TROUBLESHOOTING IN PREPARATION
A Systematic Approach

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Introduction

An old saying in the textile wet processing industry is "well prepared-half dyed." This statement is not quoted to imply that the majority of problems which occur in dyeing is due to inadequate preparation, but that in many cases problems which are not detected in preparation do lead to faulty dyeings. Grunig [l] breaks down the percentage of defects in textile wet processing according to origin as follows:

Table 1: Defects in Textile Wet Processing According to Origin [l]

Origin of Defect	Percentage of Defects
Finishing	11
Dyeing and Printing	23
Diverse -substrate quality -using wrong products -negligence -uncontrolled trace impurities	21
Biological, chemical, technical, and mechanical including storage and machinery problems	24
Preparation -process deficiencies -deposits and residues -bleach damage -mercerizing damage	21

Although 21 percent of defects in wet processing is directly attributable to preparation, many of the defects listed under the "diverse" and "biological, chemical, etc." categories (particularly substrate quality and uncontrolled trace impurities) can lead to inadequate preparation. It is possible, therefore, that up to 66 percent of the defects in finished fabrics are due to treatments or lack of treatments prior to dyeing.

Since many preparation problems that occur are due to the quality of the substrate and may not show up until later processing, it is often difficult to perceive problems during the preparation processes. Thus the objective of this discussion is thus to outline a systematic in-process approach for detecting and eliminating potential problems during preparation. The procedures suggested will require substantial testing and good, accurate recordkeeping, but they should aid in detecting problems before they show up during later processes; thereby reducing the amount of inferior quality goods produced in preparation. The specific areas which must be evaluated on a regular basis to control production quality include: (1) commodity and specialty chemicals, (2) water; (3) greige fabric, and (4) processes, including process variables and treated fabric analysis.

Commodity and Specialty Chemical Analysis

Many users of chemical products take for granted that the quality of a purchased product is always the same. This assumption may be correct most of the time, but the one time that it is not can cause quality problems. Chemical suppliers, as is the case with all manufacturers, do have quality problems from time to time. When a production lot does not meet specifications,they (like other manufacturers including textile), will initially attempt some repair procedure to get it within specifications. Although the repaired product then meets the supplier's specifications, it may not function consistently in the user's process. If the product cannot be bought to within specifications, the supplier will probably ship it to a customer that he knows is not likely to analyze it. In either, case the lot may be completely used up before the customer becomes aware that he has a quality problem. This is especially true in preparation, where defects may not show up until later processing. It is therefore imperative that each lot purchased be analyzed before use.

Every chemical should be analyzed as it is received to determine the concentration of the active‘ ingredient. Improper dilution of the compound by the manufacturer or decomposition of compounds such as enzymes or hydrogen peroxide may lead to lower activity and result in inadequate preparation treatments. In addition to checking for activity, compounds should be checked to determine whether or not they function properly under process conditions. They should be analyzed in the laboratory in the treatment in which they will by used with the appropriate temperature, pH, and other compounds, and the results compared to those obtained in a simultaneous treatment using a sample of the compound from a manufacturer's standard. It may be helpful to use a lower concentration in this analysis than actually required in the process because differences in the effectiveness of the compound may be more apparent at the lower concentration than at that used in the actual process. In using a lower concentration, however, interactions between the compound and others in the solution that lead to reduced solubility, precipitation, etc. may not be as apparent. Compatibility should therefore also be checked at concentrations equal to or higher than process conditions.

A quick way to check for the activity and composition of a compound is to compare its ultraviolet or visible spectrum to the standard spectrum of the compound. Many dyehouses are equipped with spectrophotometers for determining the strength of dye solutions. Although only colored compounds absorb in the visible portion of the spectrum, many colorless compounds used in preparation absorb ultraviolet light. Many wetting agents, penetrants, chelating agents, and even hydrogen peroxide absorb in the UV region. Beer-Lambert's Law is also obeyed in the UV, that is, absorbance is directly proportional to concentration. It is therefore wise to have absorption spectra at standard concentrations for all compounds that absorb visible or UV light. The compound must be soluble in the solvent to obtain the correct spectra, and organic solvents should be used if the compound is not soluble in water. When a new lot of a compound is received its spectrum (at the same concentration as the standard) can be easily obtained and compared to the standard. Any change in absorbance at the wavelength of maximum absorbance indicates that the activity of the new lot is different from the standard (lower absorbance, lower activity). Any change in the shape of the absorption spectra of the new lot indicates that it has a different composition from the standard.

There are standard tests for analyzing many of the compounds used in the preparation processes. These tests along with a reference for the detailed procedure are listed in Table 2.

