



Europäisches Patentamt

(19)

European Patent Office

(11) Publication number:

Office européen des brevets

0 173 528

A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 85305877.4

(51) Int. Cl.⁴: **D 06 M 15/333, C 08 L 29/04**

(22) Date of filing: 19.08.85

(30) Priority: 20.08.84 US 642435

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(43) Date of publication of application: 05.03.86
Bulletin 86/10

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(54) **Polyvinyl alcohol based wax-free size composition.**

(57) Polyvinyl alcohol based sizing solution containing a small amount of low ethylene oxide adduct of branched alcohol provides superior operability during sizing and weaving, and yields fabric that exhibits improved finishing performance.

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TITLE

POLYVINYL ALCOHOL BASED WAX-FREE SIZE COMPOSITION

BACKGROUND OF THE INVENTION

Field of the Invention

5 This invention relates to size compositions and more specifically it relates to polyvinyl alcohol based size compositions containing low ethylene oxide adduct additives.

Description of the Prior Art

10 Spun warp yarn must be sized with a water-soluble polymer which provides it with a protective surface coating; the latter is required during the weaving of the yarn into fabric. After weaving the greige fabric produced must be stripped 15 of the protective coating by desizing before it can be subjected to various finishing operations and in particular to dyeing. Sizes based on polyvinyl alcohol or combinations of polyvinyl alcohol and starch must generally be used with a wax additive 20 present in the formulation to minimize drier drum sticking in the slasher during application of the size. These wax additives are difficult to remove from the greige fabric during desizing, often requiring extraction by special solvents as well as 25 higher desize bath temperatures. As a consequence the finishing mill is faced with higher production costs due to greater process complexity, higher energy costs and a higher percentage of second quality greige fabric.

30 The use of polyvinyl alcohol-based sizing solution containing a small amount of quaternary ammonium salt or a quaternary imidazolinium salt is disclosed in U.S. Patent No. 4,383,063; these additives provide good operability in the absence of 35 wax and result in fabric exhibiting improved

finishing performance. However, such formulations have the serious deficiency of frequently exhibiting a non-reproducible sizing performance; the latter is due to an erratic and unpredictable removal of the

5 cationic additive by inter-action with anionic contaminants which tend to accumulate in the sizing solution. The primary source of these anionic contaminants is the spun yarn being sized.

The incorporation into polyvinyl
10 alcohol-based sizes of very low levels (maximum of 0.05 wt. % based on polyvinyl alcohol) of low ethoxylate adducts of linear alcohols as defoaming agents is disclosed in U.S. Patent No. 4,251,403; such materials have been found to be ineffective as
15 wax substitutes and therefore are not used as substitutes for wax in wax-free warp sizing compositions.

Summary of The Invention

According to the present invention, there is
20 provided a composition consisting essentially of (a) from about 45.5 to about 99.9% by weight of vinyl alcohol polymer selected from the group consisting of polyvinyl alcohol, vinyl alcohol/methyl methacrylate copolymer, and polyvinyl alcohol containing
25 solubilizing comonomers other than methyl methacrylate, said vinyl alcohol polymer having a saponification number of from about 1 to about 160 and a 4 percent solution viscosity of from about 3 to about 70 mPa·s at 20°C;
30 (b) from about 0.1 to about 3 percent by weight of liquid nonionic low ethylene oxide adduct of branched alcohol or mixture of branched alcohols wherein the average ethylene oxide content is from about 1 to about 7 units and the alcohol has an
35 average carbon content of from about 8 to about 18 carbon atoms;

(c) from 0 to 49.9 percent by weight of starch;

(d) from 0 to about 5 percent by weight of ethylene oxide oligomer having a molecular weight

5 (number average) of from about 200 to about 800 and

(e) from 0 to about 49.9 percent by weight of carboxymethyl cellulose,

(f) from 0 to about 1 percent by weight of at least one auxiliary ethylene oxide adduct selected
10 from the group consisting of low ethylene oxide adduct (containing an average ethylene oxide content of from about 1 to about 7 units) of a linear alcohol or of a mixture of linear alcohols (having an average carbon content of from about 8 to about 18 units) and
15 medium to high ethylene oxide adduct (containing an average ethylene oxide content of from about 8 to about 40 units) of linear or branched alcohols (having an average carbon content of from about 8 to about 18 units) provided the combined weight of
20 starch and carboxymethyl cellulose does not exceed the weight of vinyl alcohol polymer.

Further according to the present invention there is provided a concentrate of the low ethylene oxide adduct blended with vinyl alcohol polymer, a
25 wax-free aqueous size solution comprising the composition of the present invention having a solids content of 2-20% by weight, process for sizing filament yarn with wax-free aqueous solution and sized yarn comprising spun yarn having a wax-free
30 protective surface coating of the composition of the present invention.

As used herein, the term "consisting essentially of" means that the named ingredients are essential, however, other ingredients which do not
35 prevent the advantages of the present invention from being realized can also be included.

Detailed Description of the Invention

It has been found that the addition of a liquid, nonionic, low ethylene oxide adduct of a branched alcohol, in the amount of 3 percent or less, 5 to the vinyl alcohol polymer based size composition eliminates sticking of the sized yarn on the drying cans in the slasher, provides excellent weaving efficiency, and easy size removal under mild desize conditions, yielding desized greige fabric that 10 exhibits excellent dye receptivity. Size compositions of the present invention are recommended for use in the conventional sizing, heat setting and aqueous desizing operations presently employed by spun yarn textile mills.

15 For the purposes of the size compositions of the present invention the vinyl alcohol polymer can have a saponification number (mg KOH to neutralize 1 g polymer) of from about 1 to about 160 and a 4 percent solution viscosity of from about 3 to about 20 70 mPa·s.

Examples of suitable vinyl alcohol polymers include:

25 (a) Fully hydrolyzed vinyl alcohol/methyl methