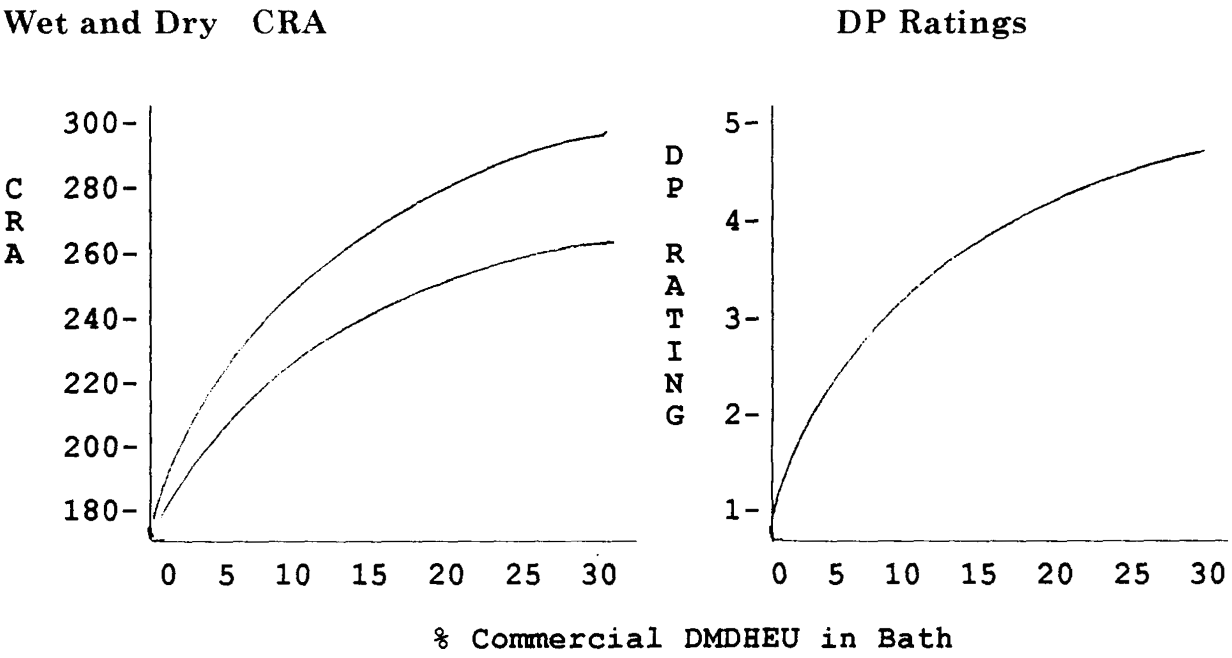
A. Durable Press Performance versus Add-on

The most obvious way to increase DP performance is to add more finish to the fabric. The relationships between fabric performance and add-on of DMDHEU can be seen in figures 46. Figure 46 shows that both wet and dry wrinkle recovery improve with increasing concentration of reagent in the bath. Also shown is the relationship between DP rating (fabric smoothness) and add-on.

1. Important Points

There is a sharp increase in wrinkle recovery with increasing resin level. As bath concentration approaches 7 % DMDHEU (15-20 % commercial product in bath), wrinkle recovery and DP Rating begin to levels-off. Above this level, the rate of improvement is less rapid and only modest gains are obtained with massive amounts of resin.

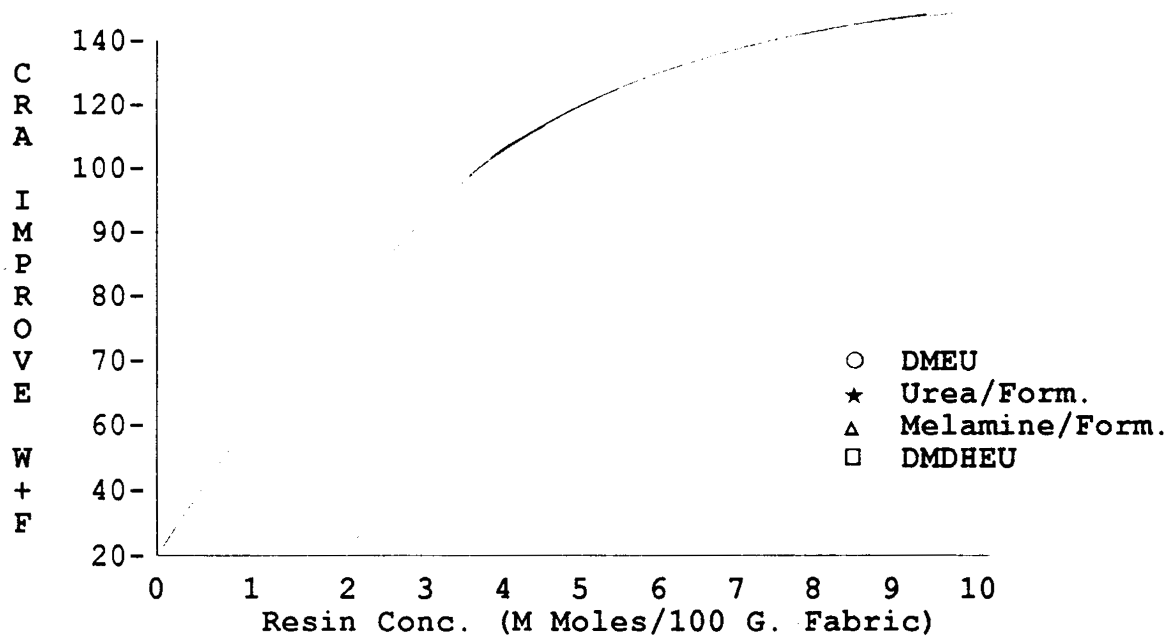
Figure 15. Relationship of DP Performance versus DMDHEU Add-on



B. Effectiveness of Different Crosslinkers

How many cross-links does it take to obtain optimum performance? Are some cross-linkers more effective than others? The answer to these questions can be seen in figure 47. Figure 47 is a composite chart where wrinkle recovery is plotted against the concentration (expressed as millimoles of reagent per 100 grams of fabric) of a number of different reagents. It is interesting to note that one curve fits all the data points. Wrinkle recover levels-off at 2 to 2.5 millimoles of reagent. While DMDHEU was not included in figure 16, 6 to 7% weight add-on calculates to be 2 to 2.5 millimoles per 100 grams of fabric and so it too follows the same general trends.

Figure 16. Crease Recovery versus Resin Concentration

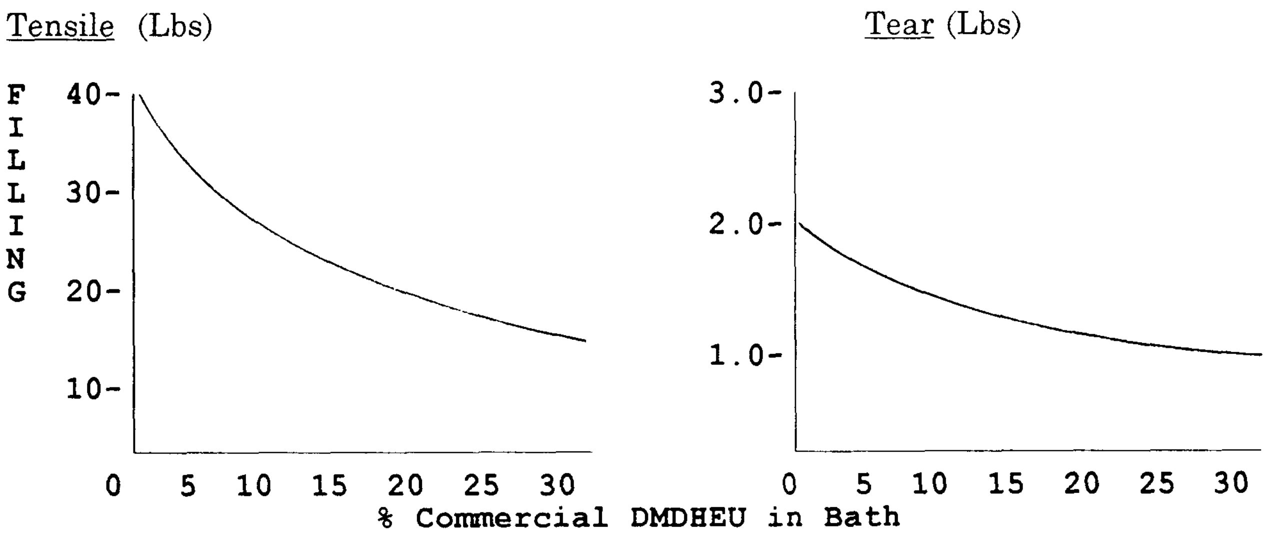


C. Tensile, Tear and Abrasion Resistance

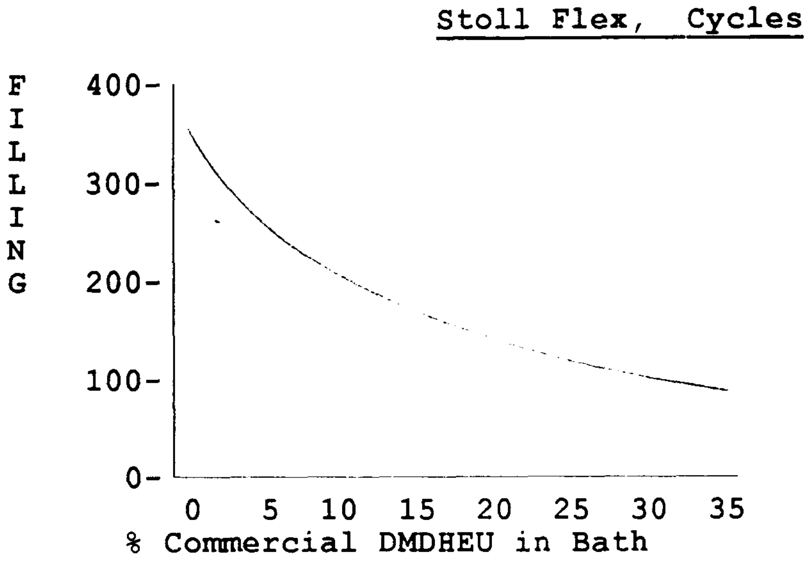
Losses in tensile, tear and abrasion resistance in 100% cotton are directly related to the number of cross-links, The relationship between abrasion resistance, tensile and tear strength versus resin add-on is seen in figure 48. The trends established in these curves mirror those seen in figures 46 and 47, except these are going the opposite direction. The steep part of each curve appears to level off at 15 % commercial DMDHEU (7 % bath solids) in the bath. Improved DP properties also tend to level off at this concentration. Strength and abrasion resistance losses will amount to between 30 to 60 % of the original fabric values.

Figure 17. Physical Properties versus Add-On

Fabric Strength



Abrasion Resistance



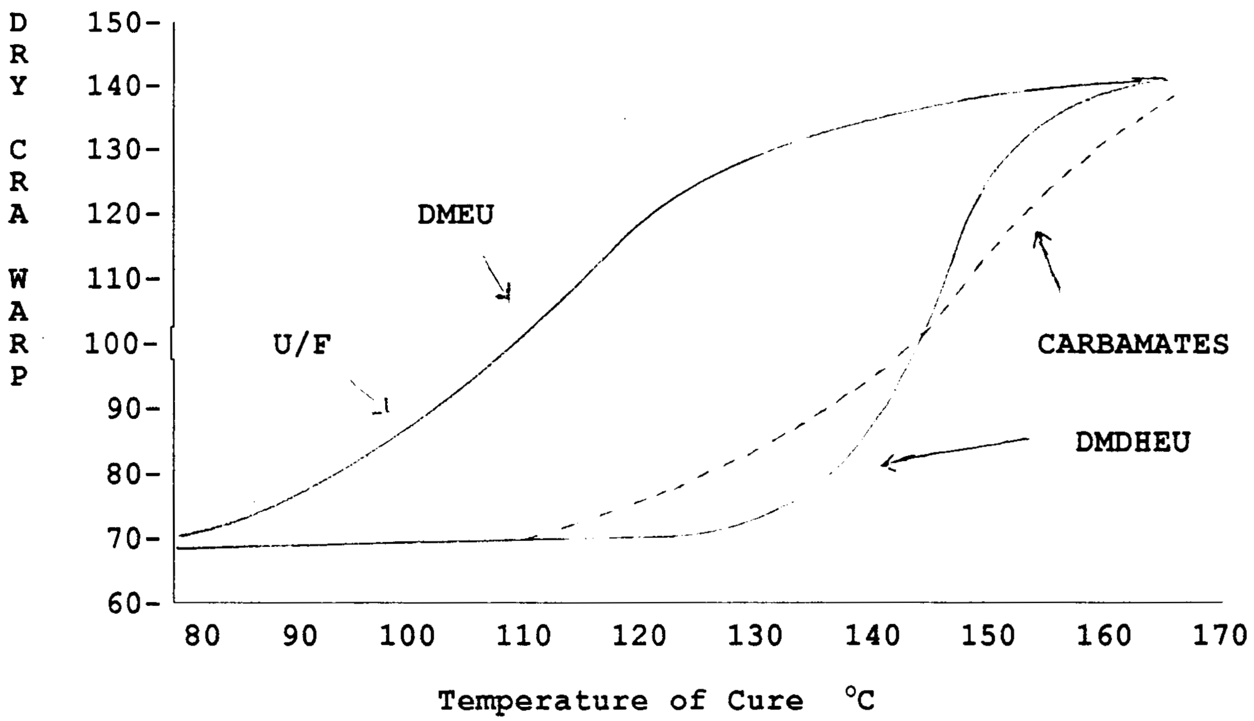
1. Points to Consider

1. Losses in physical properties due to rigidification of the fiber are unavoidable. Losses in strength due to cross-links can be recovered by a mild acid strip. Boiling for one hour in 1% phosphoric acid buffered with urea will remove almost all cross-links and restore about 70% of the lost strength. 2. Catalyst damage also lead to losses in physical properties. That portion of the loss not recovered by the acid strip was the damage of the cellulose backbone by the catalyst. Ways to minimize this damage is to avoid overly strong catalyst and to avoid over curing. 3. Tensile strength is directly proportional to fiber damage. Tearing strength. however, is affected by fiber damage and fabric stiffness. Stiff fabrics tear more easily than softer ones even if the fiber strength is not lowered. 4. From a practical point of view, the exact formulation and application conditions are determined by trial and error, first at a laboratory scale and finally under production conditions. 5. Commercially functional 100% cotton fabrics with improved DP performance can be produced by carefully balancing all of the variables. 6. In those cases where the finished fabric is too weak to function in its intended end-use, serviceable fabrics can still be made by re-engineering the greige fabric with the loss in physical properties in mind. This might include over-constructing the 100% cotton fabric or to blend in yarn strengthening fibers such as polyester or nylon.

D. Crease Recovery versus Curing Temperature

The relationship between crease recovery and temperature of cure is shown in figure 49. The temperature required to obtain cross-linking is very much a function of the reactant structure. The reactant structures included in figure 18 fall into two groups, easy to cure and hard to cure. U/F and DMEU fall into the easy to cure category. Curing starts as soon as the fabric is dry. These reagents would not be suitable for delay cure where one needs the resin to remain unreacted until after the garment is made and pressed. DMDHEU and carbamates fall in the hard to cure category where curing temperatures must exceed 130^0 C. DMDHEU has been successfully used in delay cure applications. The fabric can be handled on commercial ranges where nearly all of the resin is still uncured after drying.

Figure 18. Crease Recovery versus Temperature of Cure and Resin Type



1. Points to Consider

1. DMEU and U/F will begin curing as soon as the fabric is dry. Longer exposure time to lower curing temperatures will eventually increase the total amount of crosslinks. 2. DHEU and Carbamates, however, require fabric temperatures to reach 13 to 150° C. before crosslinking takes place. Longer times below this threshold temperature will not induce crosslinking. 3. Some commercial processes are run at what might appear to be unrealistically high curing temperatures, about 420° F. These processes are run at very high linear speeds. Since drying and curing are accomplished at the same temperature setting, the actual fabric temperature does not reach the air temperature until all the water is gone. It is unlikely that the fabric temperature ever reaches the oven setting because of the short residence time. This technique is called *Flash Curing*. There is danger of overcuring should the range slow down or stop for any reason.

E. Other Fabric Properties

1. Shrinkage

Much of a fabric's residual shrinkage is the result of tensions applied to the fabric during wet processing. Some woven fabrics will shrink both in width and length during preparation and dyeing. These must be pulled out to maintain width and yardage yields. These stresses add to residual shrinkage. Knit goods are inherently wrinkle resistant; however, some are pulled out to a width wider than the fabric's knitted gauge and this too adds to residual shrinkage. Much of the stress induced shrinkage can be eliminated by mechanically compacting the fabric. Compacting will result in reduced yardage yields. Crosslinking also reduces fabric shrinkage. For this reason, chemical stabilization of cellulosic fabric has real economic value. Without resin finishes, the fabrics described here will have excessively high residual shrinkage. Fortunately, a good resin finish will stabilize the fabric and reduce the residual shrinkage to less than 2%. The degree of stabilization required by chemical finishes will depend on the fabric's previous history. In some cases, much more finish is applied than one would reasonably consider simply to keep residual shrinkage within the required tolerances. In these cases, reduced shrinkage is the real reason for DP finishes rather than wrinkle resistance or no-iron features.

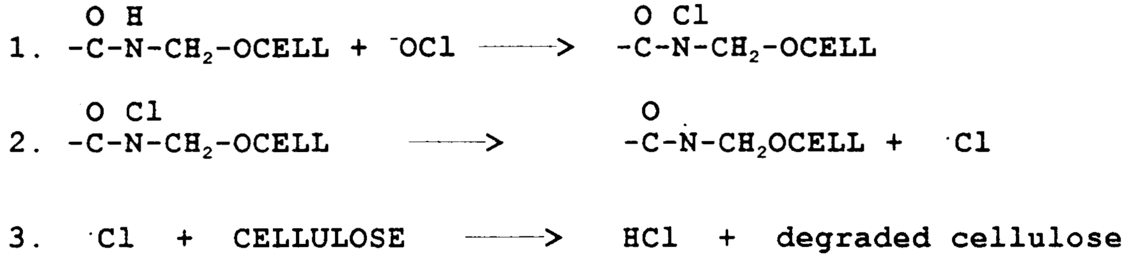
2. Yellowing

Yellowing of DP finished fabrics can be caused by a number of conditions. For example, excessive curing temperatures and /or excessive catalyst will scorch cellulosic fabrics. Some reactants have color bodies that cause yellowing. Usually nitrogenous compounds discolor with heat. Buffers are often added to commercial finishes to combat yellowing problems.

3. Chlorine Resistance

The term chlorine resistance encompasses two problems, yellowing of fabric by the bleach and tendering (strength loss). Nitrogenous finishes will react with hypochlorite bleaches to form a reaction product (chloramides) that decomposes with heat. These chloramides liberate hydrochloric acid which degrade cellulose. Fabric develops the characteristic scorched look and the fibers become very weak. Residual -NH groups are responsible for the formation of chloramides. Resins and reactants with residual -NH groups and cross-links that hydrolyze in laundering are especially prone to pick-up chlorine from a bleach bath. Both tendering and scorching are caused by the breakdown of the chloramide with heat to form hydrochloric acid. The reactions can be written as follows:

a. Mechanism of Chlorine Damage



1. $-\overset{O}{C}-\overset{H}{N}-CH_2-OCELL + {}^{-}OCl \longrightarrow -\overset{O}{C}-\overset{Cl}{N}-CH_2-OCELL$

2. $-\overset{O}{C}-\overset{Cl}{N}-CH_2-OCELL \longrightarrow -\overset{O}{C}-\dot{N}-CH_2OCELL + \cdot Cl$

3. $\cdot Cl + CELLULOSE \longrightarrow HCl +$ degraded cellulose

4. Fabric Odor

Finished fabrics are beset by two types of odors, fish odor and formaldehyde odors. Some overcured fabrics develop an unpleasant burnt or fish odor. Fish odor is trimethyl amine which is produced by the reaction of free formaldehyde with ammonia. Overcuring causes urea based chemicals to break down into ammonia and carbon dioxide so this is one source of ammonia. NH_4Cl is a popular catalyst and is also a source of ammonia. The reactions that take place are believed to be:

$$NH_3 + 6\ CH_2O \longrightarrow (CH_3)_3N + 3\ HCOOH$$

While trimethyl amine is a volatile gas, its formate salt is not. It will be trapped in the fabric and dissociate very slowly with time and humidity. Oftentimes, consumer products (drapes, comforters etc.) are shipped in sealed plastic bags. When these are first opened, a mal-odor emanates from the cloth. With time, in the open, the odor will disappear. The mal-odor is a combination of trimethyl amine and formaldehyde. Formaldehyde causes eyes to water and nasal irritation.

A simple way of checking for fish odor is to place several drops of a sodium carbonate solution on the fabric, wad it up in your hands and rub it vigorously. Any amine odor will easily be detected by smell. Scouring the fabric with alkali will permanently remove this type of odor.

X. REFERENCES

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 uses 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 hand builders. 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 padders. 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 cellulosics 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 radials 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 quantaties: 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 ($-OSO_3^-$) or a phosphate group ($-PO_4^-$). 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 addititon of H_2SO_4 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.

$$R\text{-}OH + HOSO_3H \longrightarrow R\text{-}O\text{-}SO_3H + H_2O$$

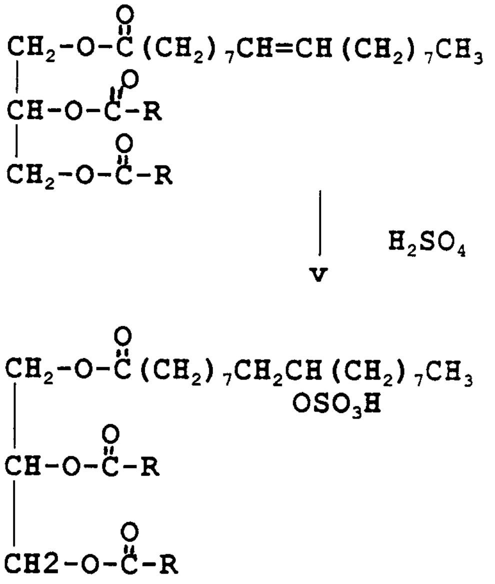
Typical products are sulfated fatty alcohols and sulfated ethoxylated fatty alcohols.

b. Sulfated Fatty Acid Esters

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

$$-CH{=}CH- + HOSO_3H \longrightarrow -CH_2-CH-OSO_3H$$

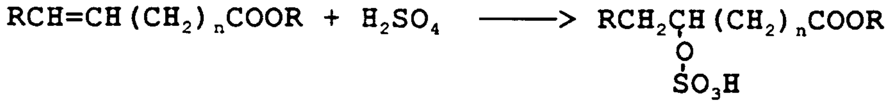
Sulfated Triglycerides. Source of fat will determine the degree of sulfation. The higher the degree of unsaturation, the greater the potential for sulfation. The hydrophilic character of the fat will depend on the number of sulfate attached to the triglyceride. Products ranging from slightly water soluble 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.



Where R= other unsaturated fatty acids

Turkey Red Oil is sulfated castor oil. Ricinoleic acid, the major acid in castor oil has both a hydroxyl group at the C_{12} position and a C=C at the C_9 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.



$$RCH{=}CH(CH_2)_nCOOR + H_2SO_4 \longrightarrow RCH_2\underset{\substack{O\\SO_3H}}{CH}(CH_2)_nCOOR$$

2. Sulfonated Fatty Amides and Esters

Sulfonates differ from sulfates. A sulfonate ($-CH_2-SO_3H$) has the sulfur atom attached directly to the carbon atom whereas the sulfate ($-CH_2-O-SO_3H$) 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 (IGEPON A)

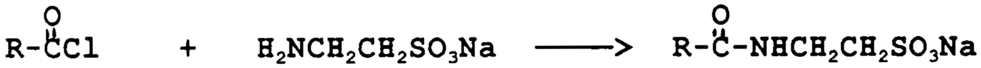
This line of surfactants is made by reacting fatty acids with sodium isethionate to yield a sulfo-ethyl ester of the acid. Isethionic acid is made by reacting ethylene oxide with sodium bisulfite, both inexpensive chemicals.

$$R-COOH + HOCH_2CH_2SO_3Na \longrightarrow R-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2SO_3Na$$

isothionate sulfoethyl ester

b. Sulfoethyl Fatty Amides (IGEPON

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.



$$R-\overset{O}{\overset{\|}{C}}Cl + H_2NCH_2CH_2SO_3Na \longrightarrow R-\overset{O}{\overset{\|}{C}}-NHCH_2CH_2SO_3Na$$

fatty acid chloride taurine fatty acid taurate

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.

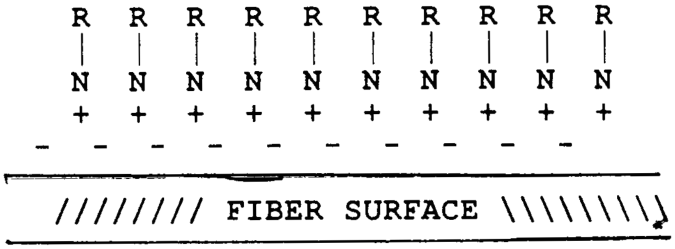
b. Disadvantages

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

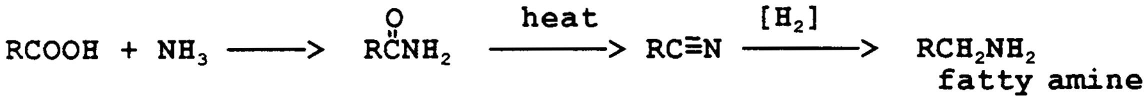


1. Amine Functional Cationic Softeners

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 protion 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



$$RCOOH + NH_3 \longrightarrow R\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow{\text{heat}} RC{\equiv}N \xrightarrow{[H_2]} \underset{\text{fatty amine}}{RCH_2NH_2}$$

b. Difatty Amines

$$RCH_2NH_2 \xrightarrow[250° \text{ C}]{\text{copper chromite}} \underset{\text{difatty amine}}{(RCH_2)_2NH} + NH_3$$

c. Fatty Diamines

$$R\text{-}NH_2 + CH_2{=}CHC{\equiv}N \longrightarrow R\text{-}NH\text{-}CH_2CH_2C{\equiv}N \xrightarrow{[H]} R\text{-}NH\text{-}CH_2CH_2CH_2NH_2$$

d. Cationic Amine Salts

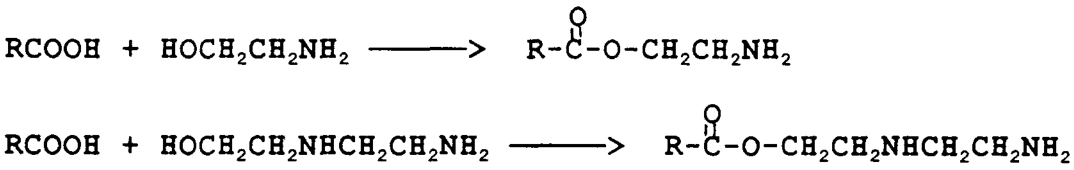
Fatty amines derived from tallow fatty acids are called tallow or di-tallow amines, those made from coconut acids would be called coco amines or di-coco amines. Fatty amines become cationic when neutralized with one mole of acid.

$$R\text{-}NH_2 + HX \longrightarrow R\text{-}\overset{+}{N}H_3\ \bar{X}$$

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



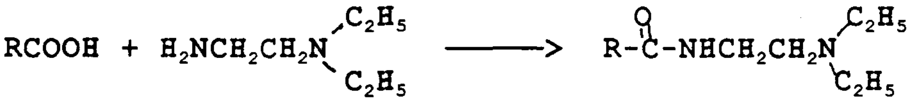
$$RCOOH + HOCH_2CH_2NH_2 \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2CH_2NH_2$$

$$RCOOH + HOCH_2CH_2NHCH_2CH_2NH_2 \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2CH_2NHCH_2CH_2NH_2$$

3. Fatty Amidoamides

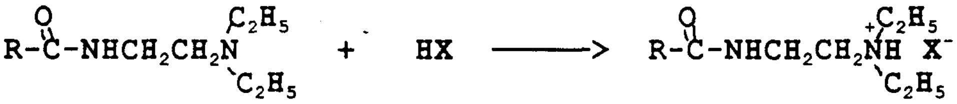
Aminoamides are made by the condensation of polyamines with fatty acids. Ethylene diamine, N,N-diethylethylene diamine and diethylene triamine are examples of polyamines that are condensed with fatty acids. Usually, the fatty acids are commercial grades such as would be derived from tallow or coconut 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



$$RCOOH + H_2NCH_2CH_2N(C_2H_5)_2 \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NHCH_2CH_2N(C_2H_5)_2$$

b. Synthesis of Amidoamide Salt

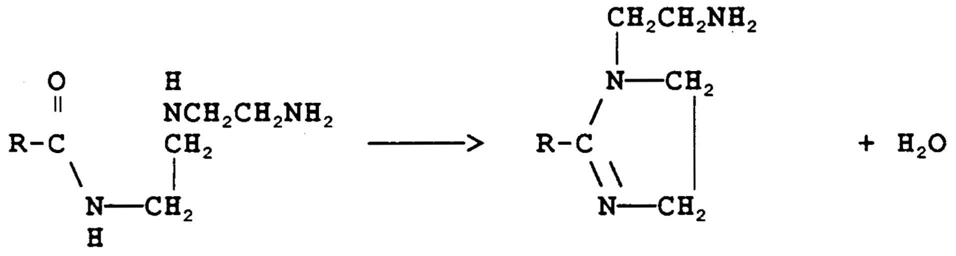


$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NHCH_2CH_2N(C_2H_5)_2 + HX \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NHCH_2CH_2\overset{+}{N}H(C_2H_5)_2\ X^-$$

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

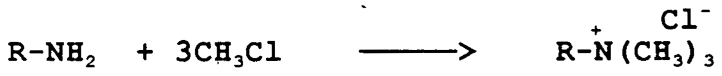


5. Quaternary Ammonium Salts

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.