Table 2: Standard Procedures for Analyzing Compounds Used in Preparation Processes

Compound	Type of Analysis	Reference
Wetting Agents	Effectiveness Rewetting For Mercerization	2, p. 49 2, p. 88 2, p. 98
Enzymes	Activity	2, p. 163
Nonionic Surfactants	Cloud Point	6 p. 695
Anionic Surfactants	Activity	3, p. 50
Chelating Agents	Activity	2, p. 264
Hydrogen Peroxide	Concentration	4, p. 162 5, p. 29
Sodium Hypochlorite	Available Chlorine	5, p. 35
Sodium Chlorite	Concentration	5, p.34

Water Analysis

The importance of water quality in textile wet processing is discussed in another article of this series. Impurities that are of particular interest in the preparation processes are trace quantities of metal ions. Calcium and magnesium ions, for instance, will precipitate soaps used or produced in scouring leading to deposition of sticky insoluble soaps on the substrate. Transition metal ions like iron, copper, manganese, zinc, nickel, cobalt, and chromium catalyze the decomposition of hydrogen peroxide and degradation of cotton in both peroxide and hypochlo--rite bleaching. In some processes specific metal ions may have beneficial effects. Calcium and particularly magnesium stabilize hydrogen peroxide and inhibit degradation of cotton in peroxide bleaching. Calcium also stabilizes alpha amylase enzymes used in desizing starch. Although the presence of some metal ions may be desireable in specific process solutions, seasonal or other variations in the level of these ions in water can lead to variations in treatments. It is therefore important to periodically analyze process water for the concentration of metal ion contaminants. Quick tests for commonly occurring metallic contaminants in water are described in the other article.

Greiqe Fabric Analysis

The greige substrate should also be analyzed to determine the type and percent of size; level of oils, fats and waxes; and trace metal ions in the fibers. This information will determine the types as well as the severity of the preparation treatments required and indicate precautions which must be taken in preparing the substrate.'

Since the technique for removing warp sizes depends on the type of size, it is imperative that the size on fabrics be identified before desizing. Most vertical processors usually know the type and level of size on woven fabrics along with other components in the size formulation. Most commission dyers, however, do not have this type of information and should carefully analyze the substrate before preparation. Even if the information is known, it is wise to confirm it. With a series of standard solutions, quick spot tests can be conducted to determine type of warp size on fabrics. Livengood [7] published a series of quick spot tests for detecting the presence of starch, polyvinyl alcohol (partially and fully hydrolyzed), carboxymethyl cellulose, starch/polyvinyl alcohol blends, acrylic and polyester sizes on fabrics. After determining the type of size, several samples of the fabric should be thoroughly desized in the laboratory to determine the percent size.

A solvent extraction should also be conducted on several samples of the fabric to determine the oil, fat, and wax content of the fabric. This analysis will indicate the amount of these impurities that must be removed in the scouring process and thus the time, temperature and chemical amounts required. It is most important for knits because these are the major impurities present.

A good general practice to follow is to determine the water, enzymes and solvent extractable content using AATCC Test Method 97-1982 [2, p. 1521, for each style, construction, etc. It is equally important to maintain good records for each test; If problems in preparation are related to specific types and/or levels of impurities, then trends will begin to show up over time. The fabric should also be analyzed for presence of iron and copper in the fibers [5, p.64]. Although trace quantities of these metals do not adversely affect bleaching, higher levels can lead to severe fiber degradation, requiring the fabric to be soured before bleaching. The fabric should also be visually assessed for the presence of rust spots or metal filings which can lead to localized degradation during bleaching. If present proper treatments (souring or treatment with oxalic acid) should again be given before bleaching.

The Preparation Processes

In this section, each specific preparation processes (desizing, scouring, bleaching, and mercerization) is discussed. The basic principles of each process are presented along with the effect that process variables (pH, temperature, etc.) and chemicals have on the process. A systematic procedure for analyzing the treated substrate after each process for determining the thoroughness of the treatment along with possible causes of inadequate treatments is also presented. Alternative procedures, if available, will also be discussed.

Desizing

Warp size is applied to warp yarns to improve their strength during the weaving process. The material coats the yarns and can act as a dye and chemical resist in textile wet processing. It must therefore be removed before any subsequent wet processing of the fabric. The desize procedure depends on the type of size. It is therefore necessary to know what type of size is on the fabric before desizing. This can easily be determined by spot tests as discussed above.

Starch is the most difficult size to remove. It does not readily dissolve in water and must be broken down chemically into water soluble compounds by either enzymes, oxidizing agents, or acids. Enzymes break down starch into water soluble sugars and dextrines, oxidizing agents oxidize starch into compounds that are soluble in alkaline solution, while acids hydrolyze starch into water soluble compounds. Enzymes are specific in their action in that they do not attack cotton, while oxidizing agents and acids can degrade cotton in addition to starch. Starch is therefore usually desized with enzymes.

Starch is actually composed on two components, a straight chain polysaccharide of glucose and a branched chain polysaccharide of glucose. Amylose, the straight chain component, is relatively low in molecular weight, water soluble, and makes up 20-30% of starch. Amylopectin, the branched chain component, is relatively high in molecular weight, water insoluble, and makes up 70-80% of starch. It is therefore the amylopectin component that is difficult to remove in desizing.

The enzyme that is specific to starch is amylase. There are also two types of amylase, alpha and beta. Alpha amylase attacks the starch chains at random leading to a rapid reduction in molecular weight and thus rapid solubilization of starch. Beta amylase, on the other hand, successively removes terminal glucose units from starch chains. Its action is also terminated at branch points in amylopectin, leaving relatively large molecular weight fractions that are difficult to solubilize. Therefore, alpha amylase should be used to obtain rapid and thorough digestion of starch. More specifically, bacterial alpha amylase prepared in cultures is preferable because it is the purestand most stable source. Other types of the enzyme include malt amylase and pancreatic amylase. Many factors affect the stability of amylase enzymes so it should be checked for activity using AATCC Test Method 103-1984, "Bacterial Alpha-Amylase Enzymes Used in Desizing, Assay of" [2, p. 163] before using. It should be pointed out also that amylase enzymes are no longer considered a specialty chemical but have now taken on a commodity status [8].

