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PROCESS OF REMOVING POLYVINYL ALCOHOL CONTAINING SIZE

Louis Kravetz, Walnut Creek, Calif., and Gerald R. Ferrante, Edison, N.J., assignors to Shell Oil Company, New York, N.Y.

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ABSTRACT OF THE DISCLOSURE

Polyvinyl alcohol-containing size is removed from fabrics by applying a solution consisting essentially of water and hydrogen peroxide and having a pH of not greater than 9 and preferably containing a wetting agent.

BACKGROUND OF THE INVENTION

This is a continuation-in-part of our copending application Ser. No. 833,295, filed June 19, 1969, now abandoned.

In the manufacture of textiles, it is common to treat warp yarns with a size coating prior to weaving into a fabric. Typically, starch is used as sizing agent. While an effective size for cellulosic fibers, such as cotton and the like, starch has relatively poor adhesion to many synthetic fibers. Polyvinyl alcohol has become increasingly important as a replacement for starch in warp sizing. Polyvinyl alcohol exhibits excellent adhesion to synthetics (particularly polyesters) and also provides a greater sizing effect per weight of size, one pound of polyvinyl alcohol being equivalent to about three to five pounds of starch, thus permittting faster processing and less thread breakage.

Following weaving of the sized fibers, the sizing agent must be removed prior to further fabric finishing operations such as bleaching, dyeing, and the like. Amylase systems are generally used to desize starch-sized fabrics but are ineffective with polyvinyl alcohol. Polyvinyl alcohol is conventionally desized with hot water-detergent combinations or hot-water mineral spirits emulsions at 190–210° F. These conventional desizing procedures require strict temperature control and still often leave relatively high levels of polyvinyl alcohol on the fabric. This residual polyvinyl alcohol may loosen in subsequent finishing operations, such as alkaline scouring or alkaline dyeing. In these later alkaline media the loosened residual polyvinyl alcohol may then gel and either redeposit on the surface of the fabric and thus prevent uniform bleaching and dyeing, or deposit on and seriously clog finishing equipment thereby adding to maintenance costs. These conventional solutions are especially ineffective for removing polyvinyl alcohol from fabrics that have been heat set.

As an alternative to conventional polyvinyl alcohol desizing agents, hydrogen peroxide solutions have recently been proposed. (Du Pont sales bulletin "Removal of Elvanol® from Fabric," pp. 7 and 8.) These previous peroxide desizing solutions have been conventional bleaching solutions, that is, containing caustic and sodium silicate in addition to hydrogen peroxide and having pH's of 9 or greater. These solutions have not proven effective. While they do remove a major portion of the polyvinyl alcohol, their high alkalinity causes gelling and redeposition of splotches of polyvinyl alcohol on the fabric surface. Also, when these solutions contact polyvinyl alcohol they develop an intense yellow color and an offensive odor which affects the quality of the treated goods. Williams and Donermeyer (Am. Dyestuff Reporter, June 3, 1968, pp. 30–37) have shown that alkaline hydrogen peroxide

solutions are, in fact, less effective polyvinyl alcohol desizing agents than solutions containing sodium hydroxide alone.

STATEMENT OF THE INVENTION

It has now been found that polyvinyl alcohol-containing sizing is effectively removed from fabric by applying to the sized fabric a desizing solution consisting essentially of an aqueous solution of hydrogen peroxide of pH 4–9 containing from about 0.01 to about 1.5% by weight hydrogen peroxide. In preferred embodiments, the desizing solution additionally contains up to about 0.15% by weight of a surface active agent.

DETAILED DESCRIPTION OF THE INVENTION

The desizing solution—The hydrogen peroxide concentration in the aqueous desizing solution is advantageously maintained between about 0.04% and 0.5% by weight, with concentrations between about 0.1 and about 0.4% by weight being preferred. Higher concentrations of hydrogen peroxide may be employed if desired.

It is essential that the pH of the desizing solution be maintained below about pH 9, desizing solutions having pHs greater than 9 being relatively ineffective. Advantageously, pH is maintained between about 9 and 5, with pH's between 6 and 8 being preferred.

Often to maintain the pH within the preferred range it is desirable to incorporate into the desizing solution a minor amount of a pH-buffering material such as an alkali metal salt of a weak or intermediate acid, for example, alkali metal bicarbonates and dihydrogen phosphates. Preferred buffering materials comprise alkali metal dihydrogen phosphates. Generally, additions of buffering material of not more than about 0.03% by weight are useful with amounts of from about 0.001 to 0.02% by weight being preferred. Higher concentrations of buffering material may be used, if needed to maintain the desired pH.