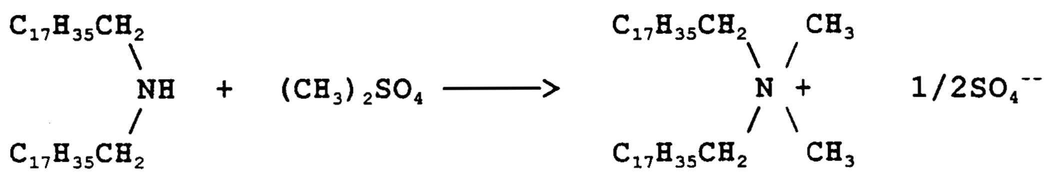
a. Synthesis of Monofatty Quats

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. Mono-fatty amines react with three moles of methyl chloride to give fatty-trimethylammonium chloride. Examples are quats derived from coco, palmito and tallow fatty acids.



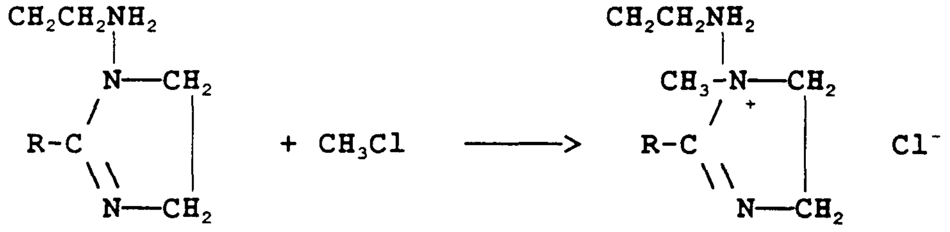
$$R\text{-}NH_2 + 3CH_3Cl \longrightarrow R\text{-}\overset{+}{N}(CH_3)_3\ Cl^-$$

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 C_{18} 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.

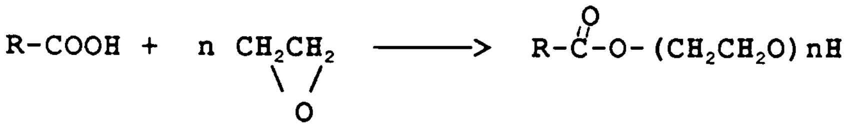
Typical Composition

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

2. Ethoxylated Nonionic Softeners

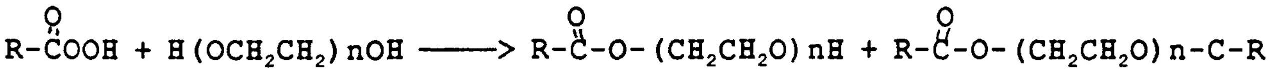
Many polyethylene glycolated hydrophobes are oily or waxy in nature and function as non-ionic fabric softeners and fiber lubricants. They are important components of fiber spin finishes because of their dual ability to lubricate and function as as antistats. Additionally, they are easily removed in downstream 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



$$R\text{-}COOH + n\ CH_2CH_2O \longrightarrow R\text{-}\overset{O}{\overset{\parallel}{C}}\text{-}O\text{-}(CH_2CH_2O)_nH$$

b. Esterification with Polyglycol



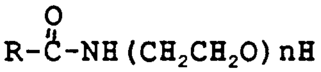
$$R\text{-}\overset{O}{C}OOH + H(OCH_2CH_2)nOH \longrightarrow R\text{-}\overset{O}{C}\text{-}O\text{-}(CH_2CH_2O)nH + R\text{-}\overset{O}{C}\text{-}O\text{-}(CH_2CH_2O)n\text{-}C\text{-}R$$

c. Typical Ethoxylates

Ethoxylated Fatty Acids: See above

Ethoxylated Fatty Alcohols: $R\text{-}CH_2O(CH_2CH_2O)nH$

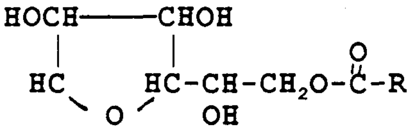
Ethoxylated Fatty Amides:



$$R\text{-}\overset{O}{C}\text{-}NH(CH_2CH_2O)nH$$

Ethoxylated Fatty Amines: $R\text{-}CH_2NH(CH_2CH_2O)n(CH_2CH_2)OH$

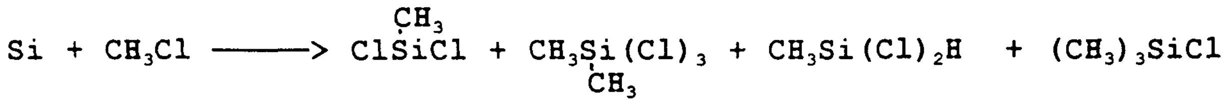
Sorbitan Fatty Esters:



3. Silicone Chemistry

In order to appreciate the role of silicones as fabric softeners, it is neccessary 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



$$Si + CH_3Cl \longrightarrow \underset{CH_3}{\overset{CH_3}{ClSiCl}} + CH_3Si(Cl)_3 + CH_3Si(Cl)_2H + (CH_3)_3SiCl$$

[I] [II] [III] [IV]

Compound	Name
[I]	Dimethyldichlorosilane
[II]	Methyltrichlorosilane
[III]	Methylhydrogendichlorosilane
[IV]	Trimethylchlorosilane

b. Reaction of Monochlorosilanes with Water

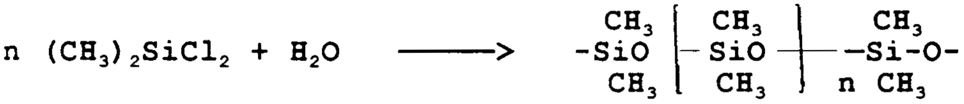
1. $(CH_3)_3SiCl + H_2O \longrightarrow (CH_3)_3SiOH + HCl$

Trimethyl silanol

2. $2\ (CH_3)_3SiOH \longrightarrow (CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3$

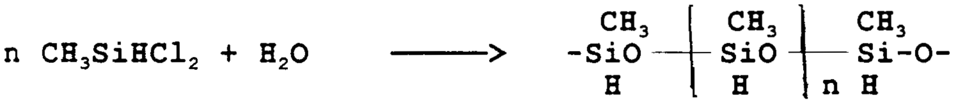
Hexamethyldisiloxane

c. Reaction of Dichlorosilanes with Water



$$n\ (CH_3)_2SiCl_2 + H_2O \longrightarrow -\underset{CH_3}{\overset{CH_3}{Si}}O \left[-\underset{CH_3}{\overset{CH_3}{Si}}O- \right]_n -\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}$$

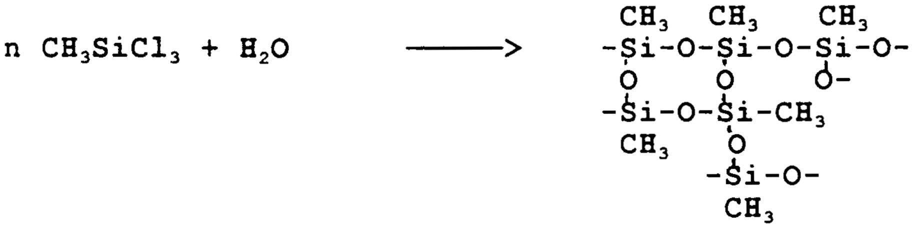
Dimethylpolysiloxane



$$n\ CH_3SiHCl_2 + H_2O \longrightarrow -\underset{H}{\overset{CH_3}{Si}}O- \left[-\underset{H}{\overset{CH_3}{Si}}O- \right]_n -\underset{H}{\overset{CH_3}{Si}}\text{-}O\text{-}$$

Methylhydrogenpolysiloxane

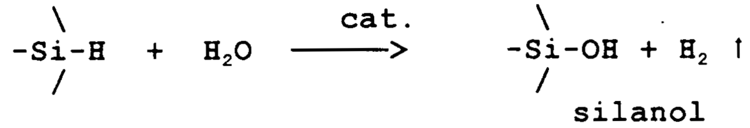
d. Reactions of Trichlorosilanes with Water



3-D crosslinked polymer

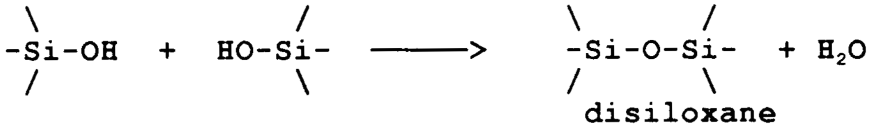
e. Reaction of Hydrogen Silanes with Water

1.



$$-\overset{\backslash}{\underset{/}{\mathrm{Si}}}-\mathrm{H} + \mathrm{H_2O} \xrightarrow{\text{cat.}} \underset{\text{silanol}}{-\overset{\backslash}{\underset{/}{\mathrm{Si}}}-\mathrm{OH}} + \mathrm{H_2}\uparrow$$

2.



$$-\overset{\backslash}{\underset{/}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{HO}-\overset{/}{\underset{\backslash}{\mathrm{Si}}}- \longrightarrow \underset{\text{disiloxane}}{-\overset{\backslash}{\underset{/}{\mathrm{Si}}}-\mathrm{O}-\overset{/}{\underset{\backslash}{\mathrm{Si}}}-} + \mathrm{H_2O}$$

From the reactions described above, it can be seen that Si-Cl bonds eventually winds up as -Si-0-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

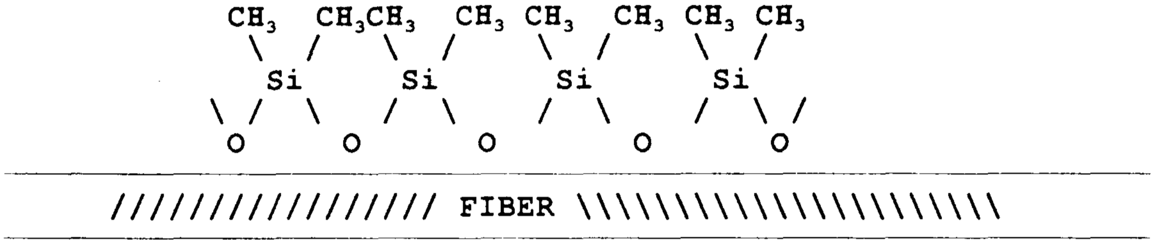
Three varieties of silicone polymers have found use as textile softeners. One variety is based on emulsified dimethyl fluids. Another variety is based on emulsified reactive fluids having Si-H groups dispersed throughout the polymer. The third variety has amino or epoxy functional groups located on the 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.

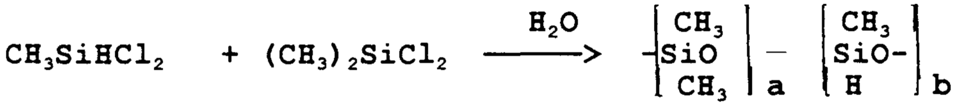
$$n\ \mathrm{Cl}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{Cl} + 2\ \mathrm{Cl}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{CH_3} \longrightarrow \mathrm{CH_3}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{O}\left[-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{O}\right]_n-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_3}$$

Figure 51. Orientation of Dimethyl Fluids on Fiber Surface.



b. Methylhydrogen Fluids

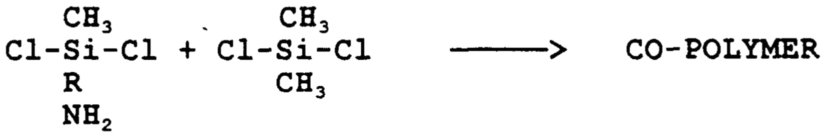
Methylhydrogendichlorosilane offers a route for making a linear polysiloxane fluid with latent crosslinking potential. Hydrolysis of the dichloro groups will occur rapidly with water to form a linear polymer. Stable emulsions can be prepared, as long as the aqueous pH is maintained between 3-4,. When 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.



$$CH_3SiHCl_2 \quad + \; (CH_3)_2SiCl_2 \xrightarrow{H_2O} \left[\begin{array}{c} CH_3 \\ SiO \\ CH_3 \end{array} \right]_a - \left[\begin{array}{c} CH_3 \\ SiO- \\ H \end{array} \right]_b$$

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.



$$\begin{array}{c} CH_3 \\ Cl-Si-Cl \\ R \\ NH_2 \end{array} + \begin{array}{c} CH_3 \\ Cl-Si-Cl \\ CH_3 \end{array} \longrightarrow \text{CO-POLYMER}$$

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 redying when salvaging off quality goods.

IV. REFERENCES

CHAPTER 9

REPELLENT FINISHES

Stain Repellency is the ability of a treated fabric to withstand penetration of liquid soils under static conditions involving only the weight of the drop and capillary forces.

Oil Repellency is tested by placing a drop of oil on the fabric and observing whether the drop resides on top the fabric or whether it penetrates. A homologous series of hydrocarbons decreasing in surface tension is used to rate the fabric's oil repellency. The hydrocarbon with the lowest surface tension to remain on top and not penetrate is indicative of the fabric's repellency. The lower the surface tension of the liquid, the better the fabric's resistance to oily stains.

Water Repellency is more difficult to define because various static and dynamic tests are used to measure water repellency. Generally speaking water repellent fabrics are those which resist being wetted by water, water drops will roll off the fabric. A fabric's resistance to water will depend on the nature of the fiber surface, the porosity of the fabric and the dynamic force behind the impacting water spray. The conditions of the test must be stated when specifying water repellency. It is important to distinguish between water-repellent and water-proof fabrics.

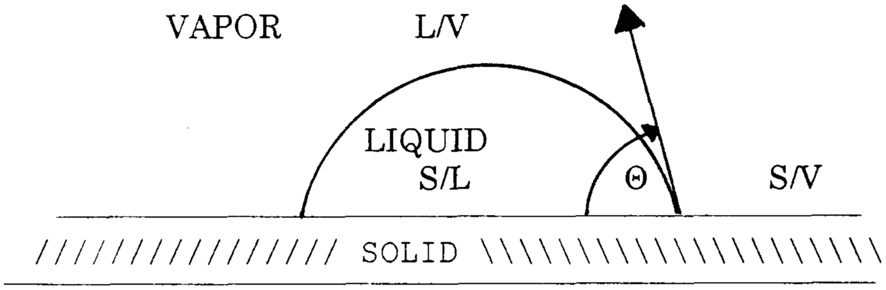
Water Repellent Fabrics have open pores and are permeable to air and water vapor. Water-repellent fabrics will permit the passage of liquid water once hydro-static pressure is high enough.

Water-ProofFabrics are resistant to the penetration of water under much higher hydrostatic pressure than are water-repellent fabrics. These fabrics have fewer open pores and are less permeable to the passage of air and water vapor. The more waterproof a fabric, the less able it is to permit the passage of air or water vapor. Waterproof is an overstatement, a more descriptive term is impermeable to water. A fabric is made water-repellent by depositing a hydrophobic material on the fiber's surface; however. waterproofing requires filling the pores as well.

I. PHYSICAL CHEMISTRY OF WETTING

When a drop of liquid on a solid surface does not spread, the drop will assume a shape that appears constant and exhibits an angle Θ, called the contact angle. The angle Θ is characteristic of the particular liquid/solid interaction; therefore, the equilibrium contact angle serves as an indication of wettability of the solid by the liquid. As seen in figure 52, the interfacial forces between the liquid and vapor, liquid and solid and solid and vapor all come into play when determining whether a liquid will spread or not on a smooth solid surface. The equilibrium established between these forces determine the contact angle **O.**

Figure 52. Spreading of Liquids on Smooth Surfaces



Where: L/V = the interfacial energy between liquid/vapor
S/L = the interfacial energy between solid/liquid
S/V = the interfacial energy between solid/vapor
Θ = equilibrium contact angle

A. Work of Adhesion

The work of adhesion between the liquid and the solid is given by the Dupre Equation:

$$W_A = \gamma_{S/V} + \gamma_{L/V} - \gamma_{S/L}$$

A liquid drop on a smooth solid surface is subject to the equilibrium forces described by the Young Equation:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\mathrm{Cos}\Theta$$

The relationship between the work of adhesion and the contact angle is derived by combining the two equations (the Young-Dupre Equation):

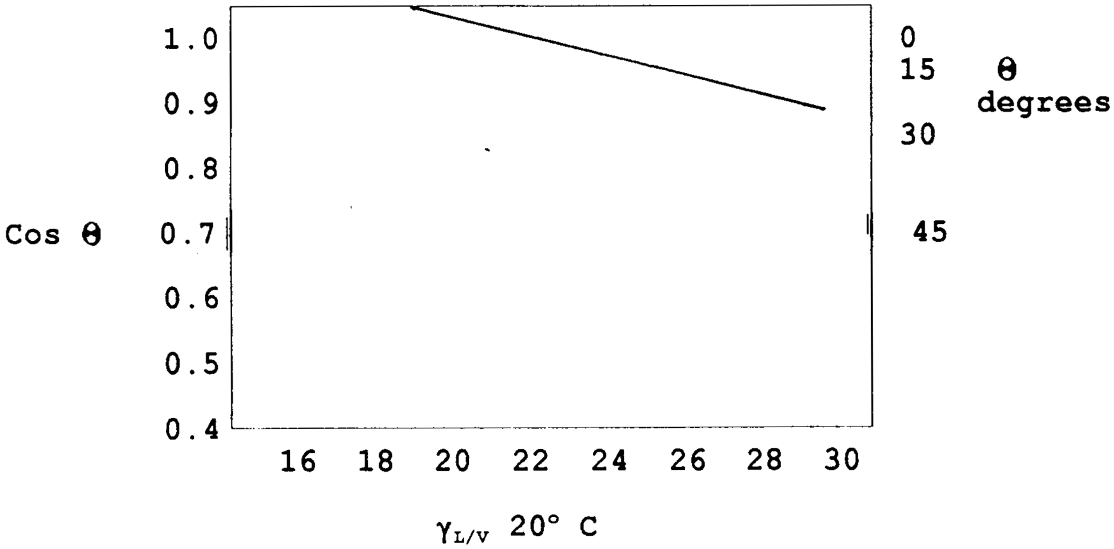
$$W_A = \gamma_{LV}(1 + \mathrm{Cos}\Theta)$$

While the interfacial energy between a liquid and its vapor can be measured directly (this quantity is the liquid's surface tension), that between a solid and air cannot. The expression above is useful in characterizing the surface energy of solids. From this equation, it can be reasoned that as the contact angle Θ approaches 180°, the work of adhesion approaches 0, and the liquid drop will not stick. As Θ approaches 0, the work of adhesion increases and reaches the maximum value, 2 γ_{LV}. The surface tension of a liquid that just spreads on a solid (Θ = 0) would be representative of the surface energy of a solid and could be used to describe the surface.

B. Critical Surface Tension

The critical surface tension of a solid γ_c is defined as the surface tension of a liquid that just completely spreads on a surface. This quantity is obtained experimentally by plotting Cos Θ verses the surface tension of a homologous series of liquids on a low energy surface. γ_c is the value obtained when the curve is extrapolated to Cos = 1,(Θ = 0). An example of this type of plot is seen in figure 53. The value for teflon extrapolates to 18 dynes /cm.

Figure 53. Critical Surface Tension of Teflon



The critical surface tension of nearly all solid polymer surfaces have been determined. Table 13. lists a few of the more important fiber polymer surfaces.

Table 3

Critical Surface Tensions of Smooth Surfaces

	γ_c dynes/cm
Poly(tetrafluoroethylene)	18
Poly(dimethyl siloxanes)	23
Poly(vinyl fluoride)	28
Poly(ethylene)	31
Poly(vinyl alcohol)	37
Poly(vinyl chloride)	39
Poly(ethylene terephthalate)	43
Poly(hexamethylene adipamide)	46

All of the above polymers are considered hydrophobic because their critical surface tensions are well below that of pure water (72 dynes/cm at 20° C). The critical surface tension is mainly influenced by the outermost layer of atoms at the solid's surface. Zisman and his coworkers measured many condensed monolayers on solid surfaces such as glass and platinum. The technique allow them to closely pack specific groups at the surface and some of their data is tabulated in the Table 14.

Table 14

Critical Surface Tension of End Groups

	γ_c
Fluorocarbon Surfaces	
CF_3-	6
CF_2H-	15
-CF_2-	18
-CF_2-CH_2-	25
Hydrocarbon Surfaces	
CH_3-	23
-CH_2-	33

C. Contact Angles in Real Systems

The contact angles observed on ideal, smooth surfaces do not correspond to those found in real systems. Nearly all surfaces exhibit a degree of roughness and textiles, in particular, deviate from the ideal system. The degree of roughness will strongly change the observed contact angles on real systems. Those finishes that yield $\Theta \geq 90$‘ when on smooth surfaces will result in much higher contact angles on textiles. Those finishes producing contact angles less than 90^0 will allow the liquid drop to quickly penetrate into the fabric. This phenomenon is put to good use in repellent fabric treatments since the repellency of textile products appear to be better than the wetting characteristics of corresponding flat films.

D. Repellent Finishes

For fabrics to be water repellent, the critical surface tension of the fiber's surface must be lowered to about 24 to 30 dynes/cm. Pure water has a surface tension of 72 dynes/cm so these values are sufficient for water repellency. This section will be devoted to describing materials that are used mainly as water repellent finishes. In a later section, it will be shown that some of these can be combined with fluorochemical finishes to enhance both water and oil repellency. Oil repellency requires that the fiber surface be lowered to 13 dynes /cm. Only fluorochemicals are able to function as oil repellents so whatever is mixed with them must not interfere with how they are deposited.

II. HYDROCARBON HYDROPHOBES

A. Paraffin Waxes

The oldest and most economical way to make a fabric water repellent is to coat it with paraffin wax. Solvent solutions, molten coatings and wax emulsions are ways of applying wax to fabrics. Of these, wax emulsions are the most convenient products for finishing fabrics. An important consideration in making water repellent wax emulsion is that the emulsifying system not detract from the hydrophobic character of paraffin. Either non-rewetting emulsifiers or some means of deactivating the hydrophilic group after the fabric is impregnated with the finish must be used.

Paraffin wax melts and wicks into the fabric when the fabric is heated. This will cause most of the fibers to be covered with a thin layer of wax, especially those that are exposed to water, and the fabric will have excellent water repellent properties. The major disadvantage of wax water repellents is poor durability. Wax is easily abraded by mechanical action and wax dissolves in dry cleaning fluids. It is also removed by laundry processes.

A typical wax emulsion consists of paraffin wax as the hydrophobe, an emulsifying agent, an emulsion stabilizer (protective colloid) and an aluminum or zirconium salt to deactivate the emulsifying agent when the fabric is heated.

Table 15

Wax Emulsion Composition

	%
Paraffin	17.0
Bone glue	2.5
Al_2O_3	3.0
Formic acid	7.0
Rosin	0.7
KOH (50°Be)	0.2
Water	to 100

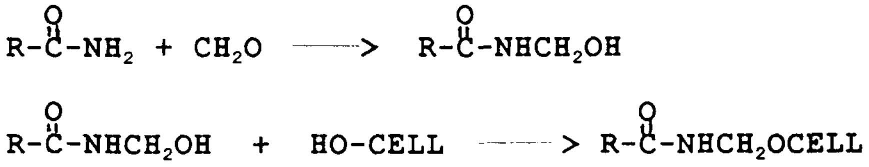
The stability of wax dispersions and the durability of wax finishes have been increased by formulating polymers such as poly(vinyl alcohol), polyethylene and copolymers of stearyl acrylate-acrylic or methacrylic acids. Wax finishes are usually co-applied with durable press reactants which also adds to the repellent's durability while imparting durable press properties.

B. Fiber Reactive Hydrocarbon Hydrophobes

1. N-Methylol Stearamide

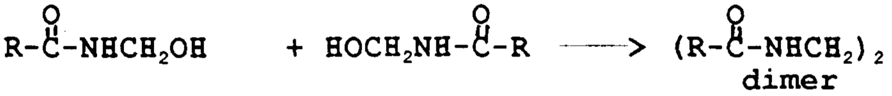
In an effort to improve the durability of hydrocarbon based water repellents, several approaches incorporating reactive groups have found commercial success. The simplest of these is N-methylol stearamide. Stearamide reacts with formaldehyde to form the N-methylol adduct. This adduct is water dispersible and either will react on curing with cellulose, dimerize or react with crosslinking reagents that are co-applied.

a. Synthesis and Reactions



$$R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NH_2 + CH_2O \longrightarrow R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NHCH_2OH$$

$$R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NHCH_2OH + HO\text{-}CELL \longrightarrow R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NHCH_2OCELL$$



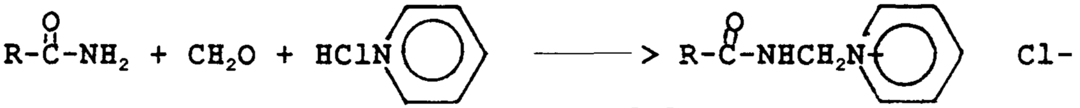
$$R-\overset{O}{\overset{\|}{C}}-NHCH_2OH + HOCH_2NH-\overset{O}{\overset{\|}{C}}-R \longrightarrow (R-\overset{O}{\overset{\|}{C}}-NHCH_2)_2$$

dimer

2. Pyridinium Compounds

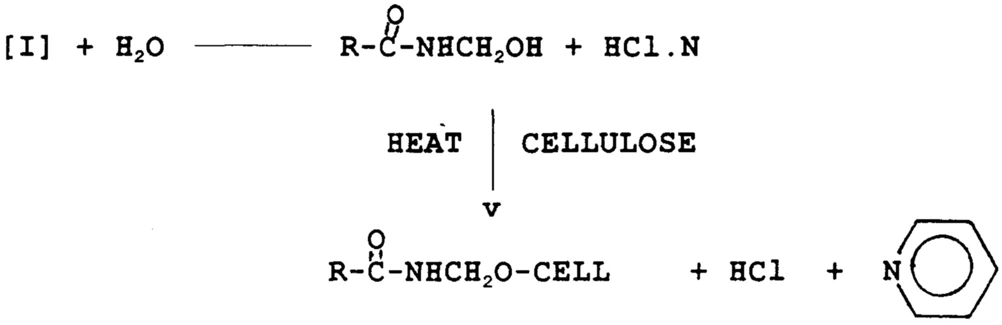
A variation of N-methylol stearamide is the pyridinium type water repellents. These were once very popular and used extensively as reactive type water repellent finishes. Toxicological considerations have curtailed the use of pyridinium-type water repellents. Workers at the US Army Quartermaster Corp discovered that pyridinium type water repellents co-applied with fluorochemical repellents resulted in a synergistic effect by providing good, long-lasting water repellency for military fabrics. The finish was durable to field laundry procedures and named Quarpel by its inventors. The concept of adding wax type water repellents to fluorochemical repellents has been broadened and other wax type called ***Extenders*** are used with fluorochemicals. More on extenders will be included in the section dealing with fluorochemical repellents.

a. Synthesis and Reactions



[I]

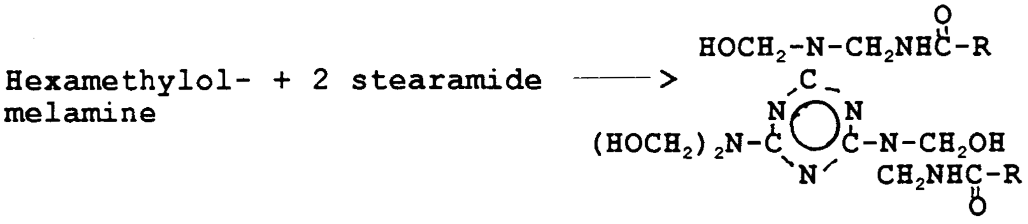
This product is self emulsifiable because of the ionic nature of the pyridinium quat. After it is applied to cellulose fabrics and cured, the pyridinium hydrochloride serves as the catalyst to promote the reaction of the N-methylol group with cellulose.



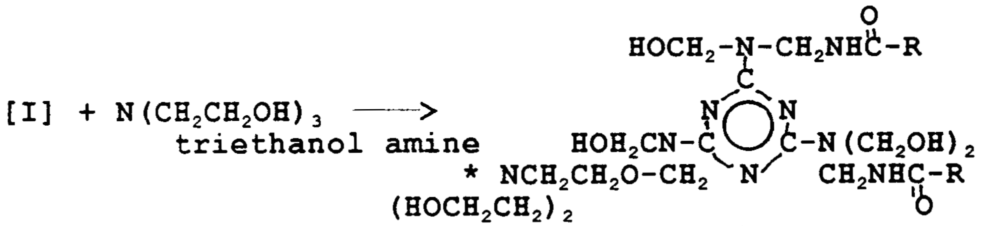
3. Resin Formers

The multiple reactive sites on methylolmelamines can be utilized for making resin-forming water repellents. The reactivity of stearamide with formaldehyde can be utilized for attaching hydrophobic groups to the melamine molecule. Part of the N-methylol groups are used to attach the hydrophobe, some are used to add a cationic site for emulsification purposes and some of the N-methylol groups are later involved in self condensation to forma resinous coating on the fiber surface or to react with added durable press reagents. An example of this type:

a. Synthesis of Melamine Wax Type Water Repellents



[I]



[II]

The *N nitrogen in becomes cationic when acidified and serves to self-emulsify the resultant waxy material. R- groups provide hydrophobicity and the remaining $N-CH_2OH$ groups in the melamine react with the OH groups brought in by the triethanol amine to form a crosslinked, three-dimensional polymer on the fiber surface.