Process parameters that affect enzymatic desizing are in general those affect the activity of the enzyme. They include pH, temperature, and compounds which enhance or decrease activity. For bacterial amylase, activity of the enzyme increases rapidly with pH up to maximum in the neutral pH range and then decreases significantly. The pH range of 6.5 to 7.5 is generally recommended, but the optimum pH may vary with supplier, temperature, and other conditions. Activity increases with temperature up to a maximum and then decreases. The maximum depends on several factors including source of amylase, presence of stabilizers in the bath, and amount of starch itself. Bacterial alpha amylase is more stable at high temperatures than other sources. Calcium ions and sodium chloride increases the heat stability of alpha amylase. The higher the level of starch, the higher the heat stability of alpha amylase. In general, maximum enzyme activity is obtained in the temperature range of 160-212°F depending on the above factors. Compounds which reduce enzyme activity and should not be allowed to contaminate the desize bath include copper and zinc ions, some anionic wetting agents, chelating agents, oxidizing and **reducing agents.**

Typical desize processes involve the following steps:

1. Saturating the fabric with the following solution at 160°F

0.l-1.0%	Bacterial amylase enzyme
10.0%	Sodium chloride
0.5%	Calcium chloride
O.l-0.2%	Wetting agent (nonionic)

2. Digestion of the starch, either

   a. Batch for 2-12 hours
   b: J-box for l0-30 minutes at 170-180°F

c. Steam for 30-120 seconds at 210-212°F

3. Thorough washing at 180°F or above

The washing step is very important in removing the dextrinized starch from the fabric.

After desizing, the fabric should be systematically analyzed to determine the uniformity and thoroughness of the treatment. It should first be weighed to determine the percent size removed. The results should be compared to those obtained in the lab. If they are lower then either the treatment or washing have not been thorough. Iodine spot tests should then be conducted on the fabric. The fabric should not be spotted randomly but from side-center-side at different points along the length of the fabric. The results of this evaluation will give some idea of the cause of any inadequate treatment as follows:

a. If none of the spots produce blue coloration, then the fabric has been evenly and thoroughly desized.

b. If the spots produce a light blue coloration of uniform intensity, a sample of the fabric should be given a hot alkaline wash. After rinsing and drying the sample, spot it again with iodine solution. If no blue coloration results, then the residual amount of size remaining in the fabric will be removed in the alkaline scour that follows.

c. If the spots produce deep blue to violet coloration of uniform intensity, the fabric should be checked as in step "b." If the iodine spots still turn blue after the hot alkaline wash, there has been'inadequate digestion of the starch, and the source of the problem must be determined.The following is a list of factors that could lead to incomplete starch removal, and each should be checked:

--Process variables
pH of bath (6.5-7.5)
Temperature of bath (150-16O°F)
Wet pick-up (100%)
Time and temperature of digestion

--Proper bath and mix preparation
for example, heating with live steam can inactivate the enzyme or introduce rust into the mix or treatment bath

--Activity of enzyme
AATCC Test Method 103-1984

--Effectiveness of wetting agent
Drop a piece of greige fabric in the bath. It should sink in 2-3 seconds.
AATCC Test Method 17-1985 12, p. 491

--Compatibility of wetting agent
    Some anionics inactivate enzymes, nonionics preferred.
    Compatibility of nonionic at bath temperature (cloud point)
    Compatibility of nonionic with electrolytes in bath

--Metals in water (copper and zinc inactivate enzymes)

--Contaminants in bath (hydrogen peroxide, chelating agents, etc)

--Wash water temperature (above 18O°F)

d. If the spots produce uniform coloration along a side or the center of the fabric, then the pad pressure is not uniform along the width of the fabric.

e. If the spots produce nonuniform coloration, that is, no coloration in some areas and variation in the intensity of blue color elsewhere, then the-fabric has not been evenly treated. There are several possible causes of nonuniform treatment which should be investigated. A poor wetting agent may lead to different degrees of wetting and penetration of the fabric by the bath. If the bath temperature is above the cloud point of a nonionic wetting agent, the insolubilized compound may settle onto the fabric leading to resist spots. If the bath level is low then there may be uneven pick-up of the solution leading to an unlevel treatment. Since the desize bath is usually covered with foam, it may be necessary to add a defoamer to accurately determine the actual bath level. If a defoamer is used, it should be checked beforehand to make sure that it does not inactivate the enzyme and extreme care taken in its use. Improper use of defoamers can lead to the formation of yellow spots on the fabric in later processing or dye resist spots. Other possible causes of an uneven treatment include water or condensation spots on the fabric, temperature variations during digestion and nonuniform washing.

Synthetic polymer sizes such as polyvinyl alcohol (PVA) and carboxymethyl cellulose (CMC) are very popular because in most cases they are very easy to remove compared to starch. Care must be taken in desizing these sizes, however, because they are available in many grades with varying solubility properties. PVA, for instance, is available in grades ranging from fully hydrolyzed (FH Grade) to partially acetylated (PA Grade). The FA Grade is more difficult to solubilize and thus requires more time and higher temperature for complete removal. The grade of PVA on sized fabrics can be determined by spotting with an iodine/boric acid solution [7]. Fabric sized with the partially acetylated grade will turn deep blue-purple when spotted with the solution while no coloration will result when fabric sized with the fully hydrolyzed grade is spotted. In general, PVA is desized with a hot water wash at 180-190°F at a neutral pH. Conditions that can make PVA ve'ry difficult to remove in desizing include overdrying of the fabric and alkaline pH during hot water desizing. The fabric should therefore not be heat set prior to desizing. PVA gels under alkaline conditions so the wash water should be neutral. All grades of CMC are readily solubilized in water and can be easily desized with a warm water wash at 150-160°F.

The desired fabric should be analyzed as discussed above to determine the source of any problems in desizing. The percent size removed should be determined and compared with laboratory results. The systematic spot test analysis should also be conducted. Fabric sized with PVA is spotted with an iodine/boric acid solution while fabric sized with CMC is spotted with a ferric chloride/potassium thiocyanate solution followed by a potassium ferrocyanide solution [7].

An alternative desize procedure is oxidative desizing with peroxides. The oxidizing agent is hydrogen peroxide or in some cases a combination of hydrogen peroxide and potassium dipersulfate, and the process is done under highly alkaline conditions. Advantages of oxidative desizing include: (1) it degrades and removes starch, PVA, and CMC so the type of size on the fabric or size blends do not affect the procedure, (2) some scouring and bleaching action are also obtained, and (3) in some cases the scouring process can actually be combined with desizing. Disadvantages include the high risk of degradation of cotton resulting in strength loss, oxycellulose formation, and possible strength loss of polyester in polyester/cotton blends. The typical desize procedure involves the following steps:

1. Saturate the fabric with the following desize solution at 140°F:

   0.06 g/l Magnesium sulfate
   3.0 g/l Diethylenetriaminepentaacetic acid (40%), DTPA
   40.0 g/l Sodium Hydroxide
   5.0 g/l Wetting agent (nonionic)
   4.0 g/l Hydrogen peroxide

2. Steam for l0-15 minutes at 212°F

3. Thorough washing at 180°F or above

This procedure is reported to produce more uniformly desized fabrics due to the high solubility of the sizes in alkaline peroxide solution [9].

Scouring

This process removes water insoluble materials such as oils, fats, and waxes from textile fibers. These impurities coat fibers and inhibit rapid wetting, absorbancy and absorption of dye and chemical solutions. In addition the scouring process softens and swells motes which facilitates their destruction during bleaching. Oils and fats are removed by saponi-. fication with hot sodium hydroxide solution. This process breaks the compounds down into water soluble glycerol and soaps and is the same process traditionally used in the home to make soaps from animal fat. Unsaponifiable materials such as waxes and dirt are removed by emulsification. This process requires the use of surfactants to disperse the water

insoluble material into fine droplets or particles in the aqueous medium. Both of these processes (saponification and emulsification) take place in the typical scouring process.

The typical scouring process involves the following steps:

1. **Saturate the fabric with the following solution at 180°F:**

   0.1-0.2% Surfactant
   0.3-0.5% Sequestering agent
   4.0% Sodium hydroxide

2. **Steaming**

   60-90 minutes at 212°F in J-box
   it: **20-30 minutes at 212°F in open-width steamer**

3. **Thorough washing at 180°F**

In **scouring polyester/cotton blends, the sodium hydroxide concentration should be reduced to 2.0% to prevent alkaline hydrolysis of the polyester.**

The choice of auxiliaries (surfactant and chelating agent) is crucial to obtain a complete **and thorough scour. The surfactant emulsifies unsaponifiable materials and is especially important in scouring polyester/cotton blends since the sodium hydroxide concentration is lower. Nonionic surfactants are generally preferred over anionics because they are excellent emulsifiers. Care should be taken in selecting a nonionic surfactant, however, because of the inverse effect of temperature on the solubility of nonionic surfactants.** If **the process temperature is above the cloud point of the surfactant, the surfactant will be ineffective and may actually be deposited on the substrate. Best emulsification of impurities by nonionics occurs at a temperature just below the cloud point, so the the surfactant used should have a cloud point temperature just above the operating temperature to be most effective. The presence of alkali or electrolytes in the bath will-lower the cloud point of nonionic surfactants, and the degree to which it is lowered increases with concentration. The cloud point should therefore be checked under use conditions to ensure that the surfactant is effective under those conditions.**

There are techniques for reducing or completely eliminating the adverse effect of temperature on nonionic surfactants. Nonionic/anionic blends which are commercially sold do not exhibit a cloud point. The same effect can be obtained by simply adding an anionIc surfactant to the scour bath in addition to the nonionic surfactant. Crypto-nonionic surfactants do not exhibit a cloud point. These are nonionic surfactants that are capped with an ionic group, and they exhibit the excellent emulsifying properties of nonionics along with the good solubilty properties of anionics. If **anionic surfactants are preferred for scouring, the phosphate ester types are generally recommended.**

Sequestering agents tie up polyvalent cations such as calcium and magnesium in water and in fibers which prevents the precipitation of soaps. Although soaps are no longer used in scouring, they are formed by the saponification reaction. If polyvalent cations are present, insoluble soaps will form, settle on the fabric, and produce resist spots. There are four major types of sequestering agents to choose from, inorganic polyphosphates, aminocarboxylic acids, organophosphonic acids, and hydroxycarboxylic acids. The inorganic polyphosphates such as sodium tripolyphosphate and sodium hexametaphosphate are probably the best overall in that in addition to sequestering most metals they also aid in cleansing the fibers. They may, however, hydrolyze at high temperature and loose their effectiveness. The aminocarboxylic acid types such as ethylenediaminetetraacetic acid (EDTA) are very good in that they sequester most metal ions and are very stable under alkaline conditions. They are the most used types. The organophosphonic acid types such as ethylenediaminetetra(methylene phosphonic acid) are also very effective but comparatively expensive. The hydroxycarboxylic acids (oxalates, citrates, etc.) are excellent for sequestering iron but not effective for calcium and magnesium.

After scouring, the fabric should be checked for thoroughness of scouring. Using a clean eyedropper place a drop of water on the fabric and measure the time required for the specular reflectance of the drop to disappear. The fabric should wet in less than 5 seconds and preferably in less than 3 seconds. AATCC Test Method 79-1986, "Absorbency of Bleached Textiles" [2] p. 1143 is a more precise method of conducting this test. Again testing should be done systematically, checking the fabric from side--center--side at different points along the length of the fabric and evaluated as follows:

a. If all the water drops wet the fabric in less than five seconds, the fabric has been adequately and uniformly scoured.

b. If the wetting time for all the drops is greater than five seconds, the fabric has not been adequately scoured. The following factors can lead to incomplete scouring and should be carefully checked:

   --Process variables
      Temperature of saturation (180°F)
      Wet pick-up (100%)
      Time and temperature in steamer
      Wash water temperature (above 180°F)

   --Proper bath preparation and chemical concentrations

   --Compatibility and effectiveness of surfactant under actual use conditions

C. If the wetting time is not uniform from side--center--side but uniform along the length of the fabric, then the pad pressure is not uniform across the width of the pad.

d. If the wetting time is not uniform along the length of the fabric, the bath should be titrated periodically for alkali content. Variations in chemical feed rates or uneven moisture content in goods coming from the desize washer may also produce this type of nonuniformity.

e. If there is no uniform pattern in the wetting times, the following factors should be checked:

--Stability of surfactant (cloud point above bath temperature)

--Water hardness (effectiveness of sequestering agent)

--Feed of chemicals into saturator (evenly distributed and no gelling of surfactant)

--Condensation or water spots on fabric

--Uniformity and effectiveness of washing

--Improper defoamer use or incomplete desizing

This systematic checking of the scoured fabric narrows the source of problems and should simplify their detection.

An alternative to aqueous scouring is solvent scouring. This process uses organic solvents such as perchloroethylene and trichloroethylene as a scouring medium instead of water. The oils, fats, and waxes on fibers are easily solubilized in the solvent. This process does not produce any fiber damage, has low energy requirements, and is excellent for removing oily impurities from wool and synthetics. It, however, does require special equipment, expensive solvents, and frequently produces hazardous waste materials. Also, it does not swell and soften motes in cotton fibers and thus does not facilitate their removal in bleaching. Emulsified solvents may also be added to-aqueous baths to aid in removal of oily impurities from fibers.

Bleaching

The bleaching process destroys color impurities in fibers producing a white substrate which is (in the case of cotton) also free from motes. This is usually accomplished by treating the fibers with oxidizing agents which oxidize the color impurities to colorless compounds. Oxidizing agents, however, can also oxidize fibers (particularly cotton) leading to a reduction in fiber strength. Conditions during bleaching must therefore be carefully controlled to maximize destruction of the color impurities but minimize fiber degradation. Hydrogen peroxide, sodium hypochlorite, and sodium chlorite are the most common bleaching agents. Hydrogen peroxide is by far the major one today as it is used to bleach at least 90% of all cotton and cotton blends. This discussion will therefore be limited to bleaching with hydrogen peroxide.

Neutral hydrogen peroxide is not an effective bleaching agent. It must be activated by adding alkali to increase pH and generate the perhydroxyl ion which is the active species in bleaching. Alkaline conditions, however, can produce undesireable results such as peroxide decomposition and fiber degradation. Table 3 shows the effect of pH in the alkaline range on bleaching effectiveness, fiber degradation and peroxide stability in bleaching cotton fibers. With increasing pH Whiteness Index (WI) as determined by AATCC Test Method 110-1979 [2, p. 172} increases to a maximum at a pH of 11.0 and then decreases. Fiber degradation as determined by CUEN fluidity (AATCC Test Method 82-1984) [2, p. 116] is at a minimum at a pH of 9.0 but that obtained at a pH of 10.1 is well within acceptable values. Above a pH of 11.0 fiber degradation is severe. Peroxide stability decreases with pH as hydrogen peroxide itself is very stable, but the perhydroxyl ion is not. The pH range of 10.2 - 10.7 is considered optimum for bleaching cotton with hydrogen peroxide. Lower pH values can lead to silicate deposition due to decreasing solubility of sodium silicate as well as lower whiteness due to less activation of the peroxide.