Alkali metal silicates are a common component of conventional fabric treating solutions especially bleaching solutions where they impart added whiteness to the fabric. While such silicates may be added to the present solutions, it is preferred to not do so as they tend to slow the desizing rate.

Surface active agents (wetting agents), both ionic and nonionic, may optionally be added to desizing solutions according to the invention. Suitable wetting agents comprise long chain alcohol ethoxylates, fatty acid soaps, petroleum sulfonates, alkali metal petroleum sulfonates, sulfated alcohols, alkylbenzene sulfonates, and the like. Preferred wetting agents comprise non-ionic wetting agents especially long-chain alcohol ethoxylates, e.g., C_{12}–C_{20}-alkylpolyoxyethyl alcohols of 3–20 oxyethyl groups. These long chain alcohol ethoxylates improve desizing performance by increasing fabric wetting. Wetting agents especially preferred comprise blends of polyoxyethylated C_{12}–C_{20} linear alkyl alcohols of from 3 to 10 oxyethyl groups.

Surface active agent concentration in the desizing solution is advantageously maintained between about 0.005 to about 0.25% by weight with concentrations of from 0.05 to about 0.15% by weight being preferred.

Conventional starch-desizing enzymes (amylases) are on occasion incorporated into solutions according to the invention to provide a desizing solution effective for the removal of polyvinyl alcohol starch combination sizings. Enzymes such as, for example, Wallerstein Co.'s Rapidase,, Premier Malt Products, Inc.'s Exsize HA and Amizyme tablets, Metro-Atlantic Inc.'s Atcozyme, Woonsocket Color and Chemical Co.'s Wooncozyme L and Jersey State Chemical Co.'s J-Zyme 30 may be suitably employed. These conventional enzymes are quite effective at the pH's of the instant desizing solutions. When enzyme is employed, concentrations of up to about 4%

by weight are suitable with concentrations of from about 0.2% to about 2% by weight being preferred.

Operating conditions.—Fabric treatment with the solution according to the invention is suitably carried out at temperatures above about 120° F. Very acceptable are temperatures between about 130° F. and 260° F. with temperatures of from about 150° F. to 212° F. being preferred and temperatures of from 190° F. to 212° F. being most preferred. With temperatures in the general range; one can ordinarily obtain suitable desizing with desizing times of from about 2.0 to about 90 minutes. With the preferred temperatures generally from about 5 to about 30 minutes are required for good desizing of most fabrics. Some heavyweight fabrics may require longer times to effect complete penetration of the desizing solution.

When fabrics sized with polyvinyl alcohol-starch combination sizings are being desized using a hydrogen peroxide-amylase solution, it is very preferred to first treat the fabric at a temperature between about 160° F. and 180° F. for from about 15 to about 30 minutes and then raise the treating solution temperature and treat the fabric at a temperature of from about 200° F. to about 212° F. for from about 5 to about 15 minutes.

Any of the conventional continuous or batch methods of applying desizing solution to fabrics can be employed in carrying out the desizing with the new desizing composition. A simple and effective procedure is to immerse the fabric in the desizing solution at the operating temperature until the desired desizing action has taken place. In a continuous process the fabric is pulled at a regulated rate through a bath of heated desizing solution. In another continuous process the fabric is, for instance, first padded in open width with the new desizing solution, either warm or cold. Then, after leaving the padding mangle, the goods are passed to a steamer or passed through a pot-eye to convert them into rope form followed by heating and piling into a J-Box where the desizing is completed by heating. The desizing is followed by the usual washing treatments. Still other procedures are applicable, the invention not being limited with respect to the method by which the new desizing solutions are applied to the fabric which is to be desized.

The fabrics treated.—The desizing process of this invention is effective with all types of fabrics, including difficult to desize heat set fabrics. Heat setting is a brief exposure to high temperatures, e.g., 10 seconds at 400° F., applied to improve the dimensional stability and "easy-care" properties of synthetic fabrics. This treatment is carried out prior to desizing. Polyvinyl alcohol exposed to this treatment is extremely difficult to remove by conventional means. The process of this invention may be used to remove all types of polyvinyl alcohol including fully hydrolyzed and partially hydrolyzed grades.

The following examples demonstrate the polyvinyl alcohol desizing effectiveness of the solutions of the invention. They are not to be construed as limiting the invention.

