

## CHAPTER 2

# CHEMISTRY OF YARN AND FABRIC PREPARATION

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### 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:

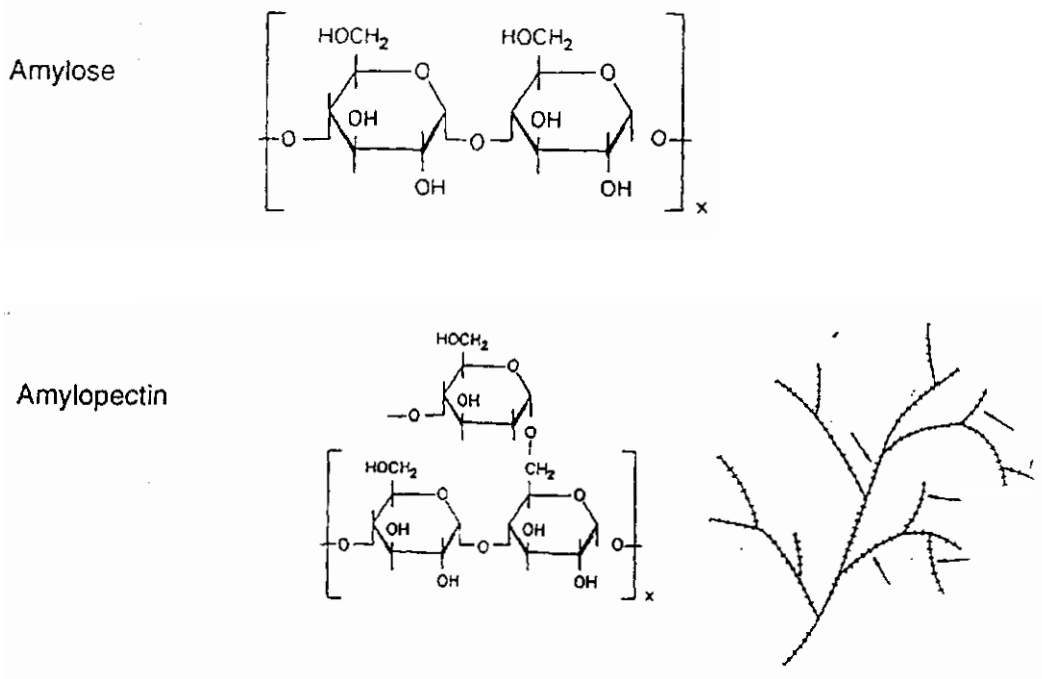
- Corn (maize)
- Tapioca (cassava)
- Wheat
- Sweet Potato
- Potato (farina)
- Sago
- Rice
- Yucca

#### 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 times 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.

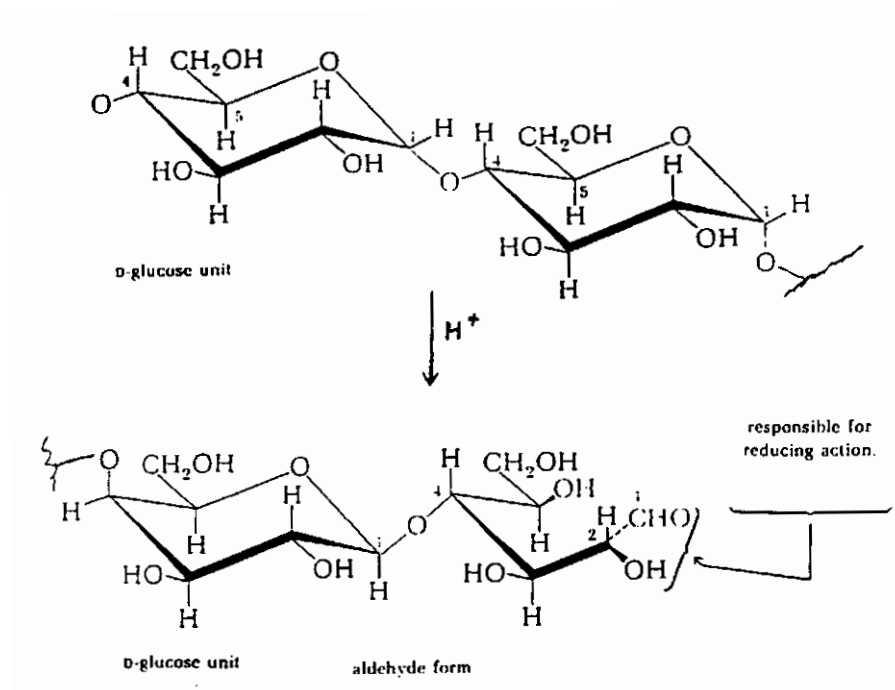
### **2. Dextrin**

Dextrine are made by heating dry starch with a mineral acid. White dextrin is made by heating at moderate temperatures and yellow dextrin 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 °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.