Table 3: Effect of pH on Bleaching Effectiveness, Fiber Degradation, and Peroxide Stability in Bleaching Cotton Fibers

Initial pH	Final pH	Whiteness Index	CUEN Fluidity	% Peroxide Remaining
8.0	4.4	66.8	5.48	72.5
9.0	8.7	67.3	1.44	71.6
10.1	9.9	71.3	2.44	63.3
11.0	11.7	72.2	7.29	7.0
12.0	12.4	69.5	17.8	2.0
Unbleached		34.2	0.96	

Formulation:

2.0 g/l Hydrogen peroxide (50%)
5.0 g/l Sodium silicate (42O Be)
0.5 g/l Magnesium sulfate
Sodium hydroxide (pH)

Time = 60 minutes
Temp = 9o°c

Sodium silicate and magnesium sulfate are usually added to hydrogen peroxide bleach solutions. The role of each is not completely understood, but it is generally thought that the combination forms magnesium silicate which in turn stabilizes the decomposition of peroxide caused by trace transition metal ions in the fibers and solution. The results shown in Table 4 indicate that the major role of sodium silicate- is that of aiding in, perhaps catalyzing, bleaching. The major role of magnesium ions is that of stabilization of pH during bleaching. In doing so fiber degradation and peroxide decomposition are reduced. The ability of magnesium ions to help maintain the pH below 11.0 reduces the formation of oxycellulose which occurs under highly alkaline conditions. It also substantially increases the stability of hydrogen peroxide as peroxide decomposition increases with pH. These results show that magnesium ions are as important in peroxide bleach solutions as sodium silicate. It may not, however, be necessary to add magnesium sulfate to the bleach solution as the quantity present in fairly hard water may be sufficient. If the water used is not hard or has been softened, then magnesium sulfate should be added.

The time, temperature, and concentration of compounds in the bleach solution are all interrelated. Hydrogen peroxide can effectively bleach cotton at low temperatures, but longer times and higher chemical concentrations are required. As the temperature of bleaching increases shorter times and lower chemical concentrations can be employed. Table 5 shows the relationship between time, temperature, and chemical concentration.

Table 4: Effect of Sodium Silicate and Magnesium Sulfate in Bleaching Cotton with 2.0 g/l Hydrogen Peroxide (50%) for 60 Minutes at 90°C.

Compound Added	Concentration (g/l)		
Sodium silicate	5.0	5.0	
Magnesium sulfate		0.5	0.5
Initial pH	10.7	10.7	10.7
Final pH	11.2	10.6	10.5
Whiteness Index	71.6	73.1	67.6
CUEN Fluidity	3.10	1.82	1.02
% Peroxide Remaining	16.5	67.4	68.8

Table 5: Relationship between Time, Temperature, and Concentration of Chemicals in Peroxide Bleaching [10]

Time (min.)	50-60	8-10	2	**12-16(hr)**
Temperature (°C)	**100**	**100**	1OO	15-25
Hydrogen peroxide, 100% (%)	0.25-0.5	0.5-1.5	1.5-2.0	2.0-4.0
Sodium silicate (%)	1.0-1.2	1.2-1.5	0.8-1.0	1.5-2.0
Sodium hydroxide (%)	0.1-0.15	0.2-0.4	0.5-0.8	1.0-1.5

All chemical concentrations are expressed as percentages based on the weight of dry fabric.

After bleaching, fabric should be visually observed for motes and pin-holes. It should be practically free of motes. Inadequate mote removal usually results when the pH is too low during bleaching, peroxide decomposition during bleaching is high, or the motes are not adequately softened in scouring. Pin-holes are the result of localized fiber degradation by hydrogen peroxide and is usually catalyzed by metal ions such as iron and copper. There are many sources of these metal ions that should be checked. They may be present in the water supply. A common source or iron is rust from water and steam supply lines. Rust may also be present on the fabric as a result of contact between wet fabric and metal. Metal shavings from previous processing may also be a source of metals in the fabric. In addition, metal ions are inherently complexed with the fibers, and the amount will vary with source of fibers and/or growing conditions.

The whiteness index (WI) of the fabric should be measured systematically from side to center to side along the length of the fabric. The WI value may vary with the instrument used for its determination, but in general should be. between 72 and 80. AATCC Test Method 110-1979, "Reflectance, Blue, and Whiteness of Bleached Fabric" [2, p. 172] outlines the procedure for measurement, and acceptable standards should be set up by the bleacher with his instrumentation. Systematic testing again will help pinpoint causes of inadequate bleaching. A uniformly low WI indicates that one or more of the process parameters is not correct. Such factors as the concentration of chemical is the bleach solution, pH or alkali of bleach solution, percent wet pickup, and time and temperature of steaming should be checked. In addition the residual peroxide on the fabric after steaming should also be checked. It should be at least 15%. If peroxide decomposes too much during steaming, the fabric tends to yellow under the highly alkaline conditions. If residual peroxide is low, stabilization of the bleach solution in not adequate., If the WI is not uniform, variation is pad pressure along fabric, variation in chemical concentration in the saturator, or variation in temperature during steaming are usually the causes. The peroxide and alkali contents of the bleach solution should be checked periodically, AATCC Test Method 102-1985, "Hydrogen Peroxide: Potassium Permanganate Method," [2, p. 162] and AATCC Test Method 98-1982, "Alkali in Bleach Baths Containing Hydrogen Peroxide" [2, p. 153].