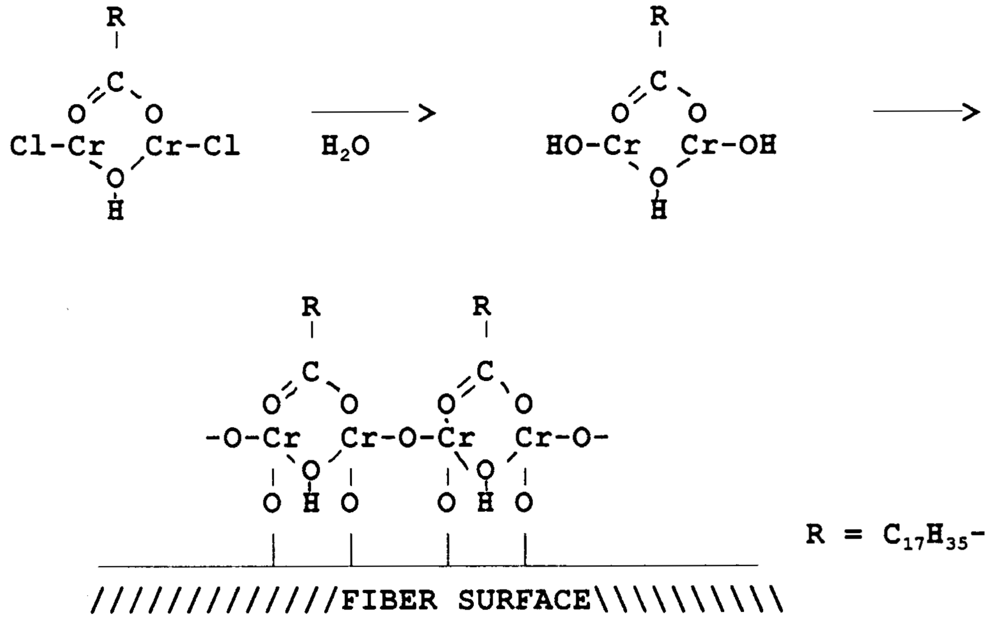
Compound [II]'s water repellency can be enhanced by incorporating paraffin wax with it. Paraffin is blended with [II] when molten. The resultant wax is sold as a solid which is emulsified prior to use. Emulsification is accomplished by melting the composition in hot water and adding tartaric or citric acid while stirring. The creamy emulsion is cooled while stirring and is ready for use. The acid also serves as the catalyst for curing the melamine.

4. Metal Complexes

Werner-type chrome complexes of stearic acid have been marketed under the trademark Quilon by DuPont. These products are especially effective on fiberglass since they can react with the glass surface. The product is made by reacting stearic acid with basic chrome chloride in an isopropanol solution. The product is diluted with water just prior to being applied to fabric causing the complex to hydrolyze.

acid with basic chrome chloride in an isopropanol solution. The product is diluted with water just prior to being applied to fabric causing the complex to hydrolyze. During application, the polymerization is not allowed to proceed so far as to cause precipitation of the polymer. On standing or when heated, the complex will polymerize to form -Cr-O-Cr-O-Cr- bonds. When the fabric is cured at 150-170” C, further polymerization of the complex occurs bonding the inorganic portion to the fiber surface. This will cause the hydrophobic tail to orient perpendicularly away from the surface, providing water repellency to the fabric.

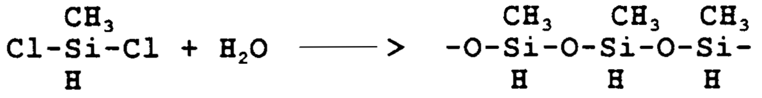
a. Synthesis and Reactions



III. SILICONE WATER REPELLENTS

Resinous polysiloxanes, on the other hand are more resistant to abrasion and less soluble in dry-cleaning fluids or laundry products. Three-dimensional crosslinked polysiloxanes fill the need provided they could be applied to fabrics. 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. As long as the aqueous pH is maintained between pH 3-4, stable emulsions can be prepared. 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 a three-dimensional resinous polymer, making the fabric highly water repellent.

A. Synthesis of Methyl Hydrogen Fluids

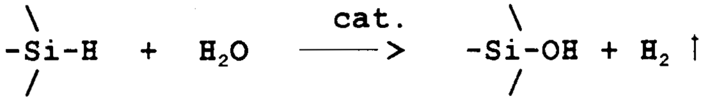


$$Cl-\overset{CH_3}{\underset{H}{Si}}-Cl + H_2O \longrightarrow -O-\overset{CH_3}{\underset{H}{Si}}-O-\overset{CH_3}{\underset{H}{Si}}-O-\overset{CH_3}{\underset{H}{Si}}-$$

Methylhydrogen fluid

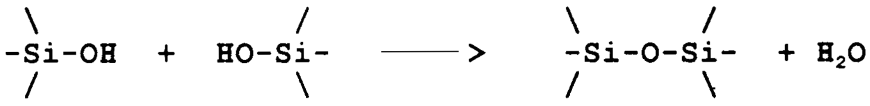
B. Crosslinking Reactions

1. Hydrolysis of Si-H



$$-\overset{\backslash}{\underset{/}{Si}}-H + H_2O \xrightarrow{cat.} -\overset{\backslash}{\underset{/}{Si}}-OH + H_2\uparrow$$

2. Condensation of Silanols



$$-\overset{\backslash}{\underset{/}{Si}}-OH + HO-\overset{/}{\underset{\backslash}{Si}}- \longrightarrow -\overset{\backslash}{\underset{/}{Si}}-O-\overset{/}{\underset{\backslash}{Si}}- + H_2O$$

3-D-crosslinked

The resinous finishes formed by polymethylhydrogensiloxanes give a harsh fabric handle. Polydimethylsiloxanes are usually mixed in to make a more pliable film, the dimethyl fluid acts as a plasticizer. Fabric hand can be controlled by the relative amounts of each component. 'It should be noted that softer films are not as strong as the more highly crosslinked ones so durability is traded for softness.

C. Application to Fabrics

Silicone finishes are applied to fabrics either from an organic solvent or from water as an emulsion. When cationic emulsifiers are used to make an emulsion, the finish may be applied by exhaustion since the negative fiber surface charges attract positively charged particles. Generally however, silicone water repellents are co-applied with a durable press finish. Durable press resins enhance the durability of the water-repellent finish. Silicone repellents are also used to make upholstered furniture stain repellent. Chlorinated solvent solutions are sprayed onto upholstery by the retailer as a customer option. The fabric is resistant to water borne stains such as coffee and soft drinks.

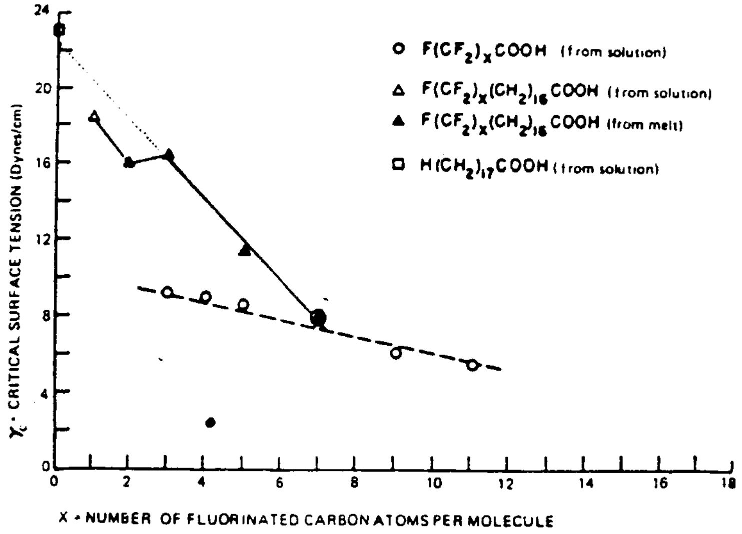
D. Advantages and Disadvantages

Silicone water repellents are durable to washing and dry-cleaning. Durability is brought about by the formation of a sheath of finish around the fiber. If the sheath cracks, durability is lost. Adsorption of hydrophilic substances found in dry cleaning and laundry products also impair water repellency. Silicones are more durable than wax repellents but less durable than fluorochemical finishes. Silicones are more expensive than wax repellents and less expensive than fluorochemical repellents. Silicone finishes resist water borne stains but not oil borne stains. Fabric hand can be made soft and pliable.

IX. FLUOROCHEMICAL REPELLENTS

Fluorochemical repellents are unique in that they confer both oil and water repellency to fabrics. The ability of fluorochemicals to repel oils is related to their low surface energy which depends on the structure of the fluorocarbon segment, the non-fluorinated segment of the molecule, the orientation of the fluorocarbon tail and the distribution and amount of fluorocarbon moiety on fibers. Low surface energy can be described in critical surface tension terms. The relationship between γ_c and structure of the fluorocarbon can be seen in the figure 54. The data was obtained by adsorbing monolayers of carboxylic acids onto a smooth surface.

Figure 54. Effect of Fluorination on Critical Surface Tension



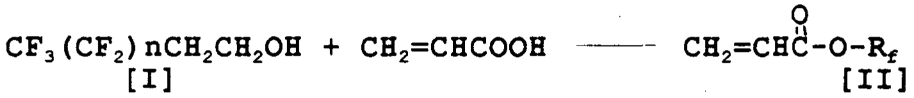
Curve A shows that as the length of fully fluorinated carboxylic acid's tail (R_f) increases, γ_c decreases. Starting with perfluoro butyric acid, γ_c slowly decreases as the perfluoro tail increases ranging from 10 down to 6 dynes/cm for perfluorododecanoic acid. Curve B shows the effect increasing the R_f portion of a long-chain hydrocarbon acid. Octadecanoic acid measures 23 dynes/cm. Once seven outermost carbon atoms are fully fluorinated, the wettability approaches that of the corresponding perfluorocarboxylic acid, 10 dynes/cm. A terminal perfluoroalkyl chain of seven carbons is sufficiently long to shield non-fluorinated segments beneath the fluorinated segments.

A. Commercial Products

Commercial fluorochemical repellents are fluorine-containing vinyl or acrylic polymers. This is a convenient method of affixing perfluoro side chains to fiber surfaces that can orient air-ward and give a reasonably close packed surface of $-CF_2-$ and $-CF_3$ groups. For example, acrylic acid can be reacted with a perfluoro alcohol to form the corresponding acrylate ester. The acrylate monomer will polymerize to form a high molecular weight polymer that can be converted to an emulsion. The emulsion dries to a continuous film, covering the fiber surface. The perfluoro segment is there as a side chain attached to the polymer backbone. Being nonpolar, it will want to orient away from polar forces, thus forcing itself toward the air interface. Heat facilitates the orientation by increasing molecular motion.

1. Synthesis and Reactions

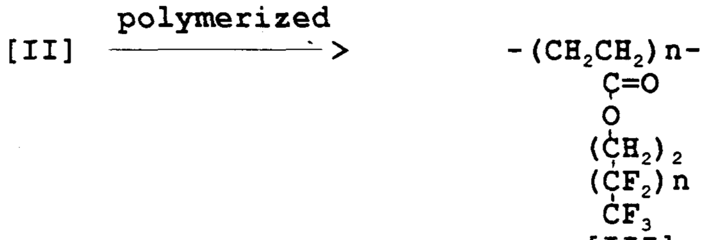
a. Monomer Synthesis



$$\underset{[I]}{\mathrm{CF_3(CF_2)nCH_2CH_2OH}} + \mathrm{CH_2{=}CHCOOH} \longrightarrow \underset{[II]}{\mathrm{CH_2{=}CH\overset{\overset{O}{\|}}{C}{-}O{-}R_f}}$$

where R_f = [I]

b. Emulsion Polymer Synthesis

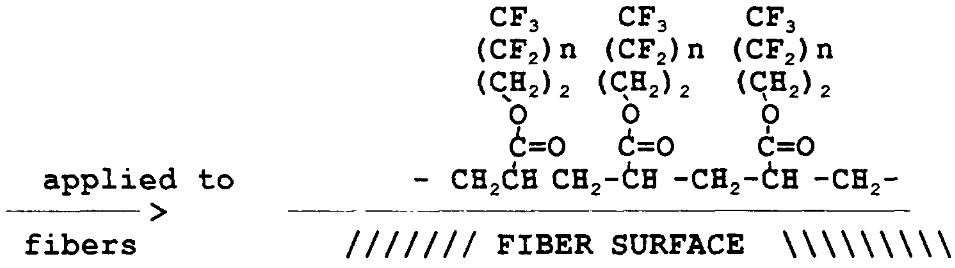


$$[II] \xrightarrow{\text{polymerized}} \begin{array}{c} -(\mathrm{CH_2CH_2})n- \\ \mathrm{C{=}O} \\ | \\ \mathrm{O} \\ | \\ \mathrm{(CH_2)_2} \\ | \\ \mathrm{(CF_2)n} \\ | \\ \mathrm{CF_3} \end{array}$$

[III]

3. Applied to Fiber

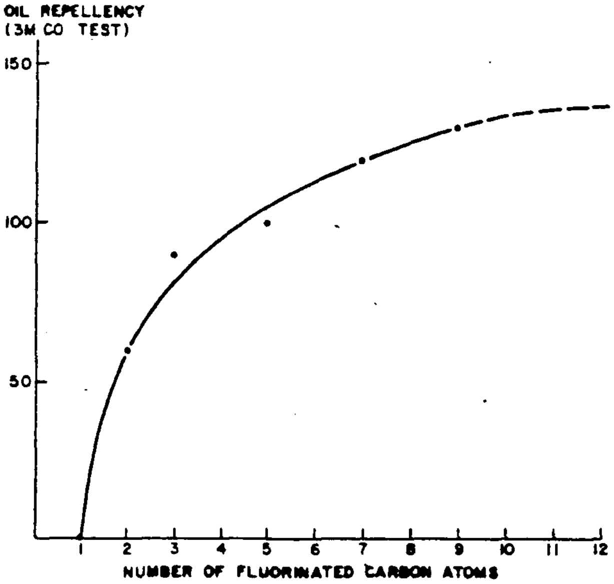
III]



B. Effect of Perfluoro Side-Chain

The data in figure 55 show the relationship of oil repellency versus the length of the fluorinated side chain of some perfluoro acrylates. For maximum repellency, the side chain must have ten fully fluorinated carbons. The critical surface tension reaches a minimum when the R_f number increases to ten. More than this is cost ineffective because adding fluorine is expensive.

Figure 22. Relationship between Oil Repellency and Length of Perfluoroalkyl Side Chain



C. Effect of Polymer Backbone

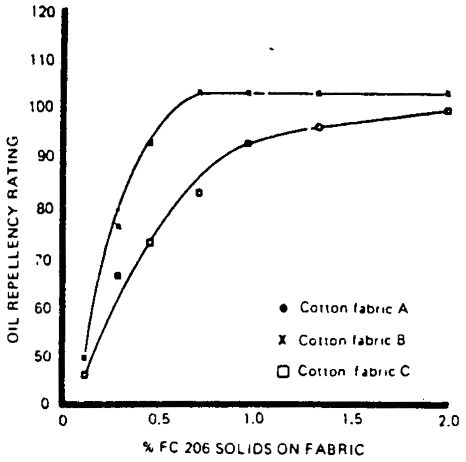
There are many articles and patents in the literature discussing a wide variety of fluorinated structures, polymers and copolymers and how they relate to repellency. It is beyond the scope of this book to review the subject in detail. However it is generally recognized that the polymer backbone must be such that it can be efficiently applied to fabric. In theory, only a one molecule thick coating is necessary to cover the fiber surface. Those polymers that lend themselves able to be spread will be more effective than those that don't. The polymer must adhere well to the fiber surface and must possess good resistance to abrasion and/or being swollen or otherwise affected by dry-cleaning and laundry products.

To achieve suitable commercial products, hydrocarbon monomers are often copolymerized with the fluoromonomers, and/or hydrocarbon polymers are admixed with the fluoropolymers. While this flies in the face of logic (diluting the fluorine content should increase the critical surface tension), the truth of the matter is that the hydrocarbon component improves both water and oil repellency over the fluoropolymer component alone. The reason for this is that the hydrocarbon portion helps in spreading the fluorochemical and reduces the temperature needed to allow the fluorinated tails to orient. It is good that this is so because fluorinated products would be prohibitively expensive as fabric finishes.

D. Add-on

The amount of fluorochemical needed to achieve oil repellency is relatively low. Figure 56 shows that on many fabrics, an add-on of 0.5% is sufficient to give optimum results.

Figure 23. Oil Repellency versus Fluorochemical Add-on



E. Extenders

Extenders are wax-type water repellents that are formulated into the fluorochemical finish bath to improve both cost and performance of the finish. The pyridinium wax type was the first to be used. In recent years, fluorochemical repellents and extenders have been co-applied with with durable press resins, all in the same bath. Durability of the finish is improved, repellency ratings are better and the finish cost is lower. Extenders serve to help spread the fluorochemical more efficiently over the fiber surface. Early experiments showed that effective extenders allowed the fluorinated tail to orient air-ward essentially acting as if the hydrocarbon material was not there. Silicone repellents reduce the fluorochemical's oil repellency and are not used as extenders.

V. REPELLENT FINISHING WITH FLUOROCHEMICALS

The oil and water repellent features of fluorochemical polymers lead to finishes applicable in two consumer product areas, durable rainwear fabrics and stain/soil resistant products. For rainwear products, superior durability to repeated laundering and drycleaning is the major advantage. For stain and soil resistance, the plus features are the fluorochemical's ability to prevent oils from penetrating into the fabric or from soils sticking to the fiber surface. Most fabric stains are caused by liquids depositing coloring matter on the fabric. Water borne stains can be held out by silicone water repellents; however, oil based stains can only be repelled by the low surface energy of closely packed fluorocarbon tails. For textiles that cannot be laundered, e.g. upholstery fabrics and carpets, stain and soil repellency is an important consumer plus. For fabrics that can be laundered or dry cleaned, stain removal is more important than stain prevention. Finishes designed to facilitate soil removal by laundering will be discussed in a later section.

A. Rainwear

A typical formulation for polyester-cotton rainwear and outerwear is shown in Table 16. The finish is applied by padding the formulation onto fabric, drying at 120°C and curing 1-3 minutes at 150-182° C. The fabric will give a 100 spray rating initially and an 80 rating after 5 home laundering-tumble drying cycles. An 80 spray rating is expected after one dry cleaning cycle. In addition, oil repellency rating of 5 initially and 4 after laundering or dry cleaning is expected.

Table 16

Typical Rainwear Formulation

	% Bath Conc.
Fluorochemical product	2.0 - 3.0
Resin wax water repellent	2.0 - 3.0
DMDHEU	10 - 15
$MgCl_2$ catalyst	2.5 - 4.0
Polyethylene softener	0.5 - 2.0
Non-rewetting surfactant	0.03 -0.05
Acetic acid	0.05 -0.1

B. Stain and Soil Retardancy

1. Upholstery Anti-Soil Finishes

Objectionable soiling of upholstery fabrics is that brought about by spilled liquids. A finish giving maximum water and oil repellency allows the consumer to wipe away the spill before it penetrates into the fabric. Fluorochemical finishes facilitate spot cleaning of any stain that is rubbed into fabric. Solvents are best used for removing oily stains. Solvent soluble fluorochemical finishes can be applied at the mill or at the retail store. Water based fluorochemicals can also be applied to upholstery fabrics. However, they must be heat treated to optimize the orientation of the fluoro tails for maximum repellency. For this reason, water based finishes are best applied in a finishing plant. Solvent based finishes are prefered for aftermarket treatments because heat isn't needed to assist the orientation of the tails, evaporation of the solvent under ambient conditions is sufficient.

Oily stains rubbed into repellent treated washable fabrics present another problem, they are much more difficult to remove than if the repellent finish wasn't there at all. For washable fabrics, a very special fluorochemical has been developed which gives both oil repellency and stain release. This will be discussed in detail in the next chapter.

VI. CARPET ANTI-SOIL TREATMENTS

A. Fluorochemical Finishes

One area where fluorocarbon finishes have met with consumer acceptance is soil retardant finishes for carpets. In this application, oil repellency per se is not what brings about the improvement, it is the fluorocarbon's extremely low surface energy which prevents soil particles from sticking to the fibers. The finish provides an anti-adhesive coating to the fiber. To function properly, the fluoropolymer must provide low critical surface tensions and at the same time be hard enough not to deform when soil particles are pressed into it. Carpet soiling is mainly hard particulate matter tracked onto the face yarns by foot traffic, the soil transfers from the shoe sole and is ground into the carpet. Polyacrylic fluoroesters tend to be soft and rubbery. While they provide the needed low surface energy, they in fact worsen carpets soiling because they deform under pressure trapping the soil particle like fly paper traps flies. This makes it even more difficult to clean the carpet. Fluorocarbon finishes that work well as carpet soil retardants have been modified to overcome the flypaper effect. Some are fluoroesters of pyromelletic acid. These products can melt at curing temperature and efficiently spread over the carpet's face yarn. At room temperature they solidify into hard, flexible low energy coatings. The way these finishes work improve carpet soiling are: 1 They reduce the transfer of soil from the shoe sole onto the carpet's face yarn. This is a function of the fluoropolymer's low surface energy. 2. They reduce the work of adhesion between the soil particle and the fiber surface. The particle tends to fall to the carpet backing and not be as visible. Reduced adhesion allows the particle to be more easily removed by vacuuming. 3. Oil repellency prevents oily surfactants from wicking up onto the face yarns from the carpet backing. Oily films on the face yarns speed up the entrapment of foot soil and the carpet will appear to be soiled much sooner than if the surfactant was not there. Shampooed rugs will appear dirty much sooner than the original unless care is taken to flush out the residual detergent. Fluorochemical treatments improve this tendency.

B. Other Carpet Antisoil Treatments

1. Light-Scattering Fibers

A new generation of soil-hiding carpet fibers have been commercialized in recent years. These fibers have been modified to enhance light scattering. As the apparent surface area of a fiber is increased, its ability to scatter light increases and the fiber becomes more opaque. Soil particles become more difficult to see therefore the carpet appears cleaner. Changing the fiber's cross section is one way of increasing light scattering. Unfortunately as light scattering increases, so does the area where particles can reside. Trilobal fiber cross sections scatter more than do round. Another method of increasing light scattering is to create holes in the fiber cross section. By keeping the cross section round, the surface area for attracting soil is at a minimum, while the internal voids provide the needed surfaces for light scattering. These modifications do not really retard soiling, they fool the consumer into thinking the carpet is cleaner than is actually so. However, these fibers have met consumer acceptance and are becoming a major force in high quality carpets.

B. Stain Blockers

Certain water borne food stains are actually acid dyes, for example the colorants in Kool Aid and cola soft drinks. Repellency of even the best of fluorocarbon treated nylon carpets will eventually be overcome by these liquids. The coloring matter will be adsorbed by the nylon fibers much the same way as nylon adsorbs acid dyes. The net effect is that these liquids are responsible for stains that cannot be prevented or removed from the best of the anti-soil products described above. A very recent innovation is the introduction of *stain blocking* technology that render nylon carpets resistant to these stains as well. The technology involves the treatment of nylon carpets with certain *Syntans* that tie up the remaining amino groups responsible for attracting food colors. Syntans are synthetic tanning agents that are used to improve the wet fastness of acid dyed fibers, e.g. wool, leather, silk and nylon. The ones that work best on carpets are sulfonated novolaks, polymethyacrylic acids and combinations of the two. The treatment can be applied by the fiber producer as part of the spin finish with fluorocarbon finishes to give the "ultimate" in carpet soil/stain protection or by the carpet manufacturer after the dyeing step. While the syntans are known to impart dye resist to nylon, the ones used are effective at room temperature allowing the pretreated fiber to be dyed at elevated temperatures. The technology has improved to the point that newer versions withstand the hot dyeing .conditions without loss of the finish during dyeing.

VII. REFERENCES

CHAPTER 10

SOIL-RELEASE FINISHES

Soil release is the term used to describe the cleanibility of fabrics by the laundering process. The preceding chapter dealt with finishes that made fabrics more resistant to soiling; however, in practice it has been found that soils have a way of penetrating even the best of repellent finishes, the textile item must be cleaned anyway. From a consumer point of view, a stain is perceived to be the worst case of soiling. With use fabrics tend to develop an overall grey and dingy look and this too is undesirable. But unless the consumer has the original fabric to compare with, the loss of whiteness is not objectionable unless it is severely discolored. A visual stain on the other hand, even a mild one, is more objectionable.

I. SOILS

Soils can be defined as unwanted substances at the wrong place. Most common soils fall into one of four categories: 1. water borne stains, 2. oil borne stains, 3. dry particulate soils and 4. composite soils involving oil and grease adsorbed on particulate matter. Water borne stains are not much of a problem, the stains are soluble in the wash water. Food stains and dried blood, although not water soluble, are responsive to proteolytic enzymes found in most commercial detergents. Dry particulate soils such as flour, clay and carbon black are mechanically entrapped in the yarn interstices and reside on the surface of the fiber. Removal of particulate soils depends on overcoming the work of adhesion between the particle and the fiber surface, facilitating the transport of detergent solution to where they reside and transporting the particle into the wash water. Mechanical energy (agitation) is important for latter.

Oily soils, e.g. salad oil, motor oil, food grease are particularly difficult to remove from synthetic fabrics such as polyester. The sorption forces between the oils and the synthetic fiber surfaces are so strong that it is virtually impossible to completely remove them by conventional laundering. For this reason oily soils, as a group, are particularly difficult to remove from many washable fabrics made from 100 % polyester and polyester blends. Lipstick, make-up, printing ink, used motor oil and atmospheric soot are examples of composite soils where bonding to the fiber is a function of the oily component. The removal of these stains is accomplished by overcoming the sorptive forces between the oil carrier and the fiber.

A. How Fabrics are Soiled

Soil can be airborne particles that settle by gravitational forces or are electrostatically attracted to the fabric. Soot is a troublesome airborne particulate that is difficult to remove from fabrics. Drapes, carpets and upholstery are items prone to being soiled by airborne soils. Soils can transfer by contact with a dirty surface and they can be ground in by pressure or rubbing. Soils can also transfer by wicking, liquid soils in contact with fabrics will wick into the structure by capillary action. Soils removed in the laundering process may redeposit back onto the fabric, emulsified oily soils may break out of solution unless the emulsion is well stabilized. Also the ionic charge of the emulsified soil may be attracted to an opposite charge on the fiber.

II. SOIL REMOVAL

A. Particulate Soil

The adhesion between particulate soil and the fiber depends on the location within the fabric structure, the forces of attraction between the soil and fiber, and the area of contact. Studies have shown that as more energy is used to grind the particulate soil into the fabric, the more difficult will it be to remove it. Both the area of contact and the location within the fabric are influenced by the force. Removal of particulate soil is brought about by breaking the adhesive bond between the particle and the fiber, wetting out the particle to make a stable dispersion, and then carry off the dispersed particle into the bulk of the wash water. The greater the area of contact, the more difficult it is to break the adhesive bond. Fine particles have a greater area of contact. The tighter the fabric, the smaller are the interfiber voids which make also make the outward transport more difficult.

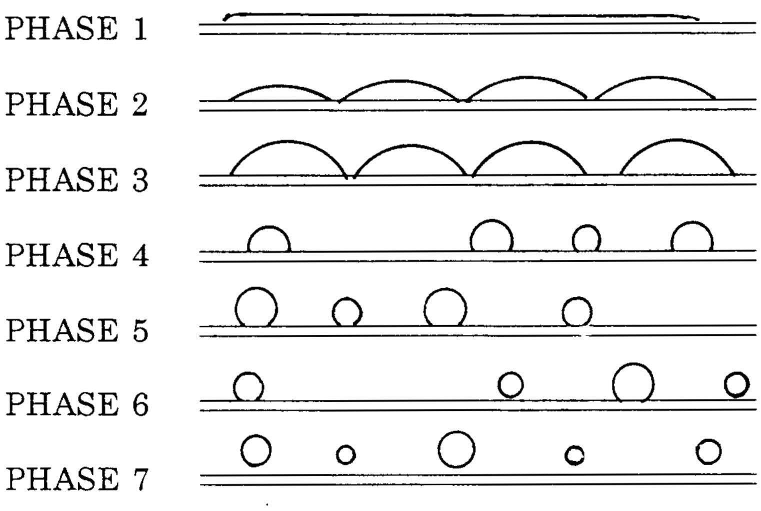
B. Oily Soils

The basic interaction between a liquid and a solid was discussed in the previous chapter on repellent finishes. It was shown that the thermodynamic work of adhesion is given by the Young/Dupree equation, $W_A = \gamma_{L/A} (1 + \cos \Theta)$. From this it follows that liquids that spread on a surface will have a zero contact angle. Since the cosine of zero is 1, the work require to remove that liquid will two times the surface tension of the liquid. Most oils have a surface tension of about 30 dynes/cm so they will completely spread on nearly all fibers except teflon.

1. Roll-up Mechanism

Oily-soil removal will depend on the three phase boundary interaction that occurs in the detergent solution. The roll-up mechanism first postulated by Adams argues that for removal to take place, the surface forces generated at the three phase boundary of fiber/detergent solution/oily soil results in progressive retraction of the oil along the fiber surface until it assumes a contact angle of 180 degrees. Here the work of adhesion is zero (Cosine of 180 degrees equals -1) and displacement is complete. The various phases of the roll-up mechanism is shown in figure 57.

Figure 24. Rolling-up Process of Soil Release



2. Roll-up Thermodyamics

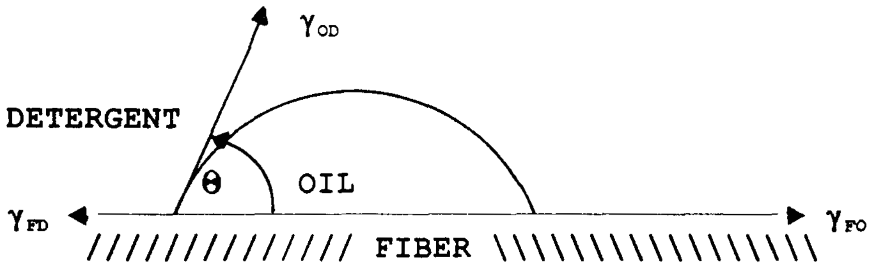
The surface forces responsible for three phase boundary between fiber-detergent and oil can be represented as interfacial tension vectors shown in figure 58. The forces responsible for roll-up is the resultant (R) of interfacial tensions as expressed by the equation:

$$R = \gamma_{F/O} - \gamma_{F/D} + \gamma_{O/D} \text{Cos } \Theta_d$$

where: $\gamma_{F/O}$ = the interfacial tension between fiber and oil
$\gamma_{F/D}$ = the interfacial tension between fiber and detergent
$\gamma_{O/D}$ = the interfacial tension between oil and detergent

Θ_d = the dynamic contact angle.

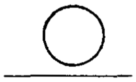
Figure 25. Fiber-Oil-Detergent Interaction



In order for the dynamic contact angle (Θ_d) to change from zero to 180 degrees, the resultant (R) must be positive. R is positive when the quantity - (fiber/oil minus fiber/detergent interfacial tension) - is greater than the oil/detergent interfacial tension ($\gamma_{F/O} - \gamma_{F/D} > \gamma_{O/D}$). It follows then that when R is greater than zero, the contact angle increases.


$\Theta < 90$


$\Theta > 90$


$\Theta > 180$

On the other hand when R equals zero, the contact angle is in equilibrium and the oil drop stops receding. However if R is less than zero, the contact angle is smaller and the drop spreads on the surface.


Θ


Smaller Θ

From this it follows that roll-up and spontaneous release occurs when:

$$\gamma_{F/O} - \gamma_{F/D} > \gamma_{O/D}$$

and that redeposition occurs when:

$$\gamma_{F/O} - \gamma_{F/D} < \gamma_{O/D}$$

It is well to remember that: 1. zero interfacial energy exist when the attractive forces operating between molecules of a liquid exactly equal the attractive forces operating between the outermost molecules of a solid. Cotton or other hydrophilic fibers will have very low interfacial tensions with water because of hydrogen bonding. 2. High interfacial energy exist when one surface is non-polar and the other is polar, for example, hydrocarbon oils in contact with hydroxyl or ionic charged solid surfaces.

It is known that cellulosic fibers have good oily soil release. For cellulosic surfaces, $\gamma_{F/D}$ is low and $\gamma_{O/F}$ is high. On the other hand polyester fibers are known to have poor soil release. For polyester surfaces, $\gamma_{F/D}$ is high and $\gamma_{F/O}$ is low. It follows therefore that for spontaneous soil release to occur, the fiber surface must be hydrophilic and the balance of interfacial energies must be:

$$\gamma_{O/F} > \gamma_{O/D}$$

Table 17 illustrates the effect of the influence of outermost molecules on a fiber surface. From thermodynamic considerations, non-polar finishes such as silicones, polyethylene and fluorochemicals increase the interfacial tension between the detergent bath and the fiber and therefore should make soil release worse. The data support these thermodynamic predictions since both the fluorochemical and the silicone finish on 100% cotton fabric reduced the amount of soil removed.

Table 17.

Effect of Hydrophobic Surfaces on Soil Release

Fabric Treatment	% Soil Removed*
Unfinished cellulose	95
Acrylic latex finish	88
Fluorochemical	60
Silicone	45

* Soil was a mixture of iron oxide suspended in oleic acid. The detergent contained an anionic surfactant. Fabric was 100% cotton.

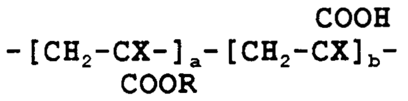
III. SOIL RELEASE CHEMICALS

The introduction of polyester/cotton blends in the early 1960's brought to light the need for soil release chemicals. Up until that era, most all washable fabrics were constructed of 100% cotton. The laundry processes included high wash temperatures, harsh chemicals (caustic, lye, bleach) and starch. Most all normal stains could be removed from these fabrics. When polyester entered the picture, oily stains became more difficult to remove. About the same time, home laundry procedures were changing; lower wash temperatures and less harsh chemicals evolved to prolong the life of durable press finishes. Also starching became unnecessary as the garment didn't require ironing.

Milliken can be credited for being first to introduce soil release durable press fabrics to the consumer. They incorporated an acrylic acid copolymer into their electron beam curable DP finish and merchandised the fabric under the VISA^{R} label. Shortly thereafter, the rest of the industry followed suit with a host of different soil release finishes. In general, soil release finishes are film forming polymers capable of imbibing water. Today the number has stabilized into three distinct varieties. Two types work well on durable press finished cotton/polyester blends, e.g. acrylics and dual-action fluorochemicals. These are added into the final DP finish bath. A third type is engineered specifically for 100% polyester fabric, e.g. exhaustibles. They are best applied in the dye cycle (thus the name exhaustible) although they may be applied by pad-dry-cure.

A. Acrylic Soil Release Finishes

The chemical composition of acrylic SR finishes may be generalized as follows:



$$-[CH_2-\underset{COOR}{CX}-]_a-[CH_2-\overset{COOH}{CX}]_b-$$

Where: X = H (acrylic) or CH_3- (methacrylic)
R = Methyl or ethyl
a = 30 to 100 % b = 70 to 30 %

1. Polymethacrylic Acid PMAA

Poly(methacrylic) acid is completely water soluble and functions as a soil release finish. However the proper amount of cross-linking is necessary before the finish to functions properly. Table 9 shows that the soil release rating are influenced by the inclusion of a diepoxide crosslinking agent. When PMAA is crosslinked with only the diepoxide, marginal SR ratings are obtained. However if a small amount of diepoxide is added with DMDHEU, the soil release ratings are vastly improved. Increasing the amount of diepoxide causes the SR rating to drop again. This data supports the contention that the ultimate properties of the cured film deposited on the surface of the fiber determines soil release.

Table 9

Poly(methacrylic acid) Soil Release Finishes

Effect of Crosslinking

	SR Rating
PMAA + 14 % Diepoxide	2.0
PMAA + 21 % Diepoxide	2.5
PMAA + DMDHEU + 1.2 % Diepoxide	4.5
PMAA + DMDHEU + 3.0 % Diepoxide	2.5

2. Methacrylic Acid - Ethyl Acrylate Co-Polymers

Monomers containing carboxylic groups can be polymerized with vinyl and acrylic co-monomers to yield a range of co-polymers with varying carboxyl content. Co-polymers of methacrylic or acrylic acid and ethyl acrylate have been found to be particularly useful as soil release agents. An acid content of 70% or less give relatively high molecular weight emulsion polymers whereas higher proportions of acid renders the polymer water soluble and of lower molecular weight. A particularly good combination for soil release is 70% methacrylic acid and 30% ethyl acrylate. The effectiveness of co-polymers can be seen in Table 19. The data shows that when a 70/30 MAA/EA co-polymer is added to a typical durable press finish containing DMDHEU, the fabric possesses excellent soil release with fair durability. The data also shows that the SR ratings are substantially lowered if a diepoxide over cross-links the polymer.

Table 19

70/30 Methyacrylic Acid - Ethyl Acrylate SR Finish

Effect of Crosslinking

	SR Ratings		
	Initial	1 wash	5 washes
70/30 MAA/EA copolymer + DMDHEU	4.0	3.5	3.0
Above + 10 % Diepoxide	2.0	2.0	2.0

a. Mechanism

The mechanism by which these finishes work involves the imbibition of water by the cured polymer deposit. Cured polymer film were shown to swell in alkaline solutions and films with water weight gains of 550% or higher correlated with fabrics with improved soil release. Below this, no improvement in soil release was noted. Durability is also a function of crosslinking. The greater the crosslinking, the better the durability. However its a delicate balance that must be struck to give optimum results. Better soil release occurs at a pH of 11 than at a pH of 8. In fact the soils can be seen to roll up and float away without the need of a detergent at a pH of 11. The reason for this is that the polycarboxylic acids are weakly anionic as the free acid. When neutralized with alkali, they become 100% ionic and develop a strong anionic charge. Under these conditions, they are extremely hygroscopic and being polyelectrolytes, increase the interfacial free energy at the soil/fiber interface.

3. Practical Considerations and Fabric Properties

1. About 6 to 10% acrylic soil release agent is needed to give good results. The polymeric films are stiff and brittle, giving the fabric a stiff and harsh hand. Being brittle and stiff, the finish tends to cause dusting, excessive needle and sewing thread breakage. 2. Most of the finish is lost after the first wash; however, the small amount remaining is effective for many launderings. The fabric is considerably softer after washing. 3. Excellent soil release results can be obtained when the optimum conditions are met. It is the most effective finish against dirty motor oil. 4. The

finish is temperamental. It takes precise condition at the finishing plant to give reproducible results. 5. The finish is cost-effective for work clothing when dirty motor oil release is a significant quality.

D. Dual Action Fluorochemical Soil Release

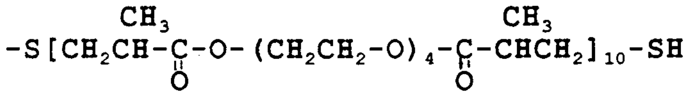
A unique block co-polymer, developed by the 3M company (Scotchgard Brand Dual-Action Fabric Protector) combines oil repellency with soil release. While conventional fluorochemical water and oil repellent finishes have an adverse affect on soil release, the co-polymer overcomes this deficiency. The hybrid polymer backbone is comprised of segments based on polyoxyethylene united with segments containing long-chain perfluoroaliphatic groups. Figure 59 shows the structure of the H portion (the hydrophilic portion), the F portion (the perfluoroaliphatic portion) and the block co-polymer. The H section is a sulfhydryl-terminated co-polymer of tetraethylene glycol dimethacrylate and hydrogen sulfide containing 50% by weight of recurring ethylene oxide units. The F section contains poly(N-methylperfluoro-octanesulfonamidoethyl acrylate). The block co-polymer has recurring units of perfluoro acrylate portion attached to the sulfhydryl-terminated glycol dimethacrylate.

The individual segments alone do not confer effective soil release; however, when combined into a single molecule, the new composition is effective both as a soil release agent and an oil repellent finish. Durable press reactants are necessary to cross-link the finish.

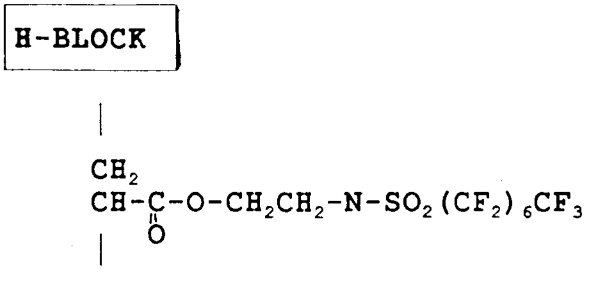
1. Composition of Polymer

Figure 28. Fluorochemical Soil Release Agent

H-BLOCK

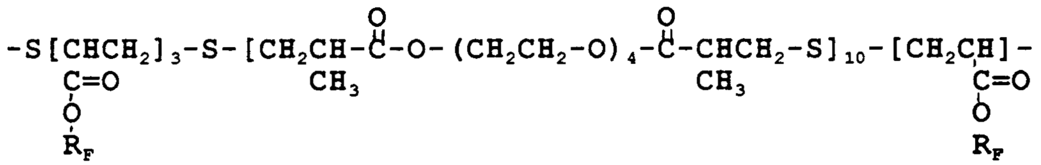


$$-S[CH_2CH-\overset{CH_3}{\underset{\underset{O}{\|}}{C}}-O-(CH_2CH_2-O)_4-\overset{CH_3}{\underset{\underset{O}{\|}}{C}}-CHCH_2]_{10}-SH$$



$$\begin{array}{l} \text{H-BLOCK} \\ | \\ CH_2 \\ CH-\underset{\underset{O}{\|}}{C}-O-CH_2CH_2-N-SO_2(CF_2)_6CF_3 \\ | \end{array}$$

POLYMER



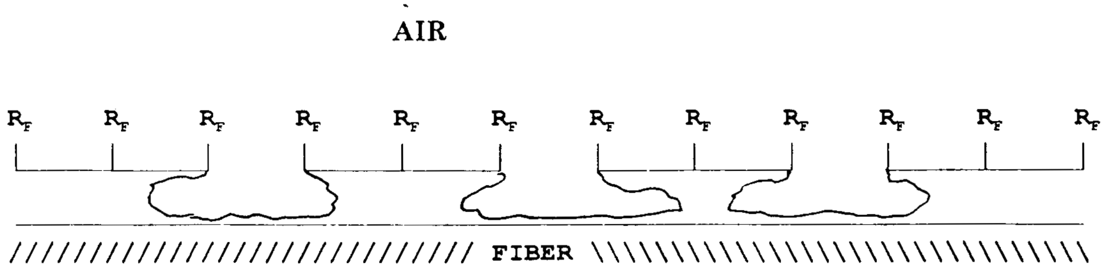
$$-S[\underset{\substack{|\\ C=O\\ |\\ O\\ |\\ R_F}}{C}HCH_2]_3-S-[CH_2\underset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-O-(CH_2CH_2-O)_4-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{CH}CH_2-S]_{10}-[CH_2\underset{\substack{|\\ C=O\\ |\\ O\\ |\\ R_F}}{CH}]-$$

2. Mechanism

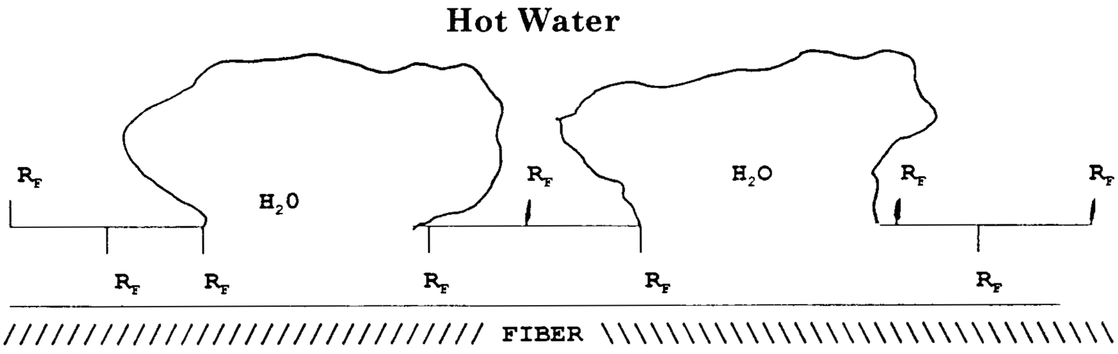
The uniqueness of this material is related to the tendencies of non-polar perfluoro alkyl side chains to orient outward towards air. During the drying and curing stage, polymer mobility allows the tails to orient outward. The oxyethylene segments are forced to the interior of the film and so the outermost film layer is richly populated by the low interfacial energy perfluoro segments. This provides a low critical surface tension which favors oil repellency. In water, the polyoxyethylene segments swell, causing the polymer to "flip-flop". The surface is now hydrophilic favoring the release of soil. The flip-flop mechanism is pictured in figure 60.

Figure 29 "Flip-Flop" Mechanism

Orientation When Dry



Orientation When Wet (During Laundry)



2. Practical Considerations and Fabric Properties

The product is very expensive; however, a small amount goes a long way. Good results can be obtained with about 0.5% add-on. Overall soil release ratings are good; however, this finish is not as effective toward dirty motor oil release as is the acrylic SR finish. The cured film properties and the very small add-on has little or no effect on fabric hand. Sewing, dusting and the other negative fabric properties associated with the acrylic SR finish are non-existent with this finish. It is important to include DP crosslinking resins to make it durable to laundering. For this reason it is used mainly on polyester/cotton blends and not on 100% cotton.

E. Hydrophilic Soil-Release Finishes for 100% Polyester

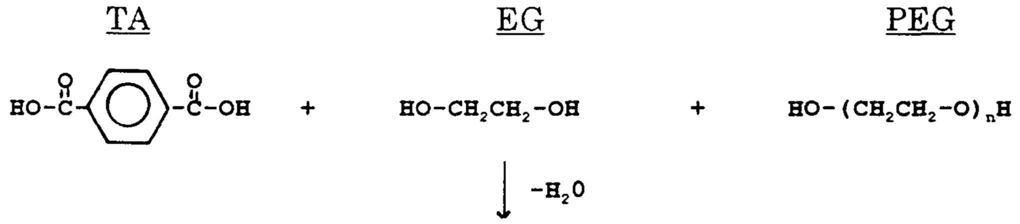
Effective soil release finishes have been developed for 100% polyester fabrics which are best applied during the dye cycle and are often called ***Exhaustible*** SR finishes. The are also called ***Co-Crystallizing*** SR finishes. This class of SR chemicals are composed of water dispersible, low molecular weight block co-polymers which have recurring blocks of hydrophilic segments attached to short blocks of PET. The hydrophilic segment is either polyoxyethylene or sulfoisophthalic acid. The PET portion provides attachment to the polyester fiber surface through secondary forces. The most effective application conditions are the same as those for exhaust dyeing polyester fibers with disperse dyes. This method results in a uniform deposition of the finish on the fiber surface. Pad applications are sometimes used; however, thermosoling temperatures are needed to get fixation.

1. Polyoxyethylene Co-Polymers

Figure 61 shows a schematic of the monomers used to make this type of co-polymer. Terephthalic acid, ethylene glycol and polyethylene glycol monomers are mixed in proper proportion and condensed to form a low molecular weight polyester. This polymer readily disperses in water and gives a product that is easy to handle and to apply to fabric. The composition of the monomers can be changed to yield products that leave the fabric with a soft slick hand or a dry stiffer hand.

Figure 30. Polyoxyethylene Type SR Finish

Monomer



Polymer

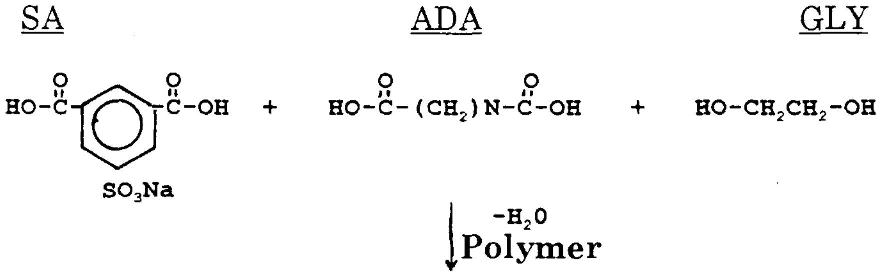
-TA-EG-TA-PEG-TA-EG-TA-PEG-

2. Sulfoisophthalic Acid Co-Polymers

Figure 62 show a schematic of a second variety of polyester SR finishes. This composition utilizes sulphoisophthalic acid as the hydrophilic portion and an aliphatic dibasic acid to control polymer softening point. The resulting co-polymer is water dispersible and being ionic in nature, requires the inclusion of an electrolyte to facilitate its exhaustion onto the fiber surface.

Figure 31. Sulphoisophthalic Type SR Agent

Monomers



-SA-GLY-ADA-GLY-SA-GLY-SA-GLY-ADA-

3. Practical Considerations and Fabric Properties

These finishes work best on loosely structured, textured polyester fabrics. Fabrics made from continuous filament or spun 100% polyester yarns are not responsive to these finishes. The driving force for exhausting the polyoxyethylene type is inverse solubility behavior exhibited by these types of materials. Polyethers are more soluble cold than hot. The high temperatures experienced in the dye bath reduces the co-polymer's water solubility favoring exhaustion. Oily-soil release on the loosely structured knits is fairly good. Oily-soil release on spun yarn and continuous filament fabrics is poor. All polyester fabrics are rendered more water wickable. Water quickly penetrates treated fabrics and is transported away from the source. This quality has been promoted as improved summer comfort, the ability to adsorb and wick away body perspiration. The finish is not effective at all on polyester/cotton blends. The finish imparts good soil anti-redeposition protection to treated fabrics and a modest measure of antistatic protection.

IV. OTHER IMPORTANT CONSIDERATIONS

A. Non-Ionic Detergents

Non-ionic detergents based on polyoxyethylene have the unique feature of becoming less soluble as the temperature rises, exhibiting a cloud point. Cloud point temperature is based on the structure of the surfactant molecule. At this temperature the surfactant is, for all practical purposes, another water insoluble oil. As a non-dispersed oil, it is capable of adsorbing onto the fiber surface and either co-mixing with the oily soil or adsorbing onto the surface of particulate soil. When the temperature drops below the cloud point, the ether linkages again form hydrogen bonds with water and the molecule resumes surfactant qualities. The phase-change induced adsorption of the surfactant onto the fiber and soil promotes the thermodynamic boundary interfacial tensions which favor spontaneous soil release. Table 11 compares the detergent qualities of anionic, cationic and non-ionic surfactants. The soil was deposited on four polymer films representing different fibers.

Table 20

Effect of Surfactant Type on Soil Removal From Polymer Films

Detergent	% Soil Removed Cellulose	PET	Nylon	Teflon
Sodium Laurel Sulfate	92	3	28	22
Cetyltrimethyl Ammonium Bromide	93	7	82	26
Ethoxylated Nonyl Phenol	94	99	99	96

This study showed that: 1. the non-ionic surfactant was equally effective and removed nearly all the soil from all four surfaces since the detergent study was carried out above its cloud point. 2. All three types of surfactants worked equally well on cellophane. One might conclude that the surfactant had little to do with soil release. 3. On the hydrophobic films, (PET, teflon and nylon) the cationic surfactant was effective on nylon but not on the other two. Apparently the fiber has an affinity for the cationic surfactant whereas PET and teflon has none. 4. None of the ionic surfactants work on PET since virtually none of the soil was removed. While the amount removed by the anionic from teflon and nylon wasn't great it was substantially more than was removed from polyester.

B. Soil Release Tests

1. AATCC Method 130

In this test, oily stains are placed on the fabric, laundered and visually rated for the severity of the remaining stain on a scale of one-to-five. The visual judgement is based on contrast, what the eye perceives to be the difference between the stained area and the rest of the fabric. There are variations of the test where a number of different staining materials are used. Regardless of the stain, judgement is still what the eye perceives. Some refinements have been attempted where optics are used rather than humans to make the judgement. From a practical point of view?these tests duplicate what the consumer does. However, from a scientific point of view, the data may be misleading or inconclusive since the quantity of soil removed is what's important. The intensity of the residual stain may or may not reflect the amount of soil remaining since it may be influenced by other factors. For example, the amount deposited on the spot may spread over a wider area during laundering and while it hasn't been removed, the intensity of the stain is less allowing one to conclude that less soil remains. Also there may be light scattering bodies in the fabric which affect the visual appearance of the stain and misleads one as to the amount of soil removed.

2. Release Point

Release Point (Rp) is defined as the surface tension of a detergent solution where oily soil just separates from fiber surfaces. This technique for quantifying soil release is based on thermodynamic considerations which state that the work of adhesion (the quantity $\gamma_{F/O} - \gamma_{F/D}$) must be overcome by the detergent for oily soil to separate from a solid surface. In a detergent solution, when the contact angle becomes 180 degrees and the oil just separates from the fiber, the interfacial tension between the oil/detergent will equal the work of adhesion.

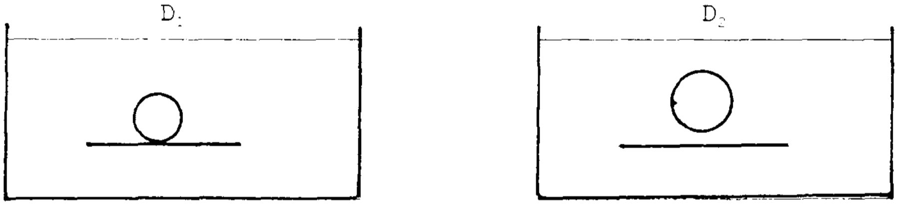
$$\gamma_{O/D} = (\gamma_{F/O} - \gamma_{F/D}).$$

The quantity $\gamma_{O/D}$ is influenced by the adsorbed surfactant. Therefore the surface tension of a bath where release just occurs is proportional to the work of adhesion between the oil and fiber surface.

a. Rp Determinations

The surface tension of a solution where oil just separates from a surface can be closely approximated by exposing the soiled surface to a series of solutions with decreasing surface tension. Consider figure 63:

Figure 32. Roll-up of Oil in Detergent Solutions



D_1 represents the roll-up condition in a detergent where the contact angle is nearing 180 degrees. The oil is just about to separate. D_2 is the detergent where the contact angle is 180 degrees and the oil has separated. The work of adhesion (the quantity $\gamma_{O/D} - \gamma_{F/D}$) is bracketed by the surface tension of the two solutions. From a practical point of view, this determination can be made by observing oil roll-up when an oily soiled specimen is subjected to a series of surfactant solutions of known surface tensions. The surface tension of the solution where the oil just floats away from the fabric is recorded as the Release Point (Rp).

b. Application of Rp Measurements

The Rp technique has been used to study the relationship between hydrophilic SR agents applied to a variety of 100% polyester fabrics. The test was conducted statically and dynamically. In the static test, the soiled samples were placed in the surfactant solution at room temperature. The dynamic test consisted of carrying out the observations in an ultrasonic bath.

Table 21 compares the data obtained on a series of SR treated polyester fabrics. Knit and woven fabrics made from the same feed yarn, textured and untextured, were tested both statically and dynamically. The same treated fabrics were stained and laundered. Afterwards, the amount of residual soil was determined by quantitative extraction.

Table 21

Rp Results Versus Residual Soil

	Rp (Dynes/cm)		Residual Soil
	Static	Dynamic	% Remaining
Woven, Spun Yarn	15.0	24.0	90
Woven Untextured	15.0	27.0	50
Knit, Untextured	23.0	35.5	66
Woven, Textured	25.0	41.0	28
Knit, Textured	28.5	45.0	11

The data shows: 1. there is good correlation between Rp and oil removal. Higher Rp numbers correlated with greater removal. 2. All of the unfinished polyester fabrics showed no release whatsoever, even in the ultrasonic bath. 3. The same experiments carried out on Mylar film gave values of 70 dynes/cm for treated Mylar and no release for the untreated film. 4. The values obtained in the ultrasonic bath were substantially higher than the static ones. This relates to the need for kinetic energy to transport the released oil droplet after the work of adhesion is overcome.

3. Geometry of Yarns and Fabrics

The geometry of the yarn and fabric influences soil release. Both the Rp data and the extraction results show that soil release from woven fabrics made from spun and untextured yarns is worse than those from textured yarns. Textured knit fabrics are more releasing than textured wovens. The data suggests that as the void spaces created by adjoining fibers become smaller, soil release becomes more difficult. Smaller capillaries require greater energy for detergent solutions to penetrate and detach the soil from the fiber surface. Also the small voids make it difficult for the detached soil to migrate to the fabric-bath interface.

V. REFERENCES

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CHAPTER 11

FLAME RETARDANT FINISHES

The desire for textiles having a reduced tendency to ignite and burn has been recognized for considerable time during man's recorded history. The use of asbestos as a flame resistant material was recorded in Roman times. Wyld (6) was issued a patent in 1735 describing a finishing treatment for cellulosic textiles based on alum, ferrous sulfate and borax. In 1882, Gay-Lussac (3) published the first systematic study of the use of flame retardants. Before delving into the chemistry of flame retardant finishes, it is necessary to first understand that there is no single test that determines whether a fabric is flame retardant or not. The test conditions used to make this determination will reflect on the specific fabric and its intended end-use. For example, all apparel fabrics are expected to pass a 45 degree flame test; however, those destined to be used as children sleep-wear are expected to pass a vertical ignition test. Drapery, upholstery and carpets all have their own ignition tests designed to evaluate how the article performs in its environment. Flame retardant tests and fabric performance specifications are discussed in detail in other references (1,2,3), and the reader is urged to consult these for a more in-depth understanding. The important point here is that the following discussions must be viewed in context with the test used to make the observations. The terms associated with flame-retardant finishing and fabric flammability in general are often confusing, for example flammable versus inflammable, fire resistant versus flame resistant. If clarification is needed, the reader is referred to Tesoro's (5) compilation of definitions associated with flammability.

Generally speaking, a fabric is deemed to be flame retardant if it does not ignite and create a self-sustaining flame when subjected to a heat source. Therefore a pile fabric made from rayon fibers is considered to be highly flammable while a tightly woven fabric made from high twist yarns easily passes the 45 degree ignition test. Neither however pass the vertical ignition test. Thermoplastic fibers present another anomaly - certain fabrics do not ignite when tested by the vertical test, the fabric melts and shrinks away from the heat source. Other fabrics made from the same fiber ignite and fail the test because the fabric construction prevents the rapid withdrawal of the melt from the flame. And finally, there are some fibers which will not ignite at all, they will however char.

I. THEORY OF COMBUSTION

When solid materials are heated, physical and chemical changes occur at specific temperatures depending on the chemical make-up of the solid. Thermoplastic polymers soften at the glass transition temperature (Tg), and subsequently melt at Tm. At some higher temperature (Tp), both thermoplastic and non-thermoplastic solids will chemically decompose (pyrolyze) into lower molecular weight fragments. Chemical changes begin at Tp and continue through the temperature at which combustion occurs (Tc). These four temperatures are very important when considering the flame resistance of fibers. Another important factor in combustion is the Limiting Oxygen Index (LOI). This is the amount of oxygen in the fuel mix needed to support combustion. The higher the number, the more difficult it is for combustion to occur. Values for these parameters for various fibers are given in Table 22.

Table 22

Flammability Parameters for Fibers

	°C				%	
Fiber	Tg soften	Tm melts	Tp pyrolysis	Tc combustion	LOI	Thermoplastic
Wool			245	600	25	no
Cotton			350	350	18.4	no
Viscose rayon			350	420	18.9	no
Nylon 6	50	215	431	450	20-21.5	yes
Nylon 6,6	50	265	403	530	20-20.1	yes
Polyester	85	255	420-427	480	20-21	yes
Acrylic	100	220	290	250	18.2	yes
Polypropylene	-20	165	469	550	18.6	yes
Modacrylic	80	240	273	690	29-30	yes
PTFE	126	327	400	560	95	yes
Nomex	275	375	410	500	28.5-30	yes
Kevlar	340		590	550	29	no
PBI	400		500	500	40-42	no

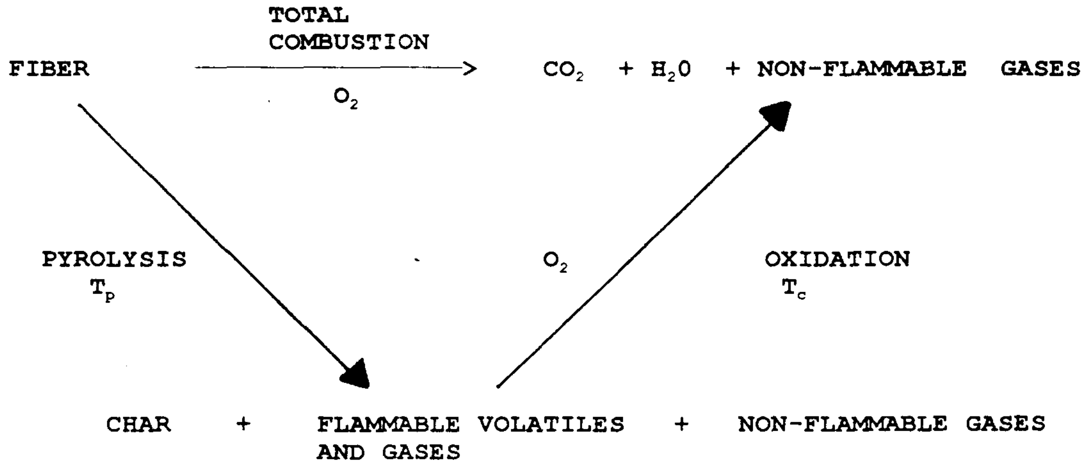
For non-thermoplastic fibers, Tp and/or Tc is less than Tg and/or Tm, however for thermoplastic fibers Tp and/or Tc is greater than Tg and/or Tm. Natural fibers are not thermoplastic, therefore when they are subjected to a heat source, pyrolysis and combustion temperatures are encountered before softening or melting temperatures are reached and eventually ignite. On the other hand, low melting thermoplastic fibers will melt and drip away from the flame before pyrolysis and combustion temperatures are reached. However if the melt doesn't shrink away from the flame front, pyrolysis and combustion temperatures are eventually reached and ignition will occur.

Natural fibers can be made flame retardant and like some synthetic fibers, e.g., Nomex, Kevlar and PBI, offer protection to a wearer because they do not shrink away from a flame. Thermoplastic fibers may appear to offer protection because they pass the ignition test by shrinking away from the flame; however, in reality this exposes to wearer to direct heat and to burns caused by contact of the molten mass with the body.

II. COMBUSTION OF CELLULOSE

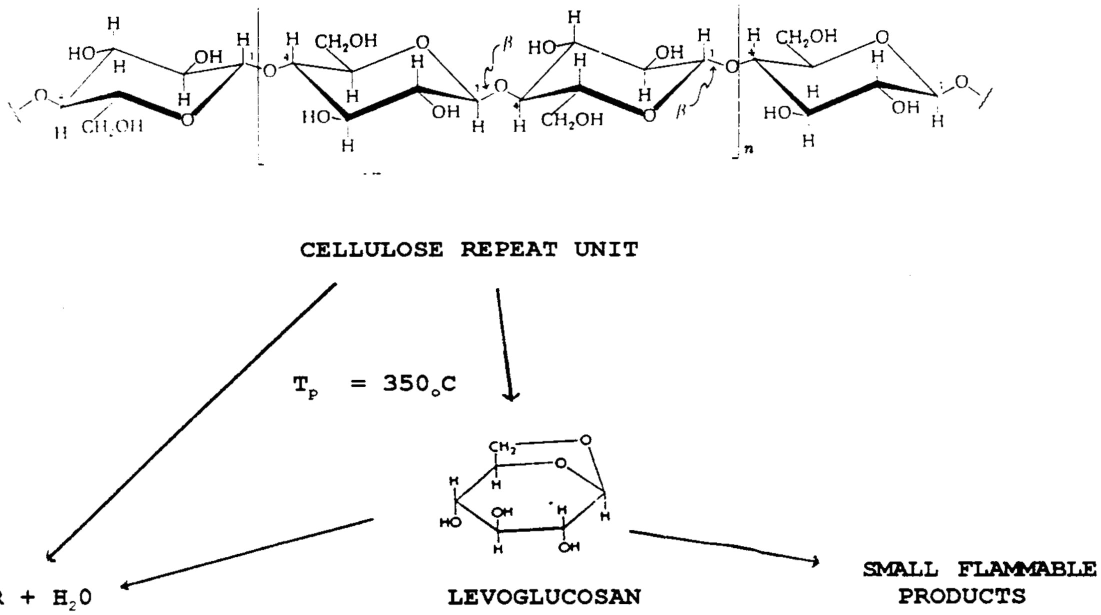
When cellulose fibers are heated, three classes of volatile chemicals are generated at pyrolysis temperature, 350° C, 1. flammable volatiles, e.g., alcohols, aldehydes and alkanes, 2. flammable gases, e.g., carbon monoxide, ethylene and methane and 3. non-flammable gases, e.g., carbon dioxide and water vapor. If oxygen is present when the pyrolysis products reach or exceed the combustion temperature, oxidation takes place (burning) and the volatiles are converted to carbon dioxide and water as shown in figure 64.

Figure 64. Combustion Cycle



Levoglucosan, shown in figure 6. is the major product formed by the pyrolysis of cellulose. It is the cyclic acetal created when the alpha-1,4-glucosidic linkage is split, and a molecule of water is lost between the C(1) and C(6) hydroxyls of the anhydroglucose unit.

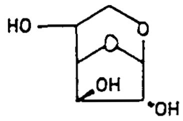
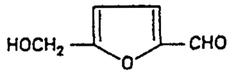
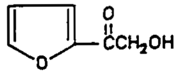
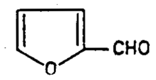
Figure 65. Cellulose Pyrolysis Products



Other products created by pyrolysis are listed in table 23. These volatile products and levoglucosan can be considered the "fuel" that when mixed with oxygen propagates the combustion process. Should these products not be present, ignition would not occur or be sustained.

Table 23

Other Pryolysis Products

1,6-Anhydro-beta-glucofuranose	
5-Hydroxymethyl-2-furfural	
2-Furylhydroxymethyl ketone	
Furfural	

III. FLAME RETARDANCY

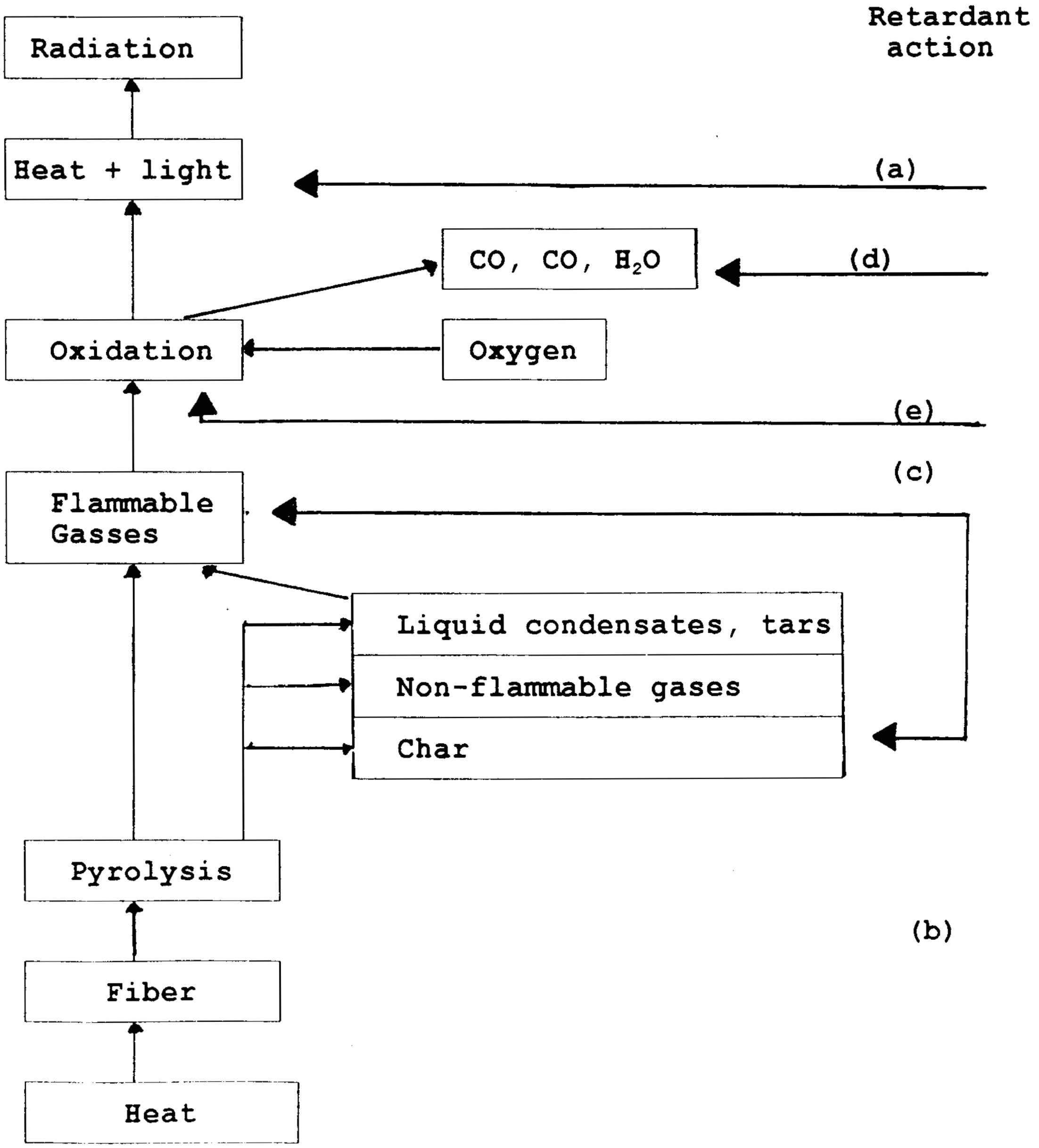
A. Feedback Mechanism

Figure 66 shows the combustion process as a feedback system which may be interrupted at various points to create flame retardancy. Thus to be effective, a flame retardant must interfere with the feedback mechanism in one or more of the following ways:

(a). Removal of heat.
(b). Increase decomposition temperature T_p at which significant volatiles form.
(c). Decrease the amount of combustible gases and promote char formation. This should happen at reduced temperatures so ignition will not occur.
(d). Prevent the access of oxygen to the flame or dilute the fuel gases in the flame to concentration below which they will not support combustion.
(e). Increase the combustion temperature, T_c, of the fuels and/or interfere with their flame chemistry.

Rarely do flame retardants function by a single mode. Today it is more common to refer to their retardant activity as either functioning in the *condensed phase* (modes (a), (b) and (c)), the *vapor phase* (modes (d) and (e), or both. Water, either from a fire hose or water from a hydrated salt will extinguish a flame by mode (a). Nomex and Kevlar function by mode (b). The structures of these polymers are such that T_p has been significantly increased. Most flame retardants for cellulose fibers function by mode (c), promoting the formation of char and reducing the amount of levoglucosan produced by pyrolysis. Some phosphorous and borate flame retardant are thought to form glassy polymers on the surface of the fibers, insulating the polymer from heat (modes (a) and (d)).

Figure 36. Combustion Feedback Mechanism



Some of the variables that must be identified in order to characterize the burning behavior of a textile material are listed in table 24. These factors are influenced by the nature of the fiber, yarn and fabric structure, density and dimensions, presence of moisture, dyes, finishes and impurities, environmental factors, e.g., temperature, humidity, oxygen availability and air velocity. Test procedures usually standardize environmental factors so the other factors may be evaluated.

Table 24

Parameters that Characterize Burning Textiles

Parameter	Detail
Ignition	Nature of ignition source, ease of ignition.
Flame propagation	Propagation velocity in all directions, and direction influence of mode of ignition, extent of burning, rate of sample consumption, rate of flame extinction, character of afterglow.
Energy	Total energy output, rate of energy evolution, rate of mass loss, rate of energy transfer to skin, rate of energy transfer across specimen.
Combustion	Gaseous products and concentrations, particulates (smoke) products and densities, toxicity of products, nature of flaming debris, nature of char.

B. Char Formation

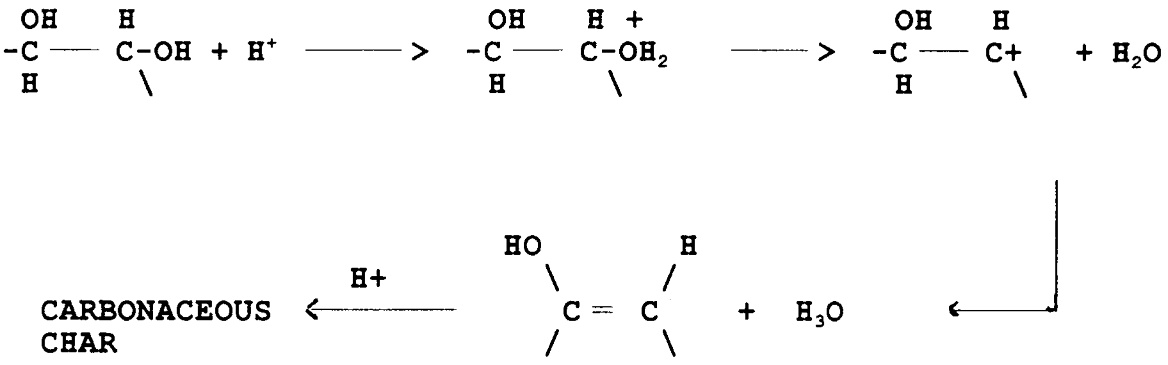
Since char is a major factor in retarding the burning of cellulosic fibers, it is beneficial for the reader to briefly look at the mechanism of its formation in order to appreciate and understand the significance of the materials that work well as flame retardants. Overall, the formation proceeds by the total dehydration of cellulose into carbon and water.

1. Reactions Leading to Char Formation

a. Overall Reaction

$$-(C_6H_{10}O_5)n- \xrightarrow{300^\circ C} 6n\ C + 5n\ H_2O$$

b. Mechanism



C. How Certain Elements Work

There are many compounds reported in the literature that function as flame retardant finishes for specific fibers. Most all of these compounds have a few elements in common that provide the necessary protection - namely boron, phosphorous, nitrogen and halogens. Before delving into the specific flame retardant compounds, it would be instructive to discuss how these elements work.

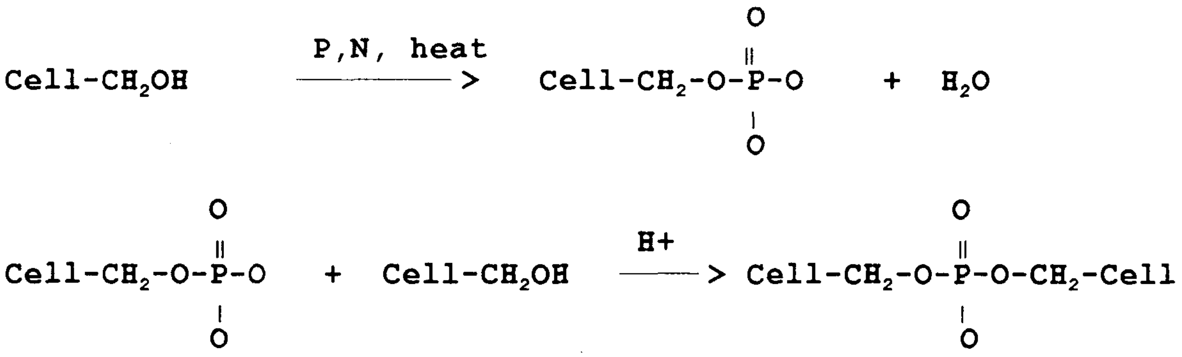
1. Boron

Boric acid (H_3BO_3) and borax ($Na_2B_4O_7$) are often used as non-durable flame retardants in applications such as cellulose batting and shredded newspaper for insulation. Boron functions in the *condensed phase* as a lewis acid and as mentioned earlier, coats the fiber with a glassy polymer to insulate the polymer.

2. Phosphorus and Nitrogen

Phosphorus and nitrogen also work in the *condensed phase*. Phosphorus compounds react with the $C_{(6)}$ hydroxyl of the anhydroglucose unit blocking the formation of levoglucosan. This reduces the amount of fuel to the flame. Additionally, phosphorous promotes char formation. The acidity associated with certain phosphorous analogues and its electrophilic nature lowers the activation energy for dehydrating cellulose. Additionally there is the possibility of crosslinking cellulose chains which further enhances char formation.

Nitrogen alone is not an effective flame retardant, however it acts synergistically with phosphorous. It is thought that nitrogen reacts with phosphorous to form polymeric species containing P-N bonds. Nitrogen enhances the electrophilicity of phosphorous thereby making it a stronger Lewis acid and also promoting the phosphorylation reaction with the $C_{(6)}$ hydroxyl of the anhydroglucose ring. This mechanism may be written as follows:



$$\text{Cell-CH}_2\text{OH} \xrightarrow{\text{P,N, heat}} \text{Cell-CH}_2\text{-O-}\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{O}}{|}}{\text{P}}}\text{-O} + H_2O$$

$$\text{Cell-CH}_2\text{-O-}\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{O}}{|}}{\text{P}}}\text{-O} + \text{Cell-CH}_2\text{OH} \xrightarrow{\text{H+}} \text{Cell-CH}_2\text{-O-}\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{O}}{|}}{\text{P}}}\text{-O-CH}_2\text{-Cell}$$

3. Halogens

Chlorine and bromine operate in the *vapor phase* by forming free radicals that scavenge hydrogen and hydroxyl free radicals. Combustion occurs by a free radical, chain reaction mechanism of which hydrogen and hydroxyl radicals are major reaction species. The halogen radicals deactivate them, causing the chain reaction to break down. Antimony and phosphorus enhances the efficiency of the halogen radicals. Phosphorus effect is additive while antimony is synergistic. The optimum ratio of Sb:X is 1:3. This suggests that SbX_3 is an important intermediate in this process. The important gas phase reactions in combustion are:

$$H\cdot + O_2 \longrightarrow HO\cdot + O\cdot \qquad +8 \text{ kcal/mole}$$

$$O\cdot + H_2 \longrightarrow HO\cdot + H\cdot \qquad -7 \text{ kcal/mole}$$

$$HO\cdot + CO \longrightarrow CO_2^{\cdot} + H\cdot \qquad -81 \text{ kcal/mole}$$

Species that remove H and or HO will slow the combustion reaction. Halogen do this in the following manner:

$$R\text{-}X \longrightarrow R\cdot + X\cdot$$

$$X\cdot + RH \longrightarrow HX + R\cdot$$

$$H\cdot + HX \longrightarrow H_2 + X\cdot \qquad \text{When } X = Cl, -1 \text{ kcal/mole}; \; X = Br, -17 \text{ kcal/mole}$$

$$HO\cdot + HX \longrightarrow HOH + X\cdot \qquad \text{When } X = Cl, -8 \text{ kcal/mole}; \; X = Br, -24 \text{ kcal/mole}$$

The X radical is much less reactive than H and HO and cannot effectively propagate chain reaction. Antimony reacts with X radicals to form SbOX and SbX_3 both of which will thermally decompose to yield halogen radicals.

IV. FLAME RETARDANT CHEMICALS AND PROCESSES FOR CELLULOSE

Durable and non-durable finishes may be used to render cotton, rayon or other cellulosic fibers flame retardant. There are many applications where non-durable flame retardants are adequate, for example, on drapery and upholstery fabrics that will not be laundered. Should the products need cleaning, the finish can be reapplied afterwards. However, there are applications where durability is important, e.g. firefighter suits, foundry worker clothing, children sleepwear.

A. Non-Durable

1. Boric Acid/Borax

A mixture of boric acid/borax (sodium borate) is a commonly used non-durable flame retardant finish for cellulosic fibers. It is the safest with regard to carbon monoxide and smoke production during burning.

2. Diammonium Phosphate and Phosphoric Acid

Phosphorus based flame retardants function in the *condensed phase*. Non-durable, semi durable and durable treatments can be obtained with phosphorus based compounds. The presence of calcium ions negates the activity of phosphorous compounds. Whereas the ammonium salts decompose thermally into phosphoric acid by the loss of ammonia, the calcium salts do not. Presumably the calcium salts are not volatile and buffer the acidity of phosphoric acid so the generation of char is diminished.

3. Sulfamic Acid and Ammonium Sulfamate

Combinations of these compounds also function as non-durable flame retardants.

B. Durable

1. Tetrakis(hydroxymethyl)Phosphonium Derivatives

The bulk of today's durable flame retardant for cellulose centers around the use of derivatives of tetrakis(hydroxymethyl)- phosphonium salts (THP). These derivatives can be applied by padding, drying, curing and oxidizing to yield serviceable flame retardant fabrics. Add-ons are high and the handle of the fabric is stiffer so the finish is normally used for protective clothing applications.

a. Tetrakis(hydroxymethyl)phosphonium Chloride (THPC)

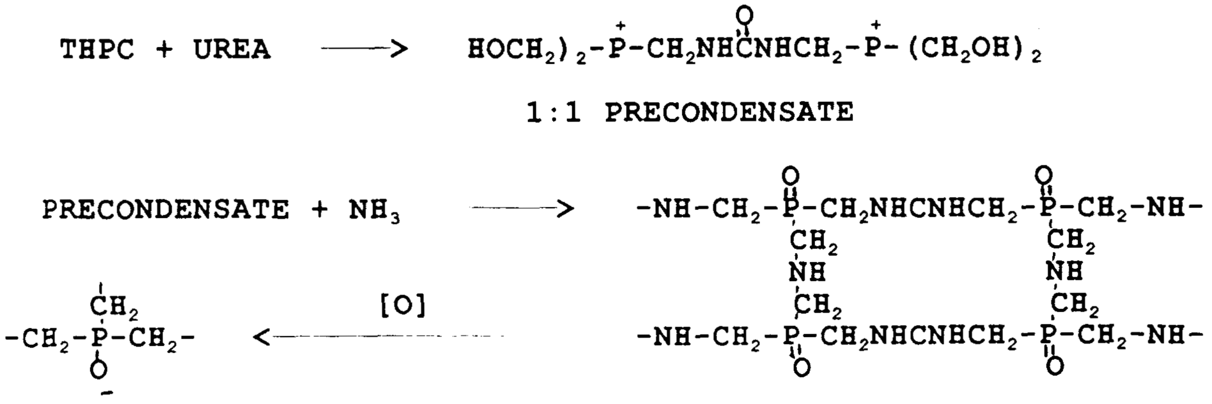
THPC is the most important commercial derivative and is prepared from phosphine, formaldehyde and hydrochloric acid at room temperature. It contains 11.5 % phosphorous and is applied by a pad-dry-cure -> oxidize -> scour process.

$$PH_3 + 4\,CH_2O + HCl \longrightarrow (HOCH_2)_4\,P^+Cl^-$$

The compound is highly reducing in character and the methylol groups condense with amines to form insoluble polymers. It is applied with urea, dried and cured. Control of pH and the oxidation state of the phosphorus is important in determining the flame retardant properties and the durability of the finish. The release of HCl may cause the fabric to tender during curing unless pH is controlled. The final step in finishing requires oxidation of P^{+3} to $P+^{5}$ with hydrogen peroxide. This step too must be controlled to prevent excessive tendering of the fabric. An alternative to the THPC is THPS. Sulfuric acid is used instead of HCl and the corresponding phosphine sulfate is formed in place of the phosphine chloride.

b. THPC-Urea Precondensate

The Proban process (Albright and Wilson) replaces heat curing with an ammonia gas curing at ambient temperature. This minimizes fabric tendering associated with heat and acids. A Precondensate of THPC with urea (1: 1 mole ratio) is applied, dried and the fabric passed through an ammonia gas reactor. An exothermic reaction creates a polymeric structure within the voids of the cotton fiber. The ammonia cure gives a P:N ratio of 12. Weight percentages of the respective elements should be P,N > 2%. To enhance durability and lightfastness of dyes, P^{+3} is oxidized to P^{+5} with hydrogen peroxide.



$$\text{THPC + UREA} \longrightarrow \text{HOCH}_2)_2\text{-}\overset{+}{\text{P}}\text{-CH}_2\text{NH}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{NHCH}_2\text{-}\overset{+}{\text{P}}\text{-(CH}_2\text{OH)}_2$$

C. Tetrakis(hydroxymethyl)phosphonium Hydroxide (THPOH)

From the forgoing discussion, THPC is usually partly neutralized with amines, amides and/or alkali. Complete neutralization of THPC with sodium hydroxide yields a compound referred to as THPOH. The distinction between THPC used in a partially neutralized condition and THPOH is difficult to define. If the curing agent is basic as is ammonia, the distinction become meaningless.

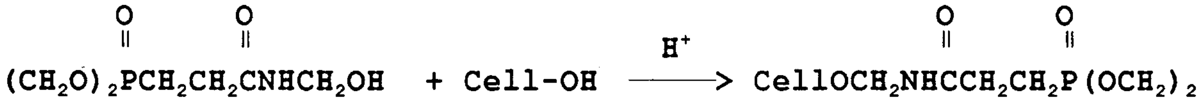
$$(HOCH_2)_4P^+Cl^- \quad + \quad NaOH \quad \xrightarrow{pH\ 7} \quad (HOCH_2)_4P^+OH^-$$

$$(HOCH_2)_4P^+OH^- \quad \longrightarrow \quad (HOCH_2)_3P \quad + CH_2O \quad + OH^-$$

THPOH-ammonia has received a great deal of commercial attention. The major advantage over THPC is reduced fabric tendering and reduced stiffness. Fabrics padded with THPOH give off formaldehyde during drying.

2. N-Methyloldimethyl Phosphonopropioamide (PYROVATEX CP)

Pyrovatex CP provides a method of attaching phosphorus to cellulose making use of N-methylol reactivity with cellulose. It is applied with a methylolated melamine resin using a phosphoric acid catalyst by a pad-dry-cure process. The high nitrogen content of melamine provides synergistic activity to the phosphorus of the flame retardant.

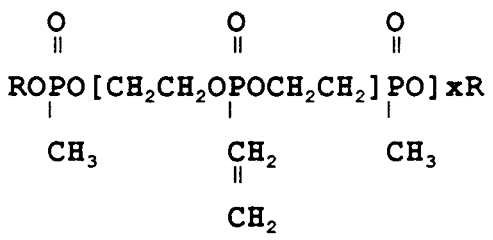


$$(CH_2O)_2\overset{O}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{C}}NHCH_2OH \quad + Cell\text{-}OH \quad \xrightarrow{H^+} CellOCH_2NH\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{P}}(OCH_2)_2$$

Fabric stiffening occurs when sufficient chemical is applied to give 2-3% phosphorus on weight of fabric. Also the acid may cause high strength loss if left in the fabric after curing; therefore, it is desirable to wash the fabric following the curing step. The finish tends to produce smoke in the curing oven. The smoke is composed of volatile fragments of the finish which condense in the cooler reaches of the oven. The condensate may drip back onto the fabric causing unsightly spots.