Example I and Comparative Experiment A

A mill trial of the hydrogen peroxide desizing process of this invention was conducted in a finishing plant. The fabric used was 50/50 polyester/cotton blend greige goods weighing approximately 4.0 oz./square yd., containing 7.2% of fully hydrolyzed polyvinyl alcohol. The desizing solution contained from 0.4% to 0.5% by weight of hydrogen peroxide. It also included 0.1% of a nonionic wetting agent and 0.2% of a chelating agent to minimize H_2O_2 decomposition. The pH of the solution was approximately 8.5 and wet pickup was approximately 66%. After padding, the fabric was steamed in a J-box for about 15 minutes at 200° F. It was then passed through two consecutive Tensitrol washers set at 190° F. and 145° F., respectively, for rinsing and finally double-bleached.

Fabric samples were removed and their pH measured prior to entering the J-box and after the J-box steaming. All pH's were in the desired 4–9 pH range. Other samples were taken after the two rinses and after bleaching and analyzed for residual polyvinyl alcohol.

As a comparative experiment, another portion of the polyester-cotton greige goods was padded with a peroxide-free desizing solution containing 0.1% of nonionic surfactant and then subjected to the same treatment as the peroxide-desized fabric. Table I compares this control with peroxide-desized fabrics.

TABLE I

Sample location	Polyvinyl alcohol remaining on fabric percent weight: With peroxide desize	Without peroxide
After first rinse	0.1	1.0
After second rinse	0.025	0.050
After bleaching	$<2.5\times10^{-4}$	5×10^{-3}

The peroxide-desized material consistently contained less polyvinyl alcohol. Ultimately it contained less than one-twentieth as much as the hot water-desized material. It was of equivalent or better whiteness.

While the amount of polyvinyl alcohol left on the fabric even with water alone may appear insignificant, the advantage of the present invention is demonstrated when the fabrics are printed.

The two fabrics were mill-printed with a bright blue dye. The control fabric took on a noticeably less brilliant hue. Upon close examination, it was seen to have taken a spotty print due to differential exhaustion of pigment on spots of gelled residual polyvinyl alcohol. The fabric treated by the invention was bright and unspotted.

Example II and Comparative Experiment B

Three 100 gram samples of polyvinyl alcohol-sized poplin were each treated with 200 grams of 0.09% wt. hydrogen peroxide aqueous solution having a pH of 7.5. The samples were maintained in the solution at 200° F. for 10 minutes, removed, rinsed in water and dried. The average weight loss due to polyvinyl alcohol desizing was 3.2% of the weight of fabric. The viscosities of the desized polyvinyl alcohol-containing peroxide solutions were between 62 and 76 cps.

For comparison, the experiment was repeated omitting hydrogen peroxide from the desizing solution. The average weight loss due to polyvinyl alcohol desizing was 2.8%. The viscosities of the used desizing solutions were higher in the absence of hydrogen peroxide, ranging from 86 to 227 cps. and averaging 133 cps., and thus more difficult to remove completely from the fabric than those with peroxide.

The polyvinyl alcohol-containing desizing solutions produced in the above experiments were stored in flasks at ambient conditions. After one week, the solution containing no hydrogen peroxide had formed a tough, difficult to remove film of a type which potentially could clog fabric processing equipment and redeposit on fabric. The peroxide-containing solution was easily and completely rinsed from the flask.

Example III

This example illustrates the use of an amylase-hydrogen peroxide solution to remove a polyvinyl alcohol-starch combination size. An aqueous desizing solution containing 0.09% by weight hydrogen peroxide, 0.1% Rapidase 800 (enzyme), 0.01% of sodium metasilicate (buffer), and 0.05% long-chain alcohol ethoxylate (wetting agent) having a pH of 7.0 was prepared. A sample of fabric containing 4.0% by weight of polyvinyl alcohol sizing and 3.0% by weight of starch sizing was padded with this solution to 100% wet pick-up and maintained at 160–170° F. for 30 minutes and then steamed at 210° F. for 15 minutes and then washed. Measurement of the polyvinyl alcohol and starch sizings remaining on the fabric showed that about 90% of the polyvinyl alcohol and about 95% of the starch was removed by the desizing solution.

Example IV

The effectiveness of hydrogen peroxide solutions as polyvinyl alcohol desizing agents is to a major extent related to the ability of hydrogen peroxide to oxidatively cleave polyvinyl alcohol molecules and produce lower molecular weight polyvinyl alcohol fragments. These lower molecular weight fragments are not only more water soluble than the parent molecules but, importantly, produce relatively lower viscosity solutions having a much reduced tendency to form gels and redeposit on the fabric or equipment. The relative polyvinyl alcohol cleavage effectiveness of hydrogen peroxide-containing desizing agents can be determined by measuring the decrease of viscosity of polyvinyl alcohol solutions following treatment with a desizing agent. Effective hydrogen peroxide desizing agents cleave the polyvinyl alcohol molecules in the solution to a substantial degree and decrease the viscosity, ineffective hydrogen peroxide-containing desizing agents producing solutions of relatively higher viscosity.