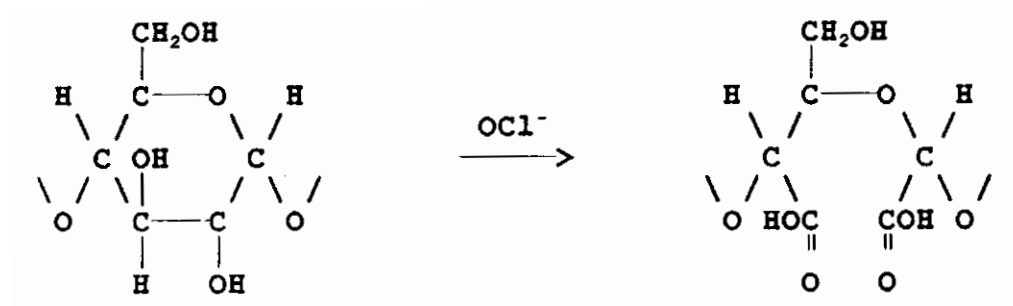
**Figure 12. Hydrolysis of Starch**



**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**





### **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 °C. Bacterial enzymes are the most thermally stable and can be used up to 100 °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 °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 <sub>2</sub>
Pancreas	6.8-7.0	40 - 55	+	+
Malt	4.6-5.2	55 - 65	-	+
Bacteria	5.0-7.0	60 - 70	0	+

**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:

Open-width Range: Steam 1 to 2 minutes at 200 to 212 °F.

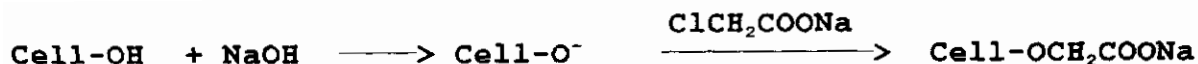
Rope Range: Store in J Box for 20 to 30 minutes at 170 to 180 °F. or over night at room temperature.

3. Thoroughly rinse with hot water, 175 °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



### B. Advantages and Disadvantages over Starch

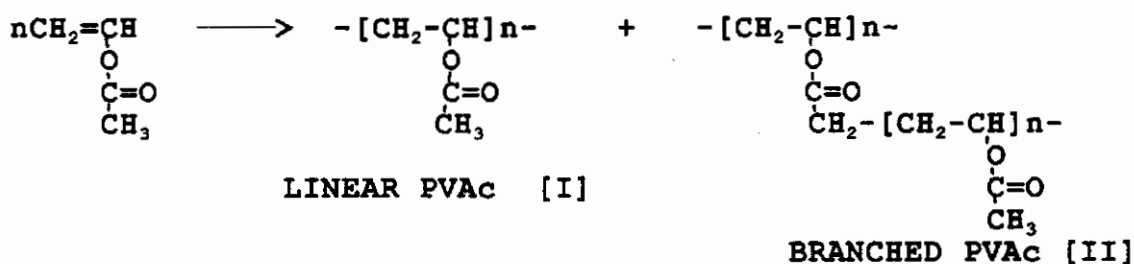
CMC is soluble in cold water and does not requiring a cooking step. Solutions remain fluid at room temperature and don't retrograde, They can be reheated and cooled repeatedly. It is easy to remove and redissolve CMC size in warm water. CMC like starch supports mildew on storage of fabrics. It is more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

## V. POLYVINYL ALCOHOL (PVA)

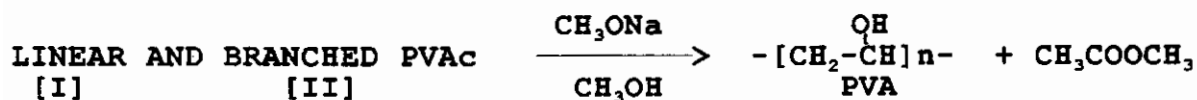
Polyvinyl alcohol comes in several grades, differing in molecular weight and solution viscosity. Polyvinyl alcohol is manufactured by hydrolysing polyvinyl acetate. The reason is because vinyl alcohol does not exist as a monomer, tautomerization favors the more stable acetaldehyde. Polyvinyl acetate, 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



#### 2. Hydrolysis to Polyvinyl Alcohol



### 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 chopped-

up, 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.