3. Fyrol 76

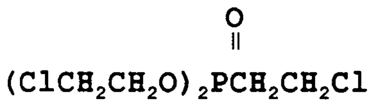
Fyrol 76 is an oligermeric phosphonate containing vinyl groups.
The finish is applied with N-methylol acrylamide with a free radical initiator (potassium persulfate), dried and cured.



$$RO\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{P}}O[CH_2CH_2O\overset{\overset{O}{\|}}{\underset{\underset{\underset{CH_2}{\underset{\|}{CH_2}}}{|}}{P}}OCH_2CH_2]\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{P}}O]xR$$

R = alkyl, CH_2CH_2OH

Antiblaze 77



$$(ClCH_2CH_2O)_2\overset{\overset{O}{\|}}{P}CH_2CH_2Cl$$

This product exhibits better abrasion resistance than THPOH-NH_3.

5. Phosphonic and Phosphoric Acid Derivatives

The literature is rich with references showing many imaginative ways of introducing phosphorus and nitrogen into cellulose fibers. Many products have been offered by chemical companies which have not succeeded as commercial ventures. It is beyond the scope of this book to completely review the full range of flame retardants, the reader is urged to consult other literature readings for a more thorough understanding (1,2,4).

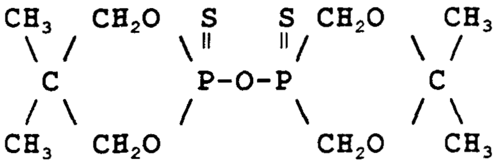
Cellulose phosphorylates with phosphoric and phosphonic acids. Urea, dicyandiamide and cyanamide are used to buffer the tendering action of the acids. Whenever levels of phosphorus attached are high enough, flame retardancy protection is good. Cellulose phosphate esters are hydrolytically unstable so durability to laundering is poor. The phosphonate esters are more durable however. The phosphates tend to chelate calcium ions when laundered in hard water. This reduces the flame retardancy of the finish as discussed earlier in the chapter. The phosphonates are less prone to do this.

V. RETARDANT SYSTEMS FOR SPECIFIC FIBERS

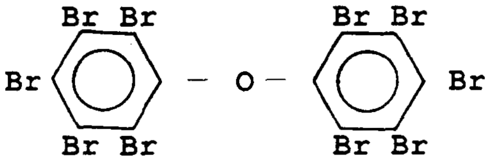
A. Rayon Additives

Flame retardant agents have been incorporated into rayon fibers during the fiber extrusion process. Listed below are several that have been used.

1. Thiophosphate (SANDOFLAM5060)

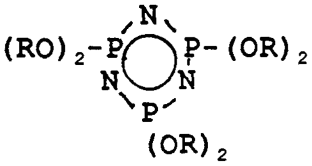


2. Decabromodiphenyl Oxide (DBDPO) and Antimony Oxide



DBDPO

3. Phosphazines



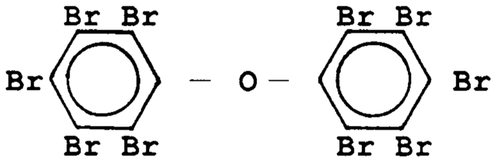
B. Polyester

Polyester fabrics, being thermoplastic, will melt and shrink away from the heat source allowing some fabrics to pass particular tests without any treatment. Certain tests however, have a melt drip specification to meet so finishes will be needed. The flame retardants that work best for polyester are halogenated compounds that function in the *vapor phase.* One of the best products to serve this purpose was tris-(2,3 dibromopropyl) phosphonate. (TRIS). The product offered good flame retardancy, acceptable fabric hand and good durability to repeated laundering. It passed the children sleepwear requirements. It could be exhausted from a dye bath or applied via the pad-dry-thermosol method. However TRIS is banned from commercial use because it failed the Ames mutagenicity test. It is on the regulated suspect carcinogen list. This finding came after the product had been on the market several years causing several million yards of treated fabric to be recalled by the Consumer Protection Agency (CPSC). The fabric producer was stuck with this inventory.

There are many halogenated compounds that improve polyester's flame retardancy. The trick is to apply the finish so that it doesn't affect the fabric hand

and still be durable to repeated launderings. Basically there are two methods of applying finishes. One method will bind insoluble compounds to the surface of the fiber. Finely ground particles are dispersed in water and glued to the surface with a binder. The second method is to find materials that are soluble in the polyester fiber and apply them as if they are disperse dyes. They can either be exhausted out of a dye bath or padded, dried and thermosoled. Listed below are several which have found some commercial success.

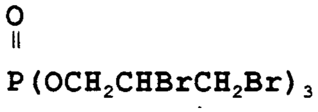
1. Decabromodiphenyl Oxide (DBDPO)



DBDPO

DBDPO is a solid material melting at 300-350 ^{0}C. which contains 83% bromine. It is sold as a water dispersion and is applied with a suitable binder to impart effective and durable flame retardancy to 100% polyester fabrics. There are many commercial formulations on the market differing in the blend of antimony oxide. One formulation, a 2:1 mixture of DBDPO and Sb_2O_3, is effective on polyester. Disadvantages of DBDPO are high add-ons needed for optimum retardancy and the stiff, boardy hand imparted due to the level of binder needed for durability. Additionally, the product is a white finely divided pigment which causes a loss in color yield.

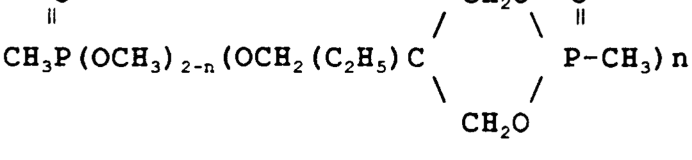
2. Tris-(2,3-Dibromopropyl) Phosphate (TRIS)



$$\overset{O}{\overset{\|}{P}}(OCH_2CHBrCH_2Br)_3$$

TRIS can be either be exhausted out of a dye bath or applied via the thermosol process. Hydrolysis products were found to be potentially carcinogenic and the product has been banned from use. All fabrics treated with TRIS have been recalled by CPSC.

3. Antiblaze 19T



$$CH_3\overset{O}{\overset{\|}{P}}(OCH_3)_{2-n}(OCH_2(C_2H_5)C\begin{smallmatrix}/ & CH_2O & \backslash \\ \backslash & CH_2O & /\end{smallmatrix}\overset{O}{\overset{\|}{P}}-CH_3)n$$

This product is a cyclic phosphonate containing 20% phosphorous. It is a clear, water soluble, oily liquid. It can be applied by the pad-dry-thermos01 process. Because of its high water solubility, it does not exhaust from a dye bath. Heat treatment causes the hand to stiffen. The finish is durable to repeated launderings.

C. Nylon

Most nylon fabrics pass flammability standards because the polymer burns at a very slow rate. However several finishes will enhance the fiber's response to flammability tests.

a. Thiourea-Urea-Melamine

This finish is applied by pad-dry-cure. It functions by lowering the melting point of nylon 40 ^{0}C.

b. Halogenated Systems

Halogenated compounds such as DBDPO and chlorinated paraffins combined with Sb_2O_3 are effective. These finishes are often used in industrial applications such as tents, tarpaulin etc.

D. Polyester /Cotton Blends

It is very difficult to impart flame resistance to polyester/cotton blends because the fibers have such different burning characteristics. One would think that blending flame retardant polyester fibers and applying THPC or THPOH technology would accomplish the job. However even this doesn't do it. Polyester normally melts and shrinks away from the flame, but in cotton blends, the melt is held in place by the charred backbone. Horrocks (2) reviews the major works on these blends.

1. Decabromodiphenyl Oxide - Antimony Oxide

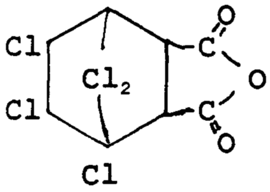
Commercially, the antimony-bromine system is one most often used. Aqueous dispersions of 2:l DBDPO and Sb_2O_3 and acrylic latex binders are preferred to give the desired durability and a safe effective finish. The finish is normally applied by the pad-dry-cure process. The level of flame retardancy is related to the add-on, more being better. However the fabric hand becomes stiff and boardy as the add-on increases. This narrows the range of acceptable fabric to those where flame retardancy is more important than aesthetics.

E. Wool

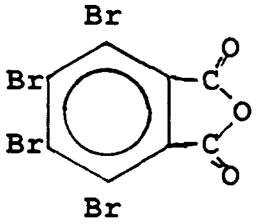
Wool is inherently a flame retardant fiber. Clean wool will pass most horizontal burning test although open pile structures fail carpet tests. Wool is blessed with a high Tc (680^0 C) and LOI index (25). However flame retardants can improve the burning characteristics of wool fabrics. Nondurable treatments which are effective on cellulose are also effective on wool, e.g. boric acid/borax, phosphates and sulfamic/sulfuric acid. Durable systems based on THPC are also applicable to wool. An inexpensive, durable system based on titanium and zirconium complexes have recently been introduced which is unique to wool.

1. Dyebath Exhaustible Finishes

a. Chlorendic Acid and Tetrabromophthalic Anhydride



Chlorendic
Acid



Tetrabromophthalic
Anhydride

Chlorendic acid and tetrabromophthalic anhydrides will exhaust into wool fibers. Add-ons of 6-18% give good flame retardancy, dye compatibility and are reasonably durable to dry cleaning.

b. TitaniumComplexes.

Titanium chloride is an effective flame retardant agent for wool. In the presence of an alpha hydroxy carboxylic acid (citric acid), a stable complex is formed which almost completely exhausts when applied at a pH < 3.5 at the boil. It is important to not allow the titanium to hydrolyse to TiO_2 because as TiO_2, titanium is ineffective. The process is good for wool used in protective clothing, carpets and upholstery. Titanium complexes yellows wool.

c. Hexafluoro-Zirconates

The need to boil wool to exhaust titanium and zirconium chelates leads to felting. low dye fastness and is energy intensive. To overcome these deficiencies, the

IWS developed a process based on titanium and zirconium hexafluoride know as the *Zirpro Process*. Hexafluorotitanates and hexafluorozirconates are extremely stable in acid solutions and exhaust onto wool well below the boil. The titanates yellow wool so the zirconates are preferred commercially. K_2ZrF_6 at a pH < 3 gives 77% exhaustion at 50^0 C, 30 minutes at 70^0 C gives good levelling. A bath containing 3 % K_2ZrF_6, 10% (37%) HCl for 30 minutes at 75^0 C, gives rise to a washfast, lightfast and improved heat and flame resistant fabric. Pad-batch and pad-dry application process may also be used. It is accepted that the hexafluorozirconate ion is bound to the cationic wool in the same manner as acid dyes.

$$ZrF_6^{=} + {}^{+}NH_3\text{-Wool} \longrightarrow ZrF_6^{=+}NH_3\text{-Wool}$$

VII. FLAMMABILITY TESTS

Determining the fammability potential of a fabric requires an understanding of a number of different tests because flammability test and specifications vary with the end-use of the textile article. Some tests have been developed as research tools to quantify the retardancy value of finishes and fibers, LOI is one that is used often. Other tests have been developed to assess the flammability hazard of fabrics. These emulate actual in-service conditions that the textile is liable to encounter. Some of the variables are: 1. the way the heat source is presented as it is being ignited, i.e., vertical, horizontal or 45 degree angle, 2. temperature of the heat source, 3. Char length, after flame and after glow and melt drip are some of the specifications of the specific test. Horrocks (1,2) presents a thorough review of the tests.

A sampling of the more important fabric flammability tests are listed in table 16. The reader is urged to consult the cited references for more in-depth information.

Table 16

Some Important Fabric Flammability Tests

FABRIC TYPE	TEST	COMMENTS
CHILDREN'S SLEEPWEAR	DCO-FF-3 DOC-FF-5	VERTICAL TEST
UPHOLSTERY FABRICS WALL COVERINGS	NFPA-701	VERTICAL TEST
MILITARY FABRICS	FED. STDS. 191-5903 191-5904	VERTICAL TEST
FABRICS	LOI TEST ASTM D-2863	TOP VERTICAL
FLOOR COVERINGS	RADIANT PANEL NFPA 253	HORIZONTAL
	PILL TEST ASTM D-2859	HORIZONTAL
PROTECTIVE CLOTHING	TPP NFPA-1971	HORIZONTAL
CLOTHING	S-191	45 DEGREE

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CHAPTER 12

OTHER FINISHES

I. ANTIPILL FABRIC FINISHING

Pilling is a condition exhibited by certain fabrics made from spun yarns. Balls of lint are firmly attached to the fabric's surface and when the condition is severe, the fabric becomes visually unappealing and irritating to the touch. Spun fabrics made from 100% synthetics fibers, i.e. acrylics and polyesters, or blends of polyester/cotton are prone to pill. The pill in a polyester/ cotton blend is made up of twisted, loose fibers still attached to the parent yarn by one or more anchor fibers. Usually the anchor fibers are polyester filaments that have partially worked their way out of the spun yarn. Pill formation is a function of rubbing against the fabric so pills are mostly found in garment areas where rubbing is most prevalent, i.e. areas near pockets, collars and cuffs.

The .most common laboratory test method for predicting a fabric's pilling tendency is the Random Tumble Pill Rating method. Squares of fabric are tumbled against a cork lining in an accelerator for specified periods of time. The squares are visually rated against photographic standards, see table 1. The number and severity of pills still attached to the surface determine the pill rating. While the method has deficiencies, it will differentiate good fabrics from bad.

A. Mechanism of Pilling

The propensity of a fabric to be classified as bad for pilling involves the equilibrium established between two ongoing actions. The first action creates fuzz balls on the fabric's surface whereas the second action breaks them off. If the rate of creation is greater than wear-off, the fabrics develops the unsightly pilled condition. However if break-off rate is greater than the formation rate, the fabric will appear to be pill-free.

1. Pill Formation

When the surface of a fabric is rubbed, pills develop because abrasion cause fibers to twist into fuzz balls. Fabric surface hairiness is a condition brought about by hairy yarns. Yarn hairiness is related to ease with which fibers migrate out of a spun yarn with one surface fiber end still firmly attached within the yarn structure.

2. Pill Build-up

Pill build-up depends on the ease with which the fuzz ball break off. If the rate of break-off is equal to the rate of formation, the fabric will appear to be pill free. However, if the rate of break-off is less than the rate of formation then the fabric will exhibit noticeable pilling.

B. Factors Affecting Pill Formation

Experience has shown that most 100% cotton fabrics are not prone to develop objectionable pilling. Some cotton fabrics will become hairy and some pills will form, however, the rate of pill break-off is greater than the rate of formation leaving the surface void of pills. The reason for this is because cotton anchor fibers are relatively weak. Experience has also shown that some fabric constructions made with polyester/cotton yarns will exhibit severe pilling. When these pills are magnified, the anchor fibers are seen to be polyester filaments. The strong polyester anchor fibers do not break off easily so pills continue to build up and not wear away.

1. Fiber Variables

a. Denier of Synthetic Fiber

Yarns made from fine denier synthetic filaments (1.5 dpf or finer) pill worse than yarns made from course filaments (2.5 dpf or higher). The reason for this is because yarn twist imparts greater cohesive forces onto larger diameter fibers than finer fibers. As the filiment denier decreases, the total number of synthetic filaments in any given weight percentage of a blend increases. This creates many more fiber ends that serve as anchor fibers. Finer fibers, because they are more limber, will move more easily through a yarn assembly than will stiff, thicker fibers.

b. Fiber Tenacity

Fiber tenacity is a major contributor to fabric pilling because fabrics made from weaker synthetic fibers pill less than fabrics made from their stronger counterparts. Synthetic fiber producers offer pill resistant varieties which are based on lower molecular weight polymers which result in lower tenacity and flex life. Low flex life alone is not enough to produce pill-free fabrics, fiber migration must also be controlled.

2. Yarn Variables

a. Yarn Twist

Yarns with low twist will pill worse than yarns with high twist. The degree of twist will influence the ability of fibers to migrate to the surface. The lower the twist, the easier it is for fibers to migrate.

b. Hairy Yarns

Hairy yarns pill worse than smooth yarns. Low twist contributes to yarn hairiness.

c. Yarn Spinning Methods

Open-end spun yarns pill worse than ring spun yarns because the yarn structure is more uneven allowing for greater fiber mobility. Air jet spun yarns with low flex life fibers result in relatively pill free fabrics. Air jet yarns have wrapper fibers holding the yarn assembly together. These act to keep the body fibers from migrating to the surface.

3. Fabric Construction

Tightly constructed knits and woven fabrics pill less than loosely constructed knits and wovens. Tighter constructions reduce the migration tendencies of the fibers within the yarns.

C. Preparation and Dyeing

Preparation and finishing will have a profound effect on fabric pilling. Some wet processes make pilling worse while others provide substantial improvement. Preparation and dyeing processes that overly work the fabric will cause excessive hairiness and lead to poor pill performance. Long preparation and dyeing cycles are especially bad. In some instances pills may be seen from just these processes alone. High temperature dyeing of fabrics containing low flex life, high shrinkage fibers improve pilling performance. Auxiliaries such as carriers also have a positive effect on these fibers.

D. Fabric Finishing

Finishing procedures have pronounced positive effect on fabric pilling. Many fabrics can be improved by selection of proper finishing conditions.

1. Film Forming Binders

Finishing with film-forming latexes will improve the pilling performance of nearly all fabrics. Whenever the final fabric hand will allow, these film-forming finishes may be considered the closest thing to a universal solution for fixing fabrics prone to pill. These finishes reduce fiber migration by bridging across filaments binding them together. About 1.5% solids deposited on the fabric is needed to do much good.

Latex binders applied to fabrics utilizing low flex life (pill resistant) fibers produce a dramatic improvement in pill ratings. Whereas the base fabric alone would be only marginally better than one made from conventional polyester fibers (still rated objectional), the latex finished fabric would be virtually pill-free. The latex finished conventional fiber fabric would be improved but not to the same degree and the low flex-life-fiber fabric.

2. Durable Press Reactants

Cellulose crosslinking resins applied to low flex-life fibers also produce dramatic improvement in pill rating. However, they have very little effect on conventional polyester fibers.

3. Fabric Softeners

Materials that reduce the coefficient of friction between fibers will make pilling worse. Fabric softeners will increase the pilling propensity of a given fabric. Those applied after dyeing and/or in the finish bath make matters worse. Laundry added softeners may also interfere with pill resistance. These materials operate on the fiber migration portion of the pilling mechanism making it easier for the filaments to move. Softeners co-applied with latexes tend to overcome the improvements noted with film-former. Those softeners that provide a soft hand (silicones, ditallow quats) are the worst offenders.

4. Singing and Shearing

Singeing and shearing are methods of reducing fabric hairiness. In many cases, pill ratings are improved because of the reduced hairiness. This improvement may last for some fabrics for many wash-dry cycles, however, for others, the onset of pilling is only temporarily postponed. Pills will start to form after several wear-wash cycles.

5. Heat-setting

Heat setting fabrics containing thermoplastic fibers is often beneficial in improving pilling performance. For some fabric constructions, the improvement may be temporary and deteriorate after multiple wash cycles. On the other hand, heat setting is a definite plus on those fabrics made with synthetic fibers having higher heat shrinkage. When high heat shrinkage is combined with low flex life, heat setting can enhance pilling performance to the point where the fabric appears to be pill-free.

E. Summary

Pill resistant fabrics need to be engineered from the ground up. Some improvement can be made on poor performing fabrics by combining elements of yarn twist, yarn spinning methods and proper dyeing and finishing procedures. However the best route to pill-free fabrics is to utilize low flex-life fibers with higher heat shrinkage characteristics and finish them with durable-press resins or latex film-forming binders. Also fiber lubricating softeners should be avoided whenever possible.

F. References

II. ANTISTATIC FINISHES

A. Causes of Static

Static is defined as the surface build-up of electrical charges whenever two unlike surfaces contact one another. Many charged particles reside on each surface. These particles may have resulted from previous treatments to the surfaces or from the presence of electrolytic impurities. When the surfaces are separated in air, a net charge transfer will occur depending on which surface attracts the charges more. If one of the surfaces is a conductor, there is an unlimited supply of electrons available to transfer to any other attractive surface. The transfer will continue until it is stopped, either by low initial concentration of ions or by the generation of a strong electric field. Rubbing the surfaces together generates heat and thermal agitation and causes an even greater separation of charges because the charged species tend to migrate away from heat. The direction of transfer, because of frictional heat, may not be in the same direction as the original transfer. For example, its been observed in some textile processes that an increase in speed or tension can actually reverse the polarity of the charged surfaces.

Materials that are non-conductors of electricity and have good electrical insulating properties are known as dielectric materials. Whenever charges build up on these surfaces, the magnitude of the charge will persist until some pathway forms to conduct away the charges. As the insulative property of a dielectric increases, the charge potential it can build up also increases exacerbating problems associated with static.

B. Problems Caused by Static Electricity

Almost all of the fiber polymers can be classified as dielectric materials. This is especially true of the synthetic fibers, e.g. nylon, polyester, polyolefins, acrylics etc. Many textile processes require that fibers and fabrics be moved rapidly over stationary objects so all the elements needed to generate static electricity exist in every phase of manufacturing as well as where consumers use textile products. For example, fibers and yarns may balloon and flare away from each other by repulsion of similarly charged surfaces. Excessive drag tension can be created when the surfaces develop opposite charges. This can cause fibers and yarns to stretch or break. Static can cause problems in the proper folding of long lengths of fabrics in the dye house. Dust can be attracted from the atmosphere to soil the textile. Static can cause garments to cling to the body, an aggravating consumer problem. Lint or other unwanted materials can be attracted to socks and pant legs from carpets and dusty floors.

These static problems are related to charge build-up potentials below the threshold electric discharge potential. However, if the built-up charge potential exceeds the threshhold potential, an electric discharge (a spark) can occur. The spark is the result of rapid ionization of the surrounding atmosphere and is identical to what happens when lightning bolts flash through the sky. For atmospheric lighting to occur, electrical charges continue to build up on water droplets in clouds until the potential is high enough for electrons to ionize surrounding air molecules. The bolt striking the ground is a pathway of ionic species for electrons to follow to earth thus restoring electrical neutrality to the environment.

Examples of static electrical discharges are the zap that occurs when one walks across a carpet on a dry, cold day and touches the metal door knob and the snap, crackleand pop that occurs when clothes are taken out of a dryer while they are still warm. While the actual shock is not life threatening unless it occurs in an explosive atmosphere (gasoline/air mixtures, hospital operating rooms, etc.), involuntary reaction to the unexpected shock can cause accidents.

D. Mechanism of Control

Methods for controlling static build-up rely either on preventing the build-up of static charges or increasing the rate of charge dissipation. One way of reducing charge build-up is to reduce friction. Certain fiber lubricants help in this respect. Another way of reducing charge build-up is to blend fibers which have the potential of developing opposite charges. The tribo-electric series is an attempt to classify fibers as to the sign and magnitude of the charge they will develop. This process has shown limited success due to the inability to accurately predict the specific compositions of materials which will produce opposite charges of the same magnitude, and due to the variation in charge produced by individual processes.

1. Static Eliminators

Since preventing static build-up is difficult if not impossible, successful antistatic control relies on increasing the rate of dissipation of the static charges. One way to do this is to "ground" the material by having it come in contact with grounding bars, metallic foil (copper or aluminum) connected by a wire lead to earth. Another way is to use static eliminators, devices that increase the electrical conductivity of the surrounding air as a means of providing sufficient opposite charges to neutralize the charges on the textile. High voltage wires or low level ionizing radioactive materials have been somewhat effective in this application. These methods have limited utility since static can again build-up as soon as the textile rubs over the next surface it come in contact with.

2. Antistatic Agents

Increasing the conductivity of the textile fiber has been a highly successful way of increasing the rate of dissipation. A wide varity of antistatic finishes have been developed which function to increase the conductivity of the fiber. Nearly all of these materials rely on water as the medium to transport the charged species and therefore their usefullness is dependant on atmospheric humidity. They are very effective in moist atmospheres but their effectness decreases as relative humidity decreases. Common reagents include hydrophylic surfactants, poly-electrolytes, long chain quaternary ammonium salts, polyethoxylated polymers and any other hydroscopic material that can be left on the surface of the fiber. Most of these agents are not permanent since they may wash or wear away. Structure/property relationships will be discussed in sections to follow. Reagents of this nature are applied to fibers by kiss rolls, spray or immersion as they are being manufactured. They are can be applied to yarns and fabrics in similar fashions. Fabric softeners that also function as antistats can be exhausted from the rinse cycle of a dyeing procedure or padded on as an ingredient in the fabric finish formulation. Consumers can add similar types of agents in the rinse bath after the wash cycle during home laundering. Dryer - added softener sheets afford the same type of static protection.

3. Fiber Polymer Modifications

Approaches not relying on moisture to provide electrical conductivity have also met with some success. The use of good electrical conductors, e.g. metals and graphite, have been successfully incorporated in some applications. For example, very fine stainless steel fibers have been blended into nylon carpet yarns. When enough steel wire is incorporated to give electrical continuity, a conductive pathway is available to dissipate the charges as they build up, keeping them below the annoyance values. Another approach is to coat fibers with a metallic coating (silver) or graphite. These coating are subject to abrasive disruptions and have limited utility. Newer developments involved the formation of bicomponent fibers where one component contains the conductive material. Graphite containing carpet fibers are available that effectively reduce static problems.

In carpets, the lack of humidity on cold dry days render the the hydroscopic antistatic agents ineffective. These materials tend to become oily or gummy and entrap foot borne soils. Therefore carpets quickly develop a heavily soiled condition and need to be shampooed more often. Vacuum cleaning is ineffective in removing the composite gummy soil.

E. Non-Durable Antistatic Agents

Many of the commercial chemical auxiliary products that function as antistats can also be classified as surfactants. Most of them have limited durability to washing and abrasion so their main use will be as temporary processing aids to overcome static problems encountered in textile manufacturing process. It is not uncommon to apply new materials along the manufacturing chain to replace those that have been removed by downstream processes. Once the textile is in consumer product form, static problems in general are nuisances and opportunities exist where antistats can be reapplied in laundering and dry cleaning. In general non-durable antistatic agents, like surfactants, belong in one of the following classes: cationic, anionic and non-ionic. Structures representative of these classes have been discussed in the chapter on Surfactants and the chapter on Softeners and will not be repeated here. The reader is reminded of ancillary problems such as smoke point, color, odor and color bleed that are associated with these compounds. What follows is a brief discussion pertaining to structure/antistatic properties of the various classes.

1. Cationic Materials

Nitrogen containing materials such as fatty amines, amides, imadazolines, and quaternary ammonium salts make up the types of materials that function as antistats. These materials exhaust and orient onto the textile surface. The ionic nature of the quats render them excellent antistatic agents. They provide good lubricating properties which is a plus in reducing the charge build-up, are somewhat hygroscopic and thus attract water molecules which provide charge dissipation and have mobile counter ions which also improve water's ability to conduct electricity. Ditallowdimethyl ammonium chloride is an effective antistat.

2. Non-Ionic Materials

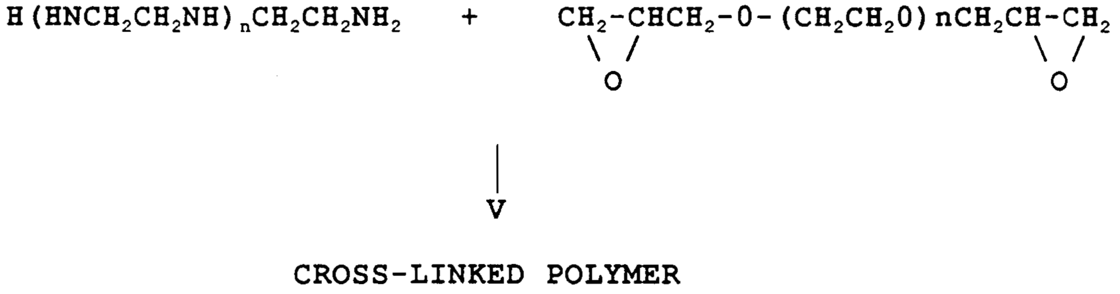
Non-ionic materials such as polyethylene glycols, ethoxylated fatty acids ethoxylated fatty alcohols and sorbitan fatty acid esters fall under the catagory of non-ionic antistats. These materials are also hygroscopic and thus function to dissipate the charge build-up. Often they are blended with the cationics as the blend has superior properties than either alone. It is believed that the non-ionic improves the water absorption while the quat provides the ionic species that improve the electrical conductivity of the surface.

F. Durable Antistatic Finishes

The basic principle behind durable antistat finishes is the formation of a cross-linked polymer network containing hydrophilic sites. To be effective, the cured properties of the resulting surface coating must be carefully controlled. As the number of hygroscopic units increase, moisture absorption increases and antistatic performances increases. However at higher levels of moisture absorption, the coating tends to swell and the resulting material becomes susceptible to abrasion during laundering. Insufficient number of hygroscopic units or over cross-linking reduces the moisture pick-up thereby reducing the effectiveness of the finish. Additionally, if the film is gummy, it will attract and hold on to carpet soil, a serious deficiency. Cationic materials also tend to interfere with the laundering process, they make soil release worse. Because of the deficiencies listed above, the use of durable antistat finishes is limited. Whenever a static problem arises, the first approach is to try a non-durable finish before attempting durable finishes. Where durability is must, blending in good conductors or modifying the fiber polymer are better choices.