Six percent by weight aqueous solutions of a higher-molecular weight polyvinyl alcchol (Air Reduction Co.'s Vinol 350), a lower molecular weight polyvinyl alcohol (Vinol 325), and a partially hydrolyzed polyvinyl alcohol (DPont's Elvanol 52–22) were prepared and their pH's were adjusted to 6. Samples of these solutions were heated at 210° F. for 15 minutes following treatment with 0%, 0.04%, 0.087%, 0.175%, 0.35% and 0.70% weight hydrogen peroxide. Post-heating viscosities of the samples were measured. As shown in Table II, hydrogen peroxide addition up to about 0.1% by weight greatly reduced the viscosities of the solutions. Increased additions of hydrogen peroxide giving little further viscosity reduction.

TABLE II

Peroxide concentration percent	Viscosity of solution, cps.		
	Vinol 350	Vinol 325	Elvanol 52–22
0.00	160	70	60
0.04	22	17	13
0.087	12	7	9
0.175	8	6	7
0.35	8	6	7
0.70	8	6	7

Example V and Comparative Experiment C

Two experiments were carried out to demonstrate the criticality of maintaining pH below about pH 9. A solution of 0.5% by weight hydrogen peroxide and 0.1% by weight Triton X–100 brand nonionic surfactant was prepared. It had a pH of 7.0. A sample of 50/50 polyester/rayon greige goods sized with 4.6% by weight of fully hydrolyzed polyvinyl alcohol was padded to 100% pick-up with this solution. The sample was steamed for 15 minutes at 212° F. and rinsed in water at 70° F. Residual polyvinyl alcohol was determined on duplicate samples.

For comparison samples of the same fabric were desized using a light bleach solution containing 0.5% by weight hydrogen peroxide, 0.5% w. sodium hydroxide, 1.0% w. sodium silicate (42° Bé.) and 0.1% w. Triton X–100.

This solution had a pH of 11.9.

The alkaline solution left 33% of the original size on the fabric, while the solution of this invention left but 20%. Additionally, the alkaline solution turned dark yellow and colored the fabric and had a pungent odor.

Example VI and Comparative Experiment D

The desizing of heat-set polyvinyl alcohol was simulated. A 10% by weight solution of Air Reduction Co.'s "Vinol 350" grade polyvinyl alcohol was prepared and cast into 0.090 inch thick wet films. These films were dried at 130° F. for two hours and conditioned at 70° F. and 65% humidity for 24 hours. The films were heat set at 385° F. for 10 seconds between the plates of an Atlas scorch tester. The dry films had a thickness of 0.002 inch. One of these heat set films was contacted with a 0.125% solution of hydrogen peroxide (pH 7.0) at 175° F. In 4 minutes it was dissolved.

Another of these films was contacted with 175° F. water. It required 7 minutes to dissolve.

We claim as our invention:

1. In a process for removing polyvinyl alcohol-containing size from fabric wherein the fabric is contacted with an aqueous solution of wetting agent at 130° F. to 260° F. for from about 2.0 to about 90 minutes and thereafter washed, the improvement which comprises applying from about 0.04% by weight to about 0.5% by weight of hydrogen peroxide to said solution and maintaining the pH of said solution in the range of from about pH 4 to about pH 9.

2. The process in accordance with claim 1 wherein the aqueous solution has a pH in the range of 6 to 8 and a hydrogen peroxide content of from 0.1% to 0.4% by weight.

3. A process for removing polyvinyl alcohol-containing size from fabric which comprises applying to the fabric an aqueous solution having a pH in the range of 4 to 9 and consisting essentially of water, from about 0.04% to about 0.5% by weight of hydrogen peroxide and from about 0.005% to 0.25% by weight of polyoxyethylated C_{12} to C_{20} alkyl alcohols of from 3 to 20 oxyethyl groups, maintaining the fabric, wetted by the aqueous solution, at temperatures in the range of 130° F. to about 260° F. for from about 2.0 minutes to 90 minutes, and then washing the fabric.

4. The process in accordance with claim 3 wherein the aqueous solution therein employed has a pH in the range of 6 to 8 and contains from 0.10% to 0.4% by weight of hydrogen peroxide and wherein the temperature is in the range of from 190° F. to 212° F.

References Cited

"Removal of Elvanol Polyvinyl Alcohol From Fabric," E. I. du Pont de Nemours & Co., Wilmington, Del., July 1966.

MAYER WEINBLATT, Primary Examiner

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