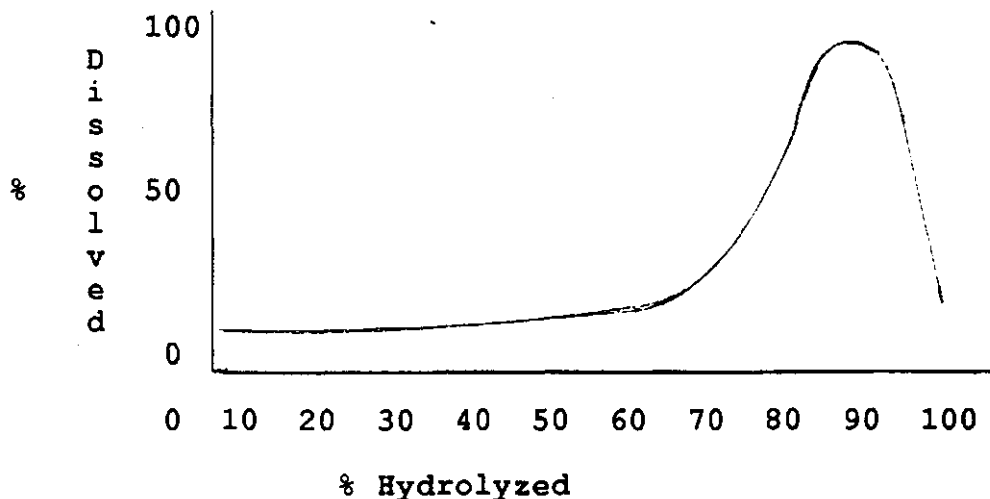
### C. Solution Properties

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.

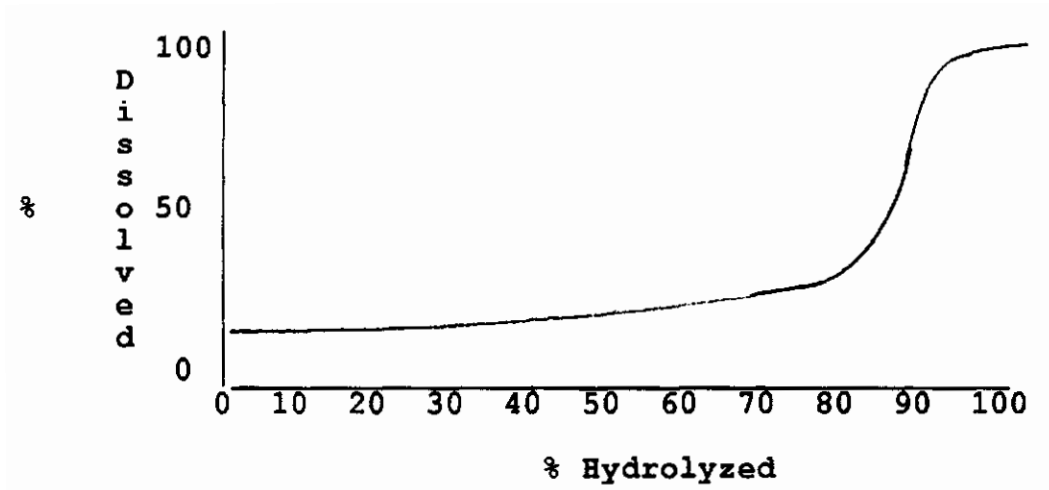
When acetate ester groups remain, the ability of the polymer chains to form H-bonds is interrupted by the pendant nature of the ester group. This allows water molecules easier access to the -OH groups and at 88 % hydrolysis, a balance between the number of hydrophilic groups and chain separation is struck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

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

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.