1. Composition

The basis for most of the durable finishes is polyamines, polyoxyethylene and some means of crosslinking them.



$$H(HNCH_2CH_2NH)_nCH_2CH_2NH_2 + \underbrace{CH_2\text{-}CHCH_2}_{O}\text{-}O\text{-}(CH_2CH_2O)nCH_2\underbrace{CH\text{-}CH_2}_{O} \longrightarrow \text{CROSS-LINKED POLYMER}$$

G. References

CHAPTER 13

MECHANICAL FINISHING

Mechanical Finishing is defined as any operation performed to improve fabric appearance or function by physical manipulation. Steam or water may accompany the physical manipulation; however, chemicals other than lubricants are seldom used. Fabric luster, smoothness, softness, residual shrinkage and hand are examples of the properties that can be altered by mechanical finishing. Topics to be covered in this chapter are:

- Compacting (Shrinkproofing)
- Calendaring
- Raising (Napping, Sueding)
- Shearing
- Polishing
- Corduroy Cutting
- Decating

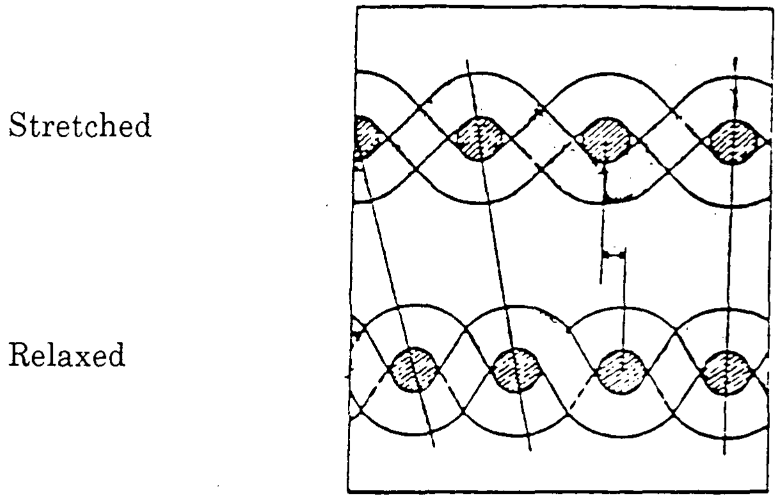
I. COMPACTING - SHRINKPROOFING

Controlled residual shrinkage is an important quality parameter for many fabrics. For example, excessive shrinkage is undesirable for fabrics to be made into garments. Here, the residual shrinkage should be less than 2% otherwise the garment will not fit after it is laundered. Drapes cut to floor length will draw up from the floor and detract from their appearance unless the residual shrinkage is controlled. Before launching into the mechanical methods of reducing shrinkage, it will be instructive to discuss the causes of fabric shrinkage.

A. Why Fabrics Shrink

Woven and knitted goods are 3-dimensional arrays of crimped yarns. Fabric forming processes take straight lengths of yarns and force them into 2-dimensional crimped lengths. The degree of crimp is a function of the yarn size and fabric construction. When fabric is completely relaxed, the crossing yarns will move around in relation to each other until a stable configuration is reached. This stable arrangement, the point where the relaxed fabric no longer shrinks in width and length, is also related to yarn sizes and fabric construction. When stretching tensions are applied to the fabric, the crimped amplitude decreases and the fabric grows in the direction of the stress. Later when the tensions are relieved and the fabric allowed to relax, the crimp amplitude returns to its stable configuration and the fabric shrinks. Many fabrics are stretched during wet processing as they are pulled from one operation to another. This is the major cause of fabric shrinkage.

Figure 67. Fabric Crimp



B. Sanforizer

Mechanical compacting is one method of reducing residual shrinkage. The process forces yarns closer together and the fabric becomes thicker and heavier. As a result of this, the net yardage yield is reduced. A Sanforizer is a fabric compactor developed by Cluett Peabody. The term ***Sanforized,*** is their registered trademark and is used to market fabrics that meet certain shrinkage specifications. The term Sanforized is now generally accepted to mean a fabric that has low residual shrinkage and the term Sanforizing is used to describe shrinkproofing processes. While the patents on the machinery have expired, the trademark is actively promoted by Cluett Peabody. The effect of Sanforizing can be seen in figure 68 which shows that open fabric structure has been closed up somewhat. The process, figure 69, consists of a range where the fabric is first moistened with steam, to make it more pliable, run through a short tenter frame (pup tenter) to straighten and smooth out wrinkles, through the compressive shrinkage head and then through a Palmer drying unit to set the fabric. The fabric is wound into large rolls under minimum winding tensions. If the winding tension are excessive, the fabric will be pulled out and the degree of compaction lessened. Usually, a lubricant is added in preceding operations to assist in the realignment of the yarns as the fabric runs through the compactor. Selection of the proper lubricant is critical for some fabrics.

Figure 68. Effect of Sanforizing

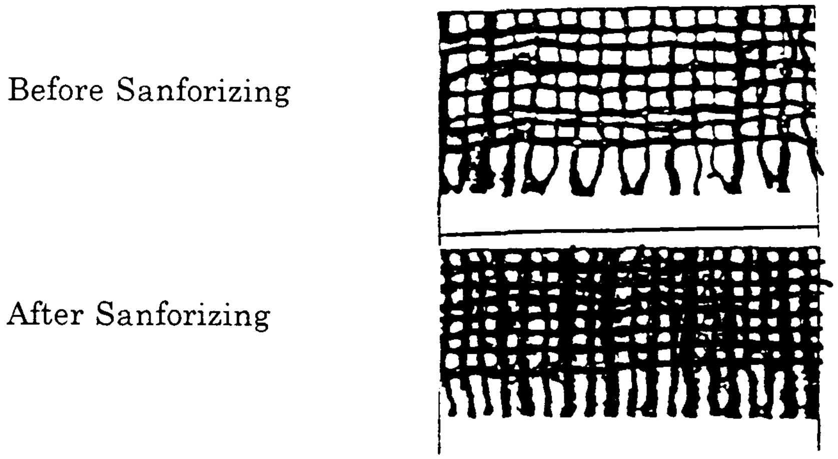
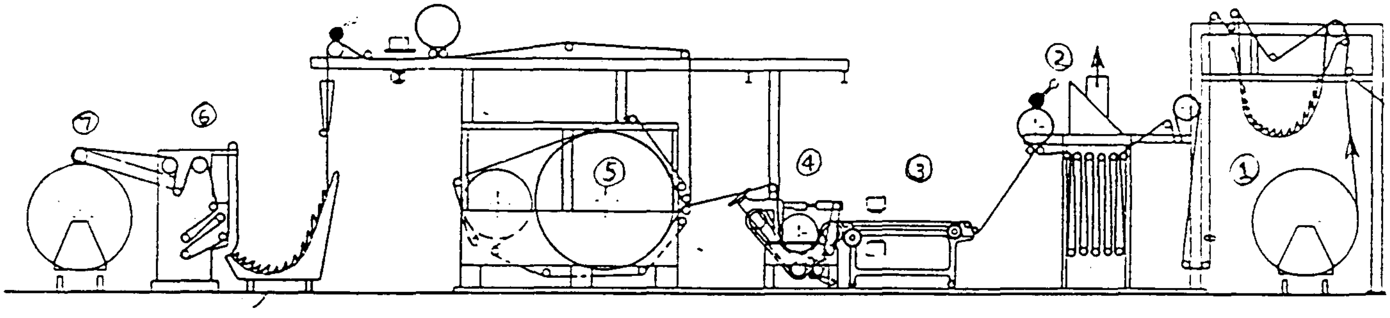


Figure 69. Sanforizing Range



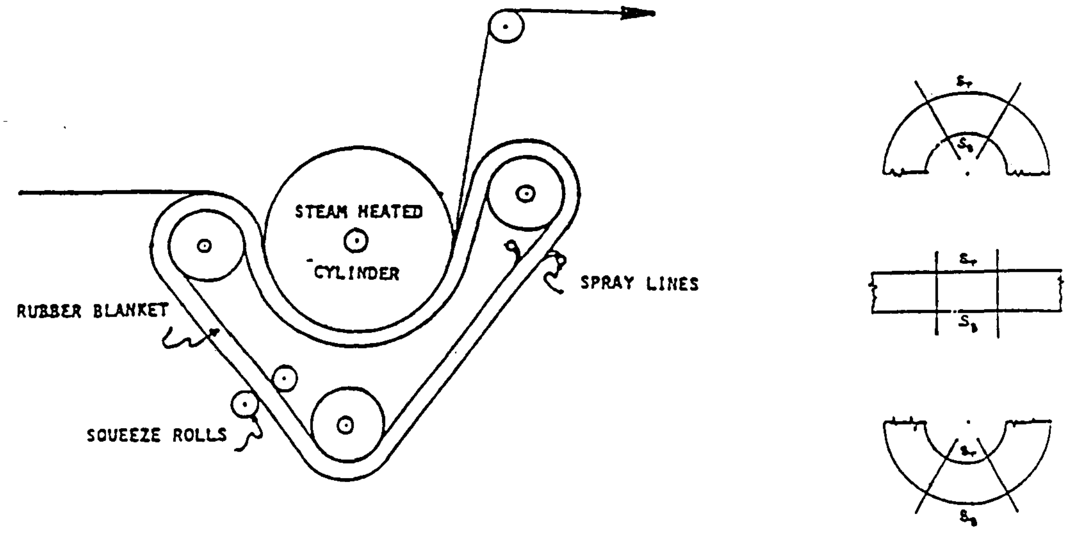
(1). Let-off (2). Steamer (3). Pup Tenter (4). Sanforizer Head (5). Palmer Unit (6). Fabric Straightener (7). Take-up

1. Compactor Head

The key to any compactor is the head where force is applied to move parallel yarns closer together. More fabric must be fed in than is taken off. A Sanforizer uses a thick rubber blanket running against a steam heated cylinder as the compacting force. The thick rubber blanket first goes over a smaller diameter roll which stretches the convex surface of the blanket. Fabric is metered onto the stretched blanket and the fabric and blanket together come in contact with the steam heated cylinder. At this point, the stretched rubber surface contracts to its original length and then is forced to contract an additional amount as it forms the concave configuration of the heated drum. Since the fabric is not elastic, an extra length of fabric is thrust between the rubber blanket and the heated cylinder. Friction between the rubber blanket and steel drum force adjacent yarns to move closer together until the unit length of fabric become equal to the unit length of rubber blanket it rests on. If the fabric construction does not allow the yarns to move, the extra fabric will buckle developing creases and wrinkles.

Figure 70 shows a schematic of the compactor head and how the fabric and blanket moves together. Heat is created by constantly stretching and relaxing the rubber blanket. The blanket is cooled by spraying water on it after the fabric exits from the unit. Insets in figure 70 also show the length variations that occur as the blanket surface goes from convex to straight to concave.

Figure 70. Sanforizer Head

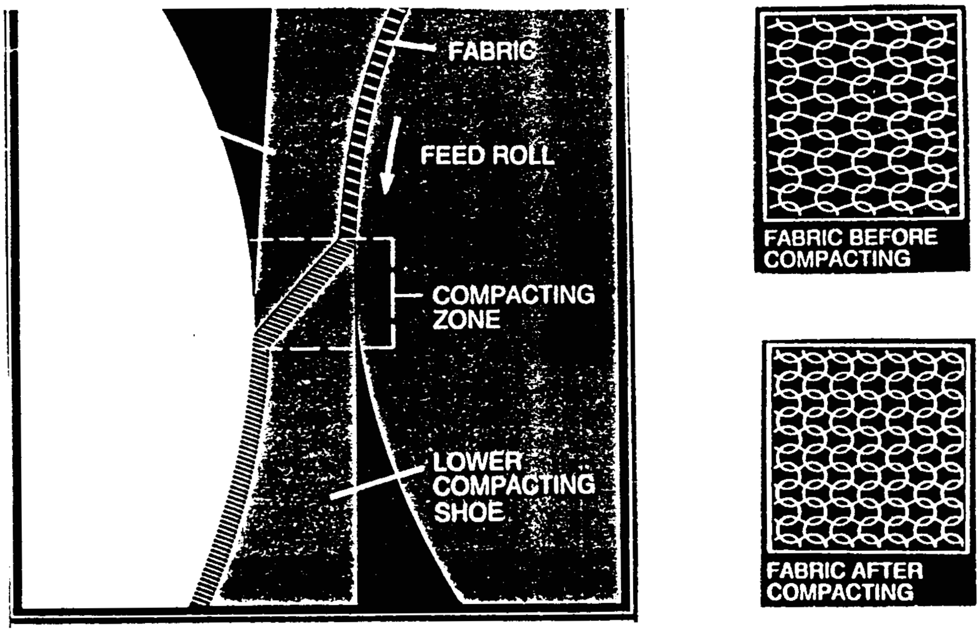


The degree of shrinkage can be controlled by the thickness of the blanket. The thicker the blanket, the greater is the stretched length at the bend. A longer length of fabric will be fed into the compactor causing the degree of compacting to be greater. Conversely if the blanket is thinner, a lesser degree of compacting will occur. Blanket thickness can be adjusted by means of a pinch roll compressing the rubber blanket. This allows for some degree of "dialing in" the degree of compacting desired. To be effective, the degree of compacting needed should be predetermined ahead of time. This is done by characterizing the shrinking behavior of the fabric by laundering. The degree of compacting should not exceed the degree of shrinking otherwise over-compacting will cause the fabric to "grow" when relaxed. This is as much a disadvantage as is shrinkage.

B. Friction Calendar Compactors

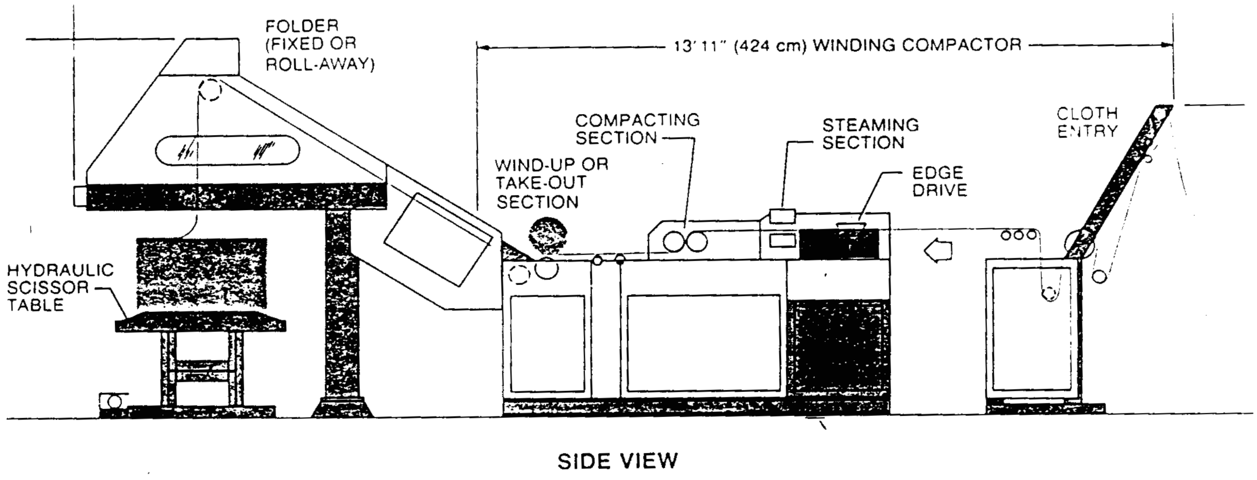
Another method of compacting fabrics is with calendar rolls. The fabric passes between two metal cylinders, one cylinder rotates faster than the other. The fabric is restrained by shoes that are positioned against the cylinders. The fabric delivery cylinder rotates faster than the take-off cylinder and the action is similar to stuffing a string into a straw. The friction causes filling yarns to move closer together and a loss of fabric length.

Figure 71. Friction Compacting Principle



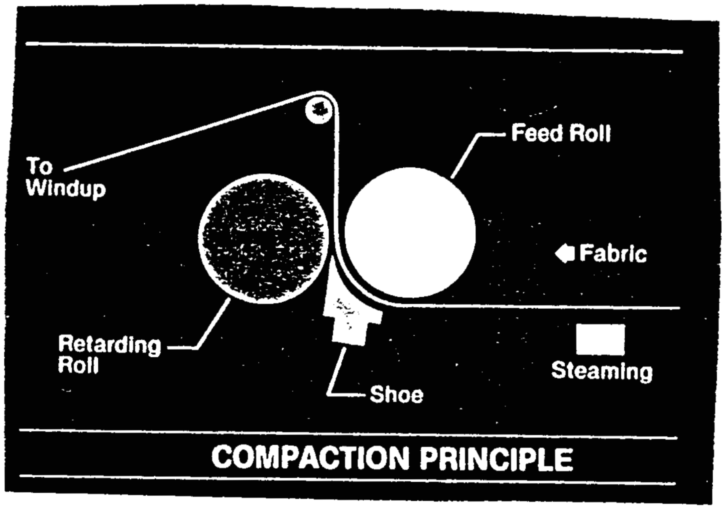
The degree of compacting can be controlled by the differential speeds of the two calendar rolls. Pac Nit II is a machine designed by Tubular Textile Company for tubular knits and operates simultaneously on both layer of the tubular fabric as it passes through the unit.

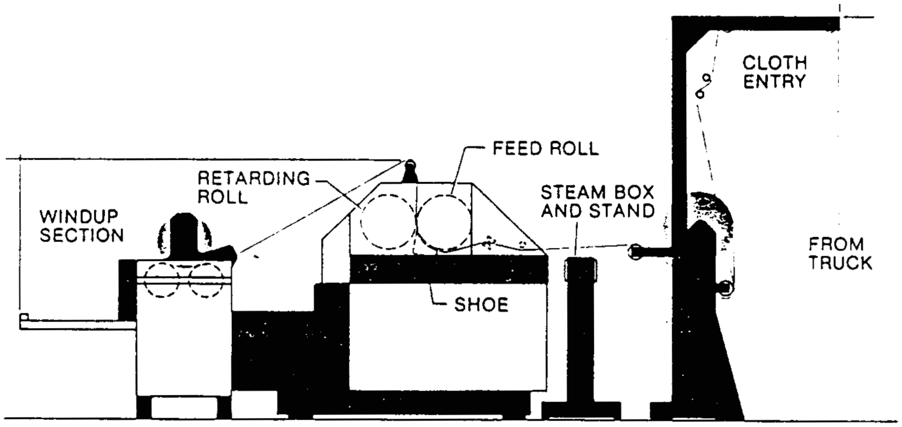
Figure 72. Tubular Knit Compactor



Tubular Textile Machinery Co has also designed a wide version compactor (Model CS 2000) that can handle single layers as wide as 90 inches. It is effective on open width knit goods such as tricots and slit circular knits.

Figure 73. Wide-Width, Single-Layer Compactor



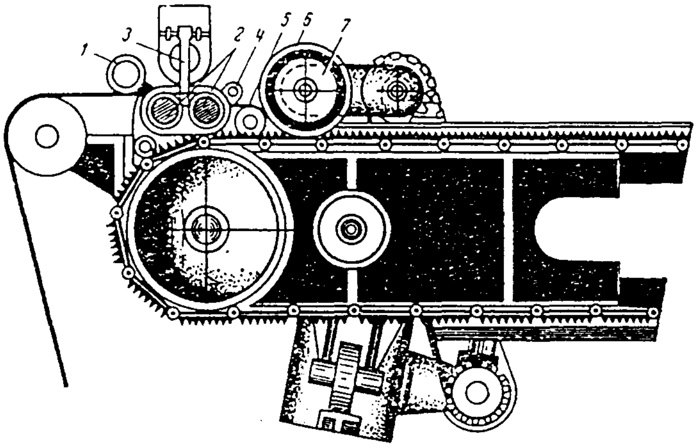


SIDE VIEW

C. Overfeed Pin Tentering

A third method of pre-shrinking fabrics is by overfeeding wet cloth onto the pins of a pin tenter oven during drying or heatsetting. Certain tenter frames are equipped with an auxiliary fabric feed drive that is independent of the tenter chain drive. These devices deliver fabric at a faster rate than the linear speed of the pin chains. The excess fabric is forced onto the pins by pinning wheels. Drying forces causes the fabric to shrink so the fabric exits the oven in a pre-shrunken state.

Figure 43. Overfeed Pin Tenter



1 — tension roller of selvedge straightener; 2 — fluted rollers; 3 — feeler; 4 — selvedge safety device roller; 5 — feed roller of the leading mechanism; 6 — pressing roller; 7 — brush for pinning the fabric

II. CALENDARING

Calendaring is a process where fabric is compressed by passing it between two or more rolls under controlled conditions of time, temperature and pressure. A calendar is a machine consisting of two or more massive rolls which are compressed by means of hydraulic cylinders applying pressure at the journals. One roll is considered the pattern roll and is responsible for the finished appearance of the fabric while the other roll is called a bowl and serves as the pressure back-up for the pattern roll and also serves to transports the fabric through the machine. There are many types of calendars, each designed to impart specific effects to cloth. The composition of the rolls, number of passes, temperature controls, moisture control and pressure can vary to fit the desired effect. For example, the pattern roll can be engraved and serve to emboss a three dimensional pattern into the fabric. The engravings can be shallow or deep depending on the desired effect. The pattern roll can be smooth, made of steel or nylon to give the fabric a high luster and sheen. The backing bowls can be made from corn husks, kraft paper, hard or soft rubber and deform to receive the pressure of the pattern roll. In calendaring, the yarns are flattened and become more oval in shape. This causes them to spread in two dimensions and closes up the fabric structure, leaving less open spaces between the yarn crossovers. In the process, the fabric becomes thinner and more lustrous.

The reason fabrics are calendared is to improve aesthetics. The major fabric changes are: 1. reduced fabric thickness. 3. increased fabric luster, 3. increased fabric cover, 4. smooth silky surface feel, 5. reduced air porosity and 6. reduced yarn slippage.

A. Types of Calendars

The type of calendar used depends on the type of cloth to be run and what the desired effect is to be. There are embossing calendars, friction calendars, swizzing calendars, chase calendars, and compaction calendars. The difference between them is the number of rolls and the drive system.

1. Swizzing Calendars

Swizzing is a British term used to denote that the fabric runs through all of the nips at the same surface speed as the rolls. Swizzing calendars usually consists of seven to ten bowls and are run at ambient temperatures. The fabric effect is closed interstices, a smooth appearance and gloss without the high glaze characteristic of a friction calendar. A schematic of 7 bowl calendar is shown in figure 75.

2. Chasing Calendars

Chasing calendars are similar to swizzing calendars. The major difference is that the thread-up is such that the cloth makes several passes through the nips before it exits to a take-up roll. This is done by having cloth pass over chasing rolls which feed it back through the nips. The cloth is compressed against itself with as many as 5 to 6 layers being in a nip. This gives the cloth a thready-linen appearance and a soft special feel.

Figure 75. Swizzing Calendar

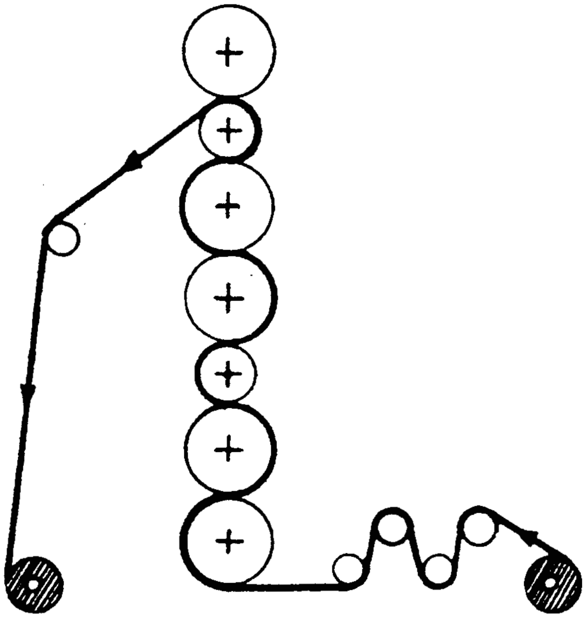
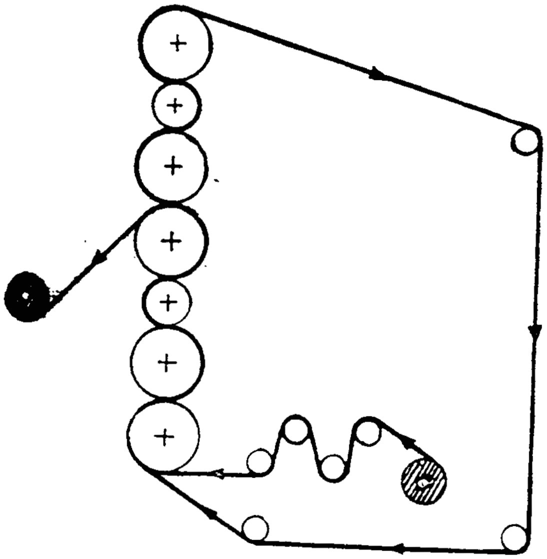


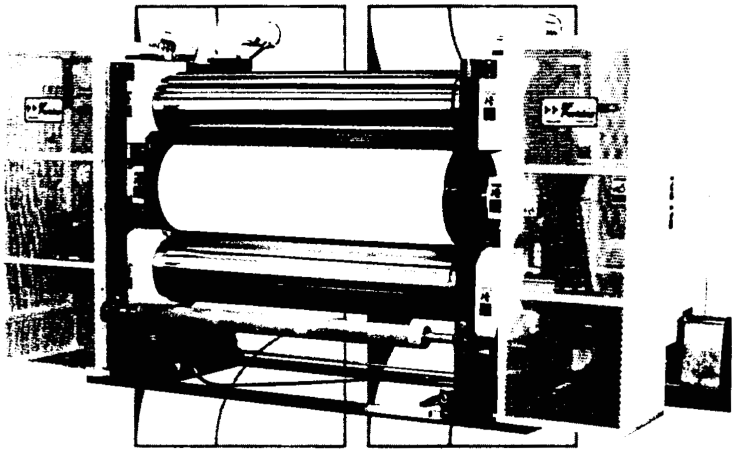
Figure 76. Chase Calendar



3. Friction Calendars

As the name implies, friction calendars (see figure 76) apply a friction force to the face of the fabric. This is done by driving the pattern roll faster than the support bowl. Friction is created by speed differentials ranging from 5% to 100% so it is necessary to have a strong fabric to withstand the strains. Frictioning produces a high degree of luster on one side and the final effect is similar to ironing with a hot iron.

Figure 76. Friction Calendar



4. Compaction Calendar

A compaction calendar has an adjustable gap between the pattern roll and bowl. This type of calendar is used to make filter media of certain thickness.

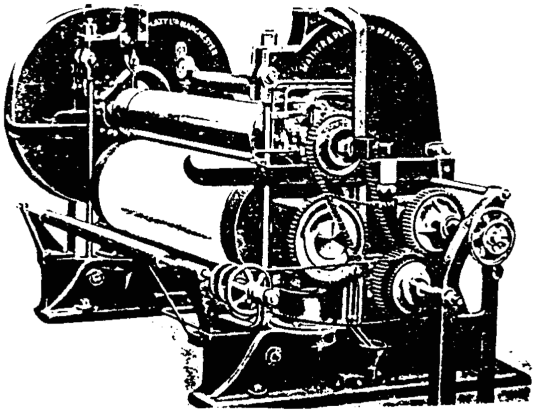
5. Embossing Calendar

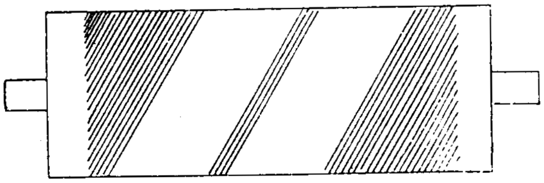
Embossing calendars are normally two or three roll calendars with one engraved roll and one or two bowls. The patterns range from polished rolls or cire' to very deep floral patterns. Moire is a watered appearance which resembles paper after it has been wet with water. The moire effect can be obtained by using a moire pattern embossing roll. Thermoplastic fabrics can be permanently embossed with heated rolls and the effect can withstand repeated laundering. Natural fibers are more difficult to emboss and usually starch is needed for the embossing to take; however, this effect is not durable to laundering. Certain melamine resins can be added prior to embossing and when properly cured, the embossing effect is more durable.

6. Schreiner Calendar

Often it is desirable to increase fabric luster without overly thinning the cloth. Schreinering is a method of doing this. Schreinering is actually embossing by the use of a very special pattern. The pattern roll has anywhere from 250 to 350 lines per inch, etched at 26 degrees from the vertical. These lines are lightly embossed into the fabric and being regular, reflect light so as to give the surface a high luster. This operation gives a silk-like brilliance to cotton fabrics. Schreinering mercerized cotton fabrics gives the nearest resemblance to silk.

Figure 78. Schreiner Calendar





Schreiner steel bowl showing the lines engraved in its surface (250 to 350 lines per in.). The 'cut' of the line into the bowl may be rounded or sharp

B. Construction of the Rolls

1. Pattern Rolls

Pattern rolls are turned from sold steel billets. The pattern is engraved onto the roll surface and the roll is heat treated to harden it and make the pattern more durable. The rolls are chromed which also increase wear resistance and protects them from rusting on storage. The center of these rolls is bored out to accommodate various heating systems. Steam, electrical heaters, natural gas and recirculating hot oil systems have been used to heat these rolls.