Several samples of the bleached fabric should be dyed with a direct dye along with a sample known to be properly bleached. The samples should be inspected for resist marks and compared to the properly bleached sample for depth of shade. Light dyeings or light patches or spots indicate either silicate deposits or oxycellulose formation during bleaching. Silicate deposition can be detected by the formation of an intense yellow color in a molybdic acid test conducted on the ashed fabric [5, p. 62]. Deposition of silicates on the fabric can be caused by several factors: (1) Improper ratio of Na20 to Si02 in the bleach solution. The ratio should be approximately 1:1. (2) Low pH during bleaching, since solubility of sodium silicate increases with pH in the alkaline range. Inadequate rinsing of bleached fabric. Sodium silicate is difficult to completely rinse from fabric because the pH decrease with rinsing leads to decreased solubility of the silicate. Potassium silicate is more soluble than sodium silicate and thus more free rinsing. There are reports of the use of potassium orthosilicate to replace sodium silicate and potassium hydroxide to replace sodium hydroxide in bleaching [11].

Oxycellulose is produced by the oxidation of chemical groups in cotton fibers. In addition to reducing the dyeability of the fiber, this also causes a reduction in fiber strength. A variety of products can result from the oxidation, and some of the damage may not show up until after subsequent alkaline treatments such as mercerization. Detection of oxycellulose is complicated by the fact that there are several different types of oxidized products and any given test may only be specific to one type of damage. A good discussion of the various types of oxycellulose and details of the test methods is presented by Garner [12]. The alkaline silver nitrate (Harrison's Reagent) test is probably most useful for detecting localized oxidative damage.

AATCC Test Method 82-1984, "Fluidity of Dispersions of Cellulose from Bleached Cotton Cloth," [2, p. 116] should also be conducted to assess the degree of fiber degradation during bleaching. The CUEN fluidity of bleached cotton should be between 0.9 and 3.3, and fluidity values above 5.5 indicate severe fiber damage. High fluidity values can result from the pH being too high, unstabilized peroxide, metal contaminants in solution or fibers, or extreme conditions of time temperature or peroxide concentration. The test should also be conducted on a sample after boiling in 2.0% sodium hydroxide for 2 hours. A large increase in fluidity after the alkaline treatment is an indication of oxycellulose damage.

Other tests that should be conducted on the bleached fabric include: (1) AATCC Test Method 79-1986, "Absorbency of Bleached Woven Cloth" [2, p. 114]. The fabric should wet immediately with the specular reflectance of the water drop disappearing in at most 5 seconds and preferably 3 seconds. (2) AATCC Test Method 97-1982, "Extractable Content of Greige and/or Prepared Textiles" [2, p. 152]. Total extractables should be less than

1.0% with the enzyme, water, and solvent extractables each being less that 0.2%. AATCC Test Method 78-1985, "Ash Content of Bleached Cellulosic Textiles" [2, p. 113]. The ash content should be less than 2.0%.

There are several alternate procedures for bleaching cotton with hydrogen peroxide. These procedures have been developed because of the problems caused by silicate deposition on fabric and machinery, and they do not incorporate sodium silicate in the bleach bath. "Silicate-Free" bleach formulations [l3] use organic sequestering agents to prevent the decomposition of hydrogen peroxide caused by metal ions. Diethylenetriaminepentaacetic acid (DTPA) is the most commonly used sequestrant. Sodium hydroxide provides the alkalinity necessary for peroxide activation, and magnesium sulfate is required to prevent peroxide decomposition caused by increasing pH during bleaching. A surfactant is also commonly added to the bleach solution as a dispersant. Other compounds incorporated in proprietary stabilizers include oxalates and phosphates. The results obtained with "silicate-free" bleaching have been satisfactory, but the cost of the organic sequestrants, compared to that of sodium silicate, has limited its use.

These non-silicate peroxide bleaching systems are widely used on knits in modern "jet" bleach ranges. Problems commonly encountered in these operations appear at first to be unrelated, but essentially all result from poor bath stability. These jet bleaching ranges typically have eight to twelve compartments through which the fabric is transported. Usually some of these compartments are used for scouring/bleaching while others are used for washing and, in producing market whites, for applying tints. When the bath foams, fabrics ballon excessively, uneven dwell times result, and this may lead to inconsistent bleaching or shade if applying tint. This uneven transport and ballooning frequently result from peroxide decomposition which produces oxygen. Addition of defoamer can cause yellowing, spotting and precipitates in the machine. The best solution to this problem is to use products which produce minimum foam, use the minimum amounts of peroxide required to produce the desired degree of whiteness, insure maximum stability of the peroxide bath by using a good stabilizer, and removing as much iron, copper, and other metals (which may cause decomposition) from the water prior to use in bleaching. It is also important to have accurate control of all chemical feeds to the bleach range, especially the tint. A tint which has slow, even exhaustion and good leveling properties at extremely low add-on levels must be chosen. Acid dyes are frequently used successfully.

An alkali-free system for bleaching with hydrogen peroxide has been developed by BASF, and products are marketed by other companies. The system does not require alkali for peroxide activation but instead a special activator is incorporated in a proprietary compound. The compound is the only one added to the peroxide bleach solution, and bleaching is normally carried out at a pH of 7.5 for 60-90 minutes at 200-212°F. Acceptable results have been obtained in bleaching 100% cotton and polyester/cotton blends with this and other alkali-free systems.