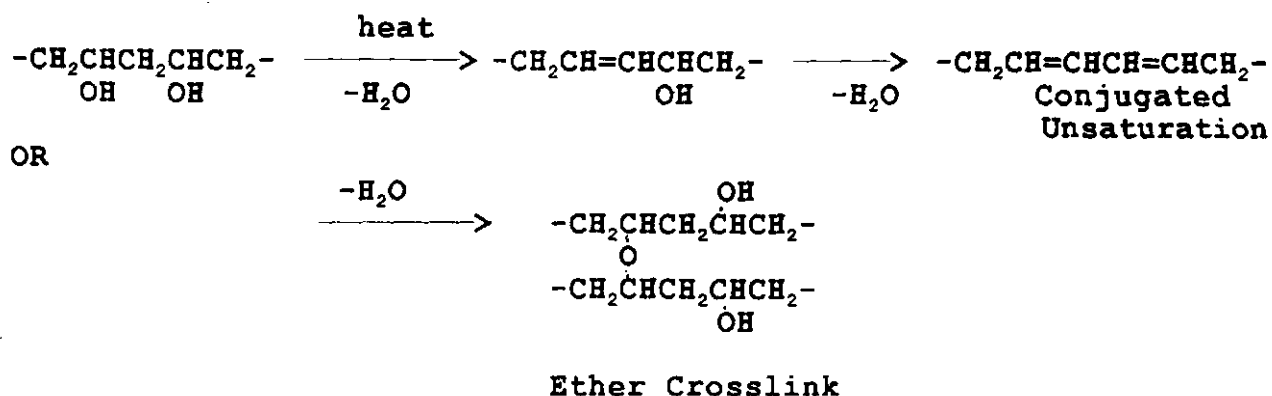
## F. Desizing PVA

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

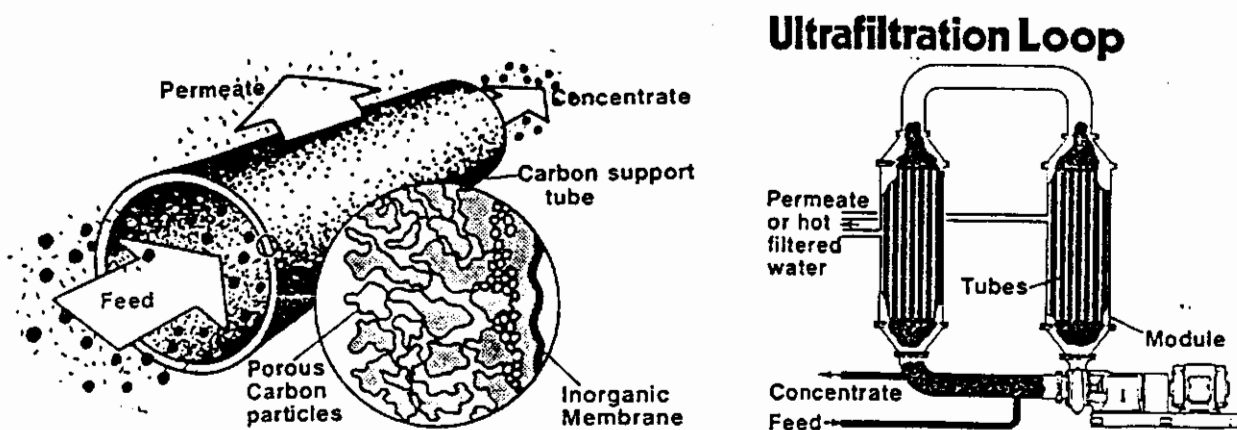


## 2. Size Recovery

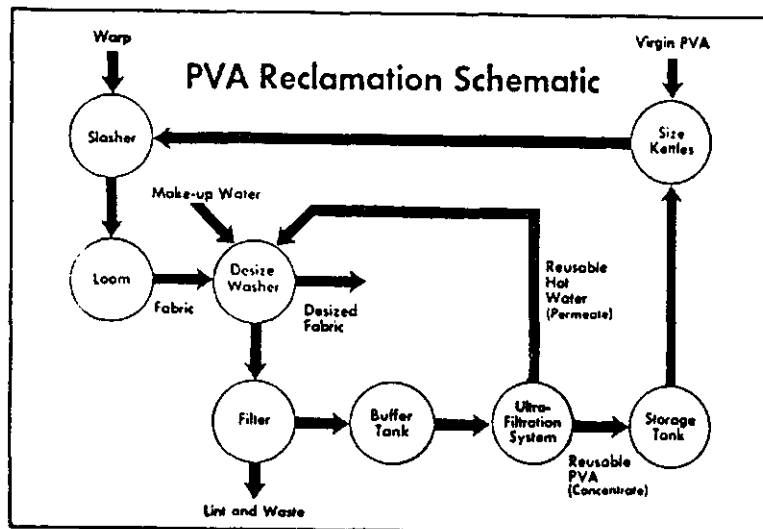
Since PVA's properties are not altered in desizing, the solids in the spent desizing liquor can be reused as warp size provided the concentration can be built back up to the level used in sizing warp yarns. This can be accomplished by passing the spent liquor through a size recovery unit. **Ultrafiltration** 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



#### 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



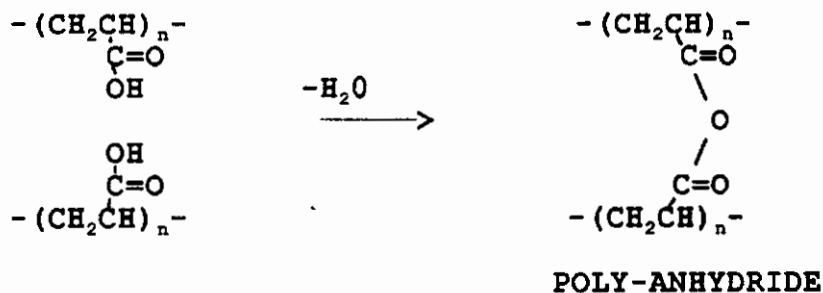
adhesion. As the free acid, the number of carboxyl groups in the copolymer are not sufficient to render the copolymer water soluble; however, when they are converted to the corresponding alkali salt, the copolymer becomes water soluble. These properties are put to good use in water jet weaving. The size 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



## 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