2. Bowls

Bowls are filled with cotton, combination of wool and cotton and/or corn husks. Cotton is used to produce very hard, dense surfaces. These are not very resilient and are susceptible to being marked or scarred should hard objects inadvertently pass through with the cloth. Wool or wool/cotton is used because the surface will be more resilient and less likely to be damaged if a seam passes through. A disadvantage of wool is that the scales on the fiber tends to pick certain fabrics and create surface defects. Corn husk is a very pure form of cellulose and makes bowls that are cheaper and more resilient than cotton, however they are weaker than cotton filled bowls. Paper is also used to fill bowls. The latest in bowl design is nylon bowls - a one inch thick nylon shell fitted over a roll. The advantage of nylon is it resiliency; it is more resistant to being marked than are the other surfaces. Seams and wrinkles can run through without having to refurbish them all the time. Cloth having selvages thicker than the body of the fabric can be run through without problems. One disadvantage, however, is that temperatures are limited to less than 375^0 F, otherwise the nylon will melt.

3. Crowning

When pressure is applied to the journals of both the pattern roll and the bowl, the rolls tend to deflect. The wider the calendar the greater will be the deflection. To take care of the deflection, all bowls are crowned, i.e. the diameter of the middle is greater than the diameter at the edges. The amount of deflection and therefore the amount of crown depends on the pressure per lineal inch. Therefore it is necessary to change the crown on the bowl to accommodate different pressures otherwise the calendaring effect will not be uniform across the width of the fabric. Too little crown will cause weak calendaring of the center as compared to the edges while too much crown over-calendars the center and under-calendars the edges. Older calendars require changing of the bowls when different pressure require a different crown profile. Also when the bowl surface is severely damaged, it must be removed and reground to true it up. Modern calendars with nylon shells are designed to alleviate these problems. There are two systems designed to overcome the need to change bowls for different crown profiles. One system uses a hydraulic reservoir under the nylon shell to change the profile. Chambers across the width of the bowl can be individually pressurized to accommodate whatever profile is desired. The second system differs from the above in that the actual calendaring pressure is applied from within the bowl and not from the pressure applied at the journals.

4. Auxiliary Equipment

Other devices are necessary for running the calendar. Let-off and take-up rolls geared-in with the calendar rolls are important. Proper tensions must be maintained to produce a consistent product. Edge guides and spreader bars are necessary to keep wrinkles from developing and being permanently pressed into the fabric. Seam detectors signaling the machine to prepare to jump the seam are necessary otherwise the seam will mark the bowl. A marked up bowl will spoil many yards of cloth.

III. RAISING

Raising is the term used to describe the creation of a pile surface on a fabric. Fibers are deliberately pulled part way out of a yarn to give the fabric a hairy or fuzzy appearance and a soft surface texture. Napping, sueding and shearing are techniques for developing a surface pile and in conjunction with calendaring are lumped into a category referred to as *Surface Finishing*. Surface finishing effects, especially raising, have been used for years to enhance the appearance and hand of fabric. Many of the finest wool and cashmere fabrics are still mechanically finished - not only to improve their hand and appearance but to increase their bulk, to impart the feeling of warmth, to increase the number of fiber ends on the surface of the fabric, to provide improved adhesion for laminating purposes and to improve the profit margin per yard sold. Many of the same techniques are used to finish woven and knitted goods made from synthetic and synthetic blended fabrics. Sueding and napping machines are used on both filament and spun constructions while shears, polishers, calendars and decaters are used singly or in combination to create specific surface effects.

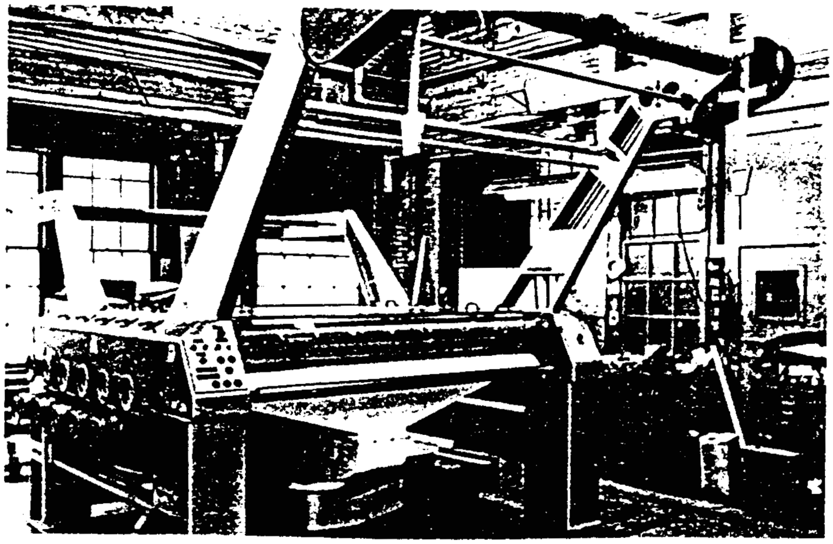
A. Sueding

A sueder is sometimes referred to as a sander since the machine consists of one or more rolls covered with sand paper as the abrasive. Fabrics traveling over these rolls develop a very low pile and the material's surface can be made to feel like suede leather. The hand will depend on the fiber composition, the filament count in the yarn and the intensity with which the fabric is worked. Filament fabrics can be made to feel like a spun fabric and generally speaking, all fabrics will have a softer hand.

1. Multi-Cylinder Sueders

There are two basic categories of sueders, multi-cylinder and single cylinder machines. The multi-cylinder machine usually has five rotating cylinders, each independently driven and they can be rotated clockwise or counter clockwise. Cylinder construction can vary between machines made by different manufacturers. Some are abrasive covered rolls either free standing or as tubes mounted around the periphery of a rotating cylinder shaft. Others are fluted cylindrical rolls with the high portions of the flutes covered with abrasive. Ahead and behind each cylinder are adjustable idle rolls which control the pressure of the fabric to a greater or lesser degree against the abrasive cylinder. Entry and exit drive rolls transport and control the fabric tension as it progresses through the machine. Figure 79 shows a multi-cylinder sueder.

Figure 79. Multi- Cylinder Sueder



2. Single Cylinder Sueder

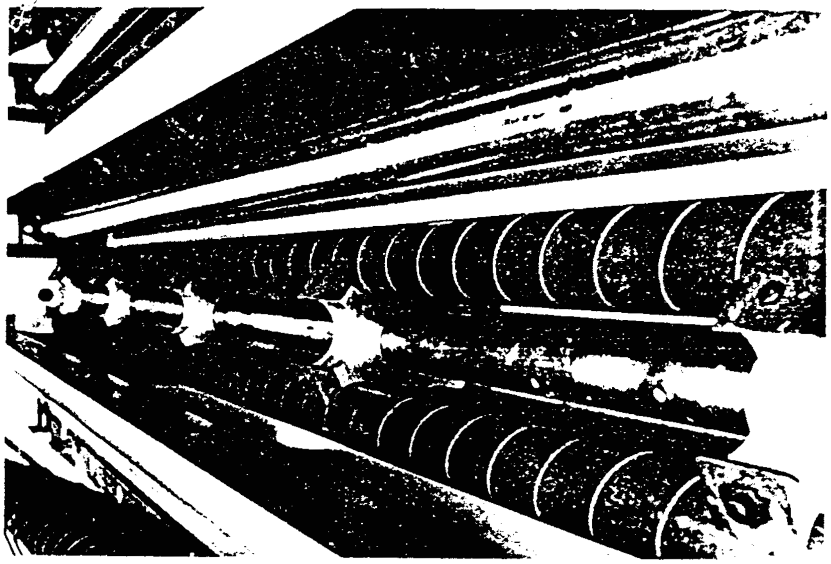
The single-cylinder sueder has one abrasive covered metallic roll and one rubber covered pressure roll. To keep the abrasive covered cylinder from expanding from the heat generated' from friction, water is circulated through the cylinder interior to keep it cool. The pressure roll presses the fabric against the abrasive cylinder and is micrometer adjustable. The abrasion of the fibers on the surface of the fabric takes place in the nip between the pressure roll and the abrasive cylinder.

3. Abrasive Covered Rolls

The quality of the nap will depend on the fabric construction and selection of abrasive grit. Fabric construction will determine the abrasive grit size, the wrong grit may over sand the fabric and either weaken woven fabrics or perforate knit fabrics. Since the abrasive material deteriorates with use, it must be changed on a regular basis to guarantee a uniform suede throughout a production run.

A new abrasive now available which last much longer than the silica based paper. The abrasive roll is made from diamond chips embedded in a Kevlar paper base.

Figure 80. Abrasive Covered Rolls



4. Advantages and Disadvantages

Both machine designs perform very well and produce very acceptable products. However one machine may have advantages over the other on a specific style. For example: 1. fabrics with knots or slubs on their backsides, or fabrics with selvages thicker than the body of the fabric are best run on a multi-cylinder machine. Knot holes or over-sanded selvages may occur on the single cylinder machine because the fabric is compressed against the abrasive cylinder. This is not the case with the multi-cylinder machine. 2. A single roll sueder is more effective on fabrics with terry loops on the face that must be broken. Also difficult styles that require shaving the face to develop a surface effect are more effectively and more efficiently sanded on a single cylinder machine. 3. Some fabrics tend to develop a directional pile when sanded on a single cylinder machine. The multi-roll machine may be operated with the cylinders rotating in opposing directions eliminating this effect.

B. Napping

Nappers also change the aesthetics of fabrics by developing a pile on the surface of the fabric. The depth of pile developed on a napper can be much greater than can be obtained by sueding, assuming the fabric construction is correct. For example fleeces, velours, high-pile fur-like effects, flannels and bed blanket finishes are produced by napping. Proper fabric construction is a prerequisite to napping. It is important that the yarns acted on by the napper are not the ones responsible for the strength and integrity of the fabric. The reason for this is that the napped yarns are weakened by the napping action. Fabric to be napped should have a napping lubricant or softener applied prior to napping to allow the fibers in the yarn to slide more freely during the napping operation.

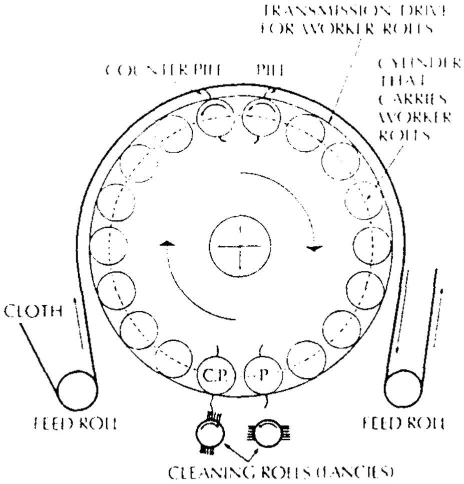
1. Nappers

Wire nappers, known as planetary nappers, are the most commonly used machines in the industry. The basic design of a wire napper is 24 to 36 small, pile wire clad rolls (worker rolls) mounted on the periphery of a large main cylinder. The large napper cylinder rotates in the same direction as the flow of the fabric at a constant speed while the worker rolls rotate on their own axis in a direction opposite to the rotation of the main cylinder. Cleaning rolls or brushes below the main cylinder remove lint and entangled pile to keep the wires at high efficiency. The speed of the worker rolls, the type of wire, the angled direction of the wire all influence the degree of nap. There are many arrangement of these components each designed for their individual specialty.

a. DoubleActingNappers

The double acting napper is the most commonly used machine in the industry. The main cylinder carries 24, 30, or 36 napper rolls. Every other worker roll is wound with napper wire angled in the same direction as the rotation of the cylinder. This roll is called the pile worker roll. The alternating worker roll, called the counter-pile roll, is wound with counter-pile wire having points angled in the opposite direction. Adjustments of the counter-pile and pile roll speeds relative to the speed of the fabric travel results in the raising of fibers. The napping action is such that the counter-pile rolls dig into the yarn to pull out fibers while the pile roll felts or tucks the fiber ends into the base of the fabric producing a product that roughs less and retains better appearance after laundering. The double acting napper develops a dense, tangled nap which is very desirable on many fabrics

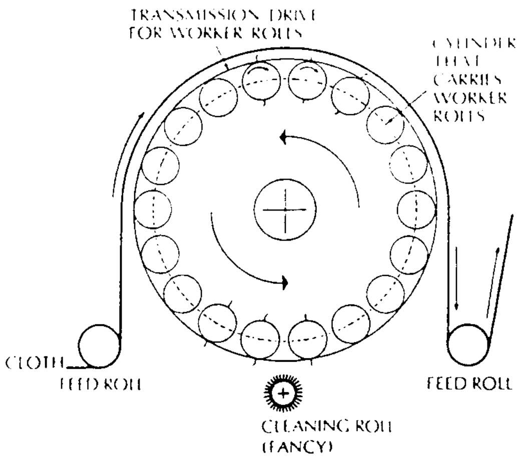
Figure 81. Double Acting Napper



b. Knit Goods Napper

The knit goods napper is designed to be used almost exclusively in the knit industry. These machines can handle tubular fabrics as well as open-width knits. The knit goods napper differs in that the main cylinder rotates on its own axis in a direction opposite to the flow of the cloth. Half of the worker rolls are covered with straight wire called traveler wire and the other half are covered with hooked wire whose points face the rear of the machine. While it looks like pile wire, it act like counter-pile wire because of the direction of rotation of the main cylinder. Both sets of worker rolls rotate on their own axis in a direction opposite of the cylinder rotation. Fourteen to 24 worker rolls are mounted on the main cylinder. The hooked wire roll does the napping and the traveler wire roll speed is adjusted to control the tension of the fabric on the cylinder. Correct speeds prevent wrinkles from forming in tubular goods and longitudinal wrinkles in flat goods.

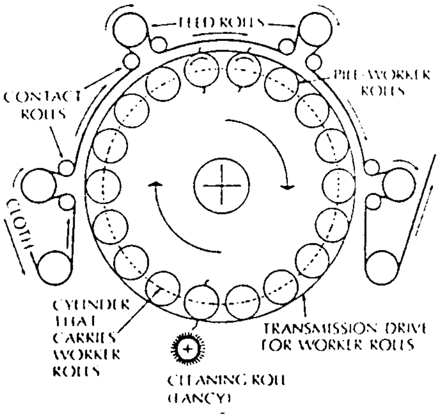
Figure 82. Knit Goods Napper



c. Single Acting Napper

The single acting napper is generally used as a finishing napper. The double acting and knit nappers generally develop a directional nap with parallel fibers that can be lofty or flat. The purpose of the single acting napper is to untangle and comb the fibers parallel. The single acting napper's main cylinder rotates in the same direction as the flow of the cloth. There are 20 to 24 pile worker rolls in the cylinder whose wire points face the rear of the machine. The pile worker rolls rotate in a direction opposite to the main cylinder. A distinguishing feature of this machine is the way the cloth is fed to contact the main cylinder. The cloth is fed over contact rolls that permit 2 to 4 tangential contacts. Were the cloth to hug the entire cylinder, the wire ends all pointing in the same direction would tear it to shreds.

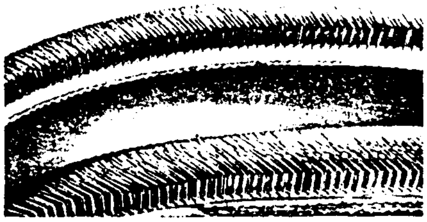
Figure 83. Single Acting Napper



d. NapperWire

The characteristics of the napper wire are just as important as the machine design. Most wires have a 45 degree bend at the knee and are ground needle sharp. The wire protrudes through a tough flexible backing, built-up and reinforced to securely hold the wires. The backing and wire are wound spirally over a hollow supporting roll to become the worker roll.

Figure 52. Napper Wire



For certain fabrics, e.g. tricot warp knits, it has been found that a bumped or mushroomed wire point with tiny barbs underneath will develop a denser nap in fewer runs, As the wire point withdraws from the yarn bundle, the minute barbs will raise more fiber than a single needle point producing more fiber coverage per napping run. Wires with less severe knee bends can be used to raise unbroken loops from filament yarns. In this instance, the wire raises the filament from the yarn and drops it off without breaking the yarn.

IV. SHEARING

Shearing is the process where a raised fiber is cut at an even height. Some spun fabrics are sheared close to the fabric as a means of removing the raised hairs giving the fabric a clear, smooth surface. Shearing is an alternative to singeing. More often however, shearing follows napping to: 1. clear out random lengths of fibers and produce a uniform and level pile., 2. reduce the height of wild fibers and prevent pilling, 3. to produce a certain hand, 4. improve color and appearance and 5. produce sculptured effects.

Knitted and woven fabrics with loops on the face or back are not necessarily napped first - they can be sheared directly to cut off the tops of the loop and produce plushy velours such as knit velours and plush towels. Terry looped bath towels can be sheared on one or both faces to produce a plush pile surface.

A. Shearers

The shearer head consists of a spiral blade revolving on its own axis in contact with a ledger blade. This creates a shearing action similar to that produced by a pair of scissors. When fibers are presented to this cutting head, they will contact the ledger blade and be cut off by the rotating blade. The fabric travels over a cloth rest (bed) in front of the ledger blade and the design is such that an acute angle is formed by the fabric. This sharp angle causes the pile to stand erect and be more easily cut. The distance between the bed and the ledger blade is adjustable so the height of the pile can be regulated.

Most shearers are equipped with expander rolls to straighten and flatten the fabric as it approaches the bed and a vacuum system to remove the lint produced at the cutter. Specially designed support beds, i.e. embossed rolls in place of the support bed, endless embossed support aprons acting as support rests are available for producing sculptured patterns on high pile fabrics. Variations can produce stripes, zig-zag, checks etc. Very often the fabric is brushed prior to shearing. The object of brushing is to lay the fibers in one direction and thus facilitate the cutting process.

Figure 85. Shearer Head

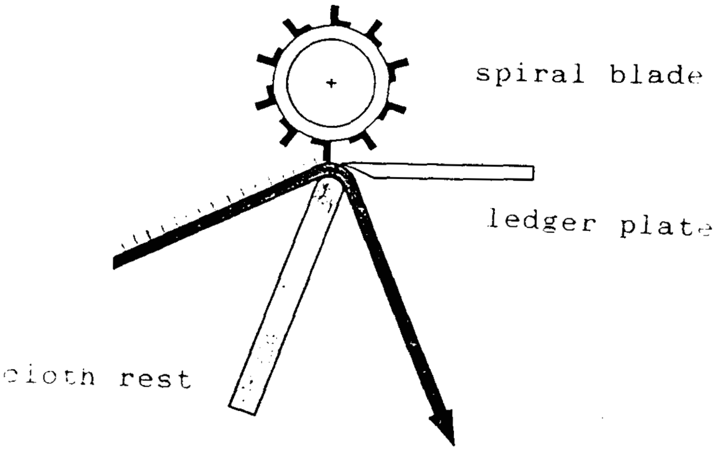
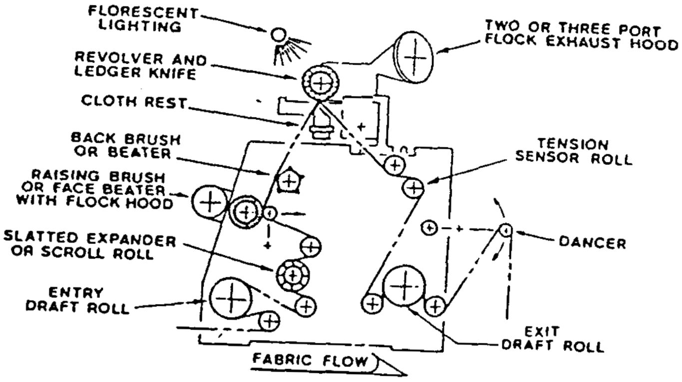


Figure 86. Shearing Machine

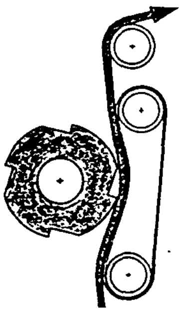


V. POLISHING

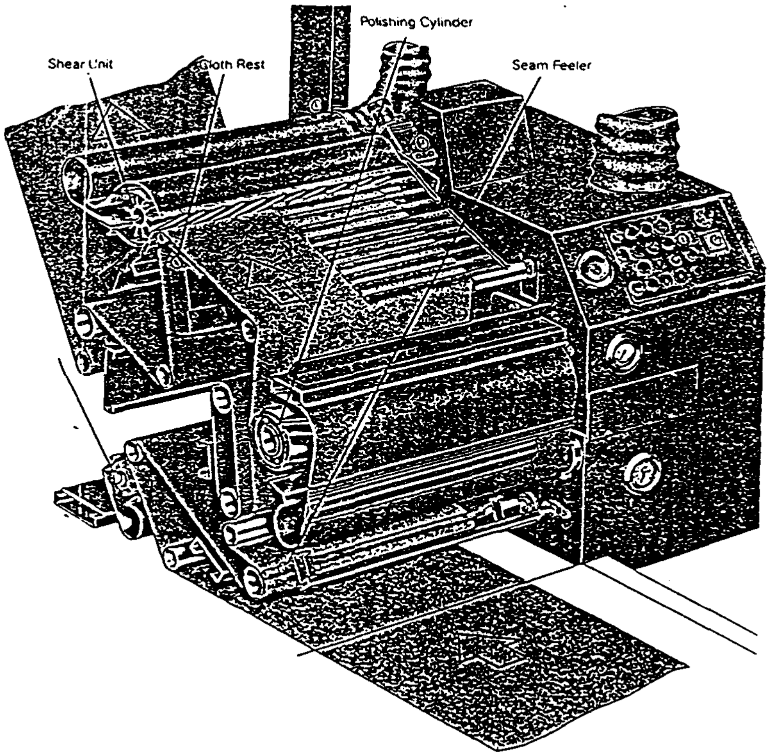
Polishers are primarily used on synthetic pile fabrics when either an erect lustrous pile or a laid down pile is required. The machine consists of a fluted heated cylinder driven by a variable speed motor and an endless felt blanket. The fabric passes over the endless blanket which is adjustable and brings the fabric face in contact with the heated cylinder. The serrations on the cylinder draw through the fibers to raise and parallelize them. Heat facilitates the straighten process and sets the fibers. Polished fabrics appear more lustrous because the parallel fibers result in more uniform light reflection. By running the cylinder so that the edges of the serrations revolve against the fabric flow, the pile will be made to stand more erect. However if the edges of the serrations run in the same direction as the cloth, the pile will be made to lay flat.

Figure 54. Polisher

POLISHING HEAD



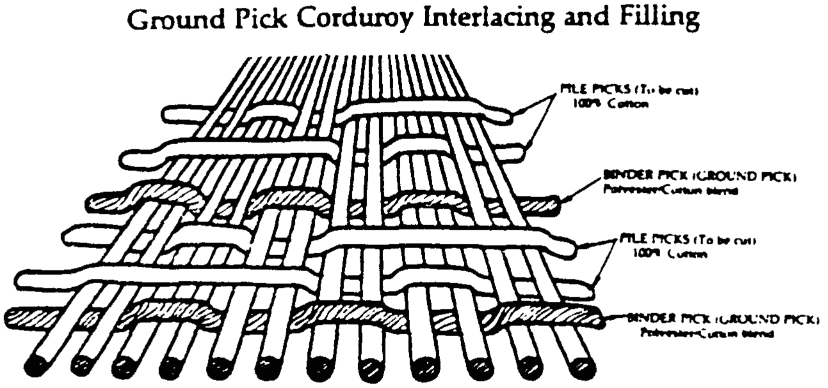
POLISHER



VII. CORDUROY CUTTER

Corduroy fabrics are distinguished from other fabrics by parallel pile ribs running lengthwise in the warp direction. The pile ribs. called wales, are produced by passing the fabric through a cutter which slit specific filling yarns across the face of the fabric. The design of the fabric is such that the filling consist of ground yarns and pile yarns. The ground yarns provide fabric strength and integrity while the pile yarns, will be cut later to form the rib or wale. Figure 88 shows a weave arrangement for anchoring the pile.

Figure 88. Corduroy Fabric as it Come off the Loom

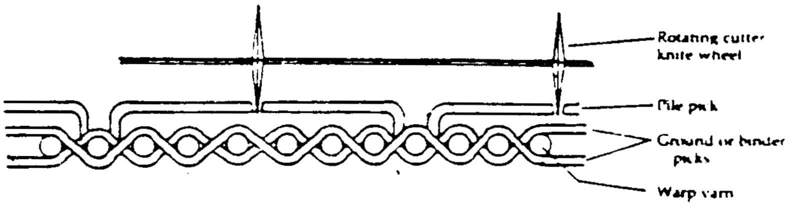


The principle of raising the pile is relatively simple, the filling yarn is slits in two places creating two legs anchored by warp yarns. The two legs become erect when brushes traverse the fabric in the filling direction. The brushing action also causes the individual fibers in the two legs to disentangle and become a single rib.

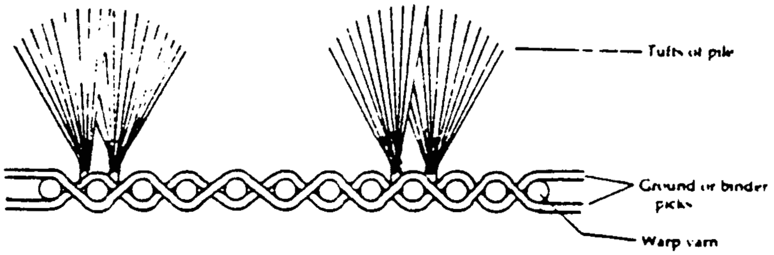
The cutter too is a simple device. It consists of circular knife blades positioned over a slotted base plates. The slotted base plates resembles thin needles which are inserted under the floating filling yarns that are to be cut. Each wale requires two cutters so the number of cutters will depend on the number of wales per inch. Once the fabric is threaded onto each base plate, the fabric is pulled through the machine at an angle. Some fabric require that they be run through the machine more than once. The reason for this is that there are limitations as to how close the cutters can be placed together. For fine wale corduroys, it would take two or more passes before all the appropriate cuts can be made. As mentioned earlier, brushing is necessary to stand the pile and brushing follows the cutting operation. In addition, an adhesive is applied to the back of some styles to improve the anchoring of the pile. It is not very difficult to pull the pile from the back unless it is well anchored in.

Figure 89. Corduroy Cutting

Cutting the Pile



Appearance after Cutting and Brushing



VIII. DECATING

Decating is normally the last finishing process for some fabrics. It is a method of steaming fabric between two layers of cotton press cloths. The process is used to: 1. improve the hand and drape, 2. brighten the colors and enhance natural luster, assist in setting the finish, or refinish fabrics after sponging or cold water shrinkage. Decating is a normal step for many wool and wool blend fabrics. It is an effective mechanical softening treatment resulting in a luxurious, soft, smooth handle. The process is also effective on acetate, acrylic, rayon, spun polyester and other synthetic blends.

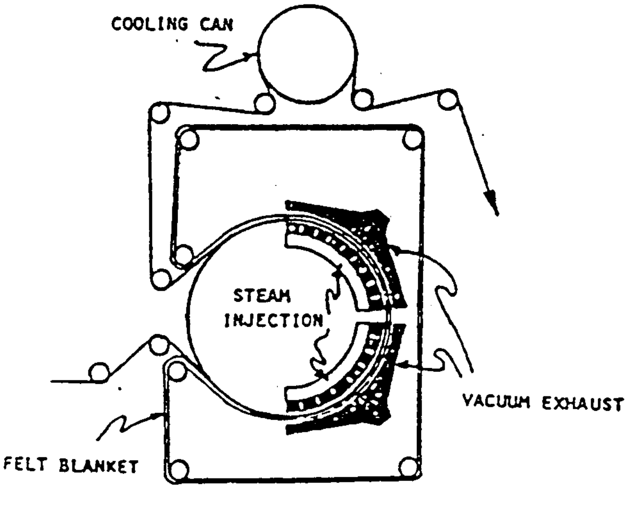
A. Semi-Decating

Semi-decating is a bach process requiring three steps: 1. winding the fabric onto a perforated cylinder between a cotton decating apron, 2. steaming and followed by cooling the fabric and 3. unwinding and batching the finished fabric. Proper pressure, heat, moisture, cooling and time are prerequisites for quality results. The procedure requires that the fabric be wound onto a perforated drum between the interleaving cotton decating apron to form a reasonably thick roll. Steam is forced through the roll (inside - out) for several minutes to provide moisture and heat. Compressed air is then blown through the roll in much the same manner as the steam to remove some of the moisture and cool down the fabric. To insure that the effect is uniform from the inside to the outside of the roll, the fabric and blanket are rewound onto another perforated drum so that the outside layers become the inside layers and the cycle is repeated. At the end of the cycle, the fabric and blanket are separated and wound into individual rolls.

B. Continuous Decating

The continuous decater has one steaming cylinder and one cooling cylinder. An endless decating apron carries the fabric around the steaming cylinder and around the cooling cylinder. The fabric is continuously moving so the time element of the process is affected by the speed of the machine - being somewhat less than the batch-wise semi-decating process. Nonetheless, excellent results are obtained on many fabrics.

Figure 90. Continuous Decater



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