Mercerization

Mercerization is the treatment of cotton under tension with a strong sodium hydroxide solution. This process improves many properties of cotton fibers and may actually reduce or eliminate some dyeing problems. Some of the properties of cotton fibers that are improved by this process include absorptivity, dyeability, tensile strength, luster, and dimensional stability. The process produces cotton with more uniform properties which is particularly helpful in reducing some of the dyeing problems caused by immature cotton. Mercerization can be done at any stage during preparation--from before desizing to after bleaching. Fewer problems are encountered, however, when mercerizing bleached fabric.

Mercerization is generally accomplished by padding fabric through a strong sodium hydroxide solution, allowing time for the alkali to penetrate and swell the cotton fibers, framing to provide the tension required for luster development, and thorough rinsing to remove the alkali. The sodium hydroxide concentration should be maintained between 25 and 30% (48-54° Tw). Lower concentrations will result in a lower degree of mercerization and less luster. Higher concentrations have no additional effect. A good wetting agent or penetrant should also be added to the bath. It should be stable and effective at the high alkaline concentrations used (AATCC Test Method 43-1985) [2, p. 98]. Only those designed specifically for mercerization should be used. The temperature of the bath can affect the degree of mercerization. Swelling of cotton and thus mercerization decreases with increasing temperature. The temperature should be maintained between 70 and 100°F. Lower temperatures do not affect the process if the sodium hydroxide concentration is in the proper range. At lower concentrations degree of mercerization will increase as temperature decreases. Lower degrees of mercerization are obtained as temperature increases above 100°F.

Wet pick-up in padding can affect mercerization in several ways. Less swelling will occur at low wet pick-up leading to incomplete mercerization. The caustic solution also plasticizes the fabric so that it is easily stretched. At low wet pick-ups less plasticization occurs and the fabric may tear during stretching on the frame. Wet pick-up should be about 100%. After padding at least 30 seconds should be allowed for the caustic to swell the cotton fibers before tension is applied on the frame. Shorter times will result in incomplete mercerization.

As cotton fibers are swollen by the alkali, the fabric shrinks. To obtain luster and shrinkage control the fabric must be stretched on a frame. It should be stretched in the filling direction to its greige width or slightly more. No stretching in the warp direction is required unless extreme luster is desired. If warp stretching is required, the frame speed should not exceed the padder speed by more than 5 percent.

Removal of caustic from the fabric is very crucial for the development of luster and shrinkage control. The caustic solution concentration in the fabric (not the rinse solution) should be reduced to less than 5% with the fabric still on the frame. If not, low luster and shrinkage of the fabric will occur. If the fabric shrinks as it comes off the frame, the caustic concentration in the fabric has not been reduced sufficiently. After the fabric comes off the frame the remaining caustic should be thoroughly rinsed out. It is difficult to remove the residual amounts of caustic from the fabric by rinsing alone, so residual amounts are usually neutralized with a dilute acid solution. Care should be taken in using acetic acid for neutralization as some of the sodium acetate formed may remain in the fabric and alter the pH of the subsequent process.

The mercerized fabric can be analyzed for degree of mercerization, AATCC Test Method 89-1985, "Mercerization in Cotton" [2, p. 127]. The Barium Number obtained from this test should be at least 130 and preferable 150. Low numbers-result from incomplete swelling of cotton fibers which can be caused by factors previously discussed. The test should be conducted at different points along the length of the fabric. Decreasing Barium Numbers along the length indicates that the bath concentration is decreasing or that the bath temperature is increasing. Both of these conditions can result in mercerizing wet fabric. Not only can the bath become diluted, but the reaction between caustic and water generates heat which may increase the bath temperature. When mercerizing wet fabric, the time allowed for swelling of the fibers must also be increased.

The test for determining Barium Numbers is long and tedious. A quick test for analyzing for the degree of mercerization is to dye samples of the mercerized fabric along with a sample known to be properly mercerized using a direct dye such as C.I. Direct Blue 80. Any differences in the depth of the dyeings are indicative of different-degrees of mercerization. A red or blue dye should be used since it is easier to visually observe differences in depths of these colors.

There is no standard test for analysis of the luster of mercerized fabric. It must be judged visually. Many factors can result in the fabric having low luster. They include low caustic concentration in the mercerizing bath, bath temperature too high, low wet pick-up, inadequate time for swelling the fibers, inadequate stretching on the frame, or too must caustic in the fabric as it comes off the frame.

Summary

It is impossible to discuss all the problems along with possible causes that can occur in the preparation processes. The approach taken here is to prevent many problems before they occur and to detect problems before large quantities of inferior quality goods are produced. Analysis of raw materials such as the fabric, water, and chemicals for contaminants or activity provides essential information on the types and amounts of impurities that must be removed and any changes in process conditions that may be necessary, impurities that may interfere with the process, and the actual concentration of active chemicals which may vary due to decomposition or improper dilution by the manufacturer. The technical aspects presented for each process along with the systematic approach to in-process analysis provides a basis for detecting and pinpointing the cause of problems during the process so that large quantities of inferior quality goods are not produced and possibly dyed. Although most of the procedures discussed are for continuous preparation of cotton and polyester/cotton blends, the principles and systematic approach to analysis can be applied to other fibers and batch processes with some modifications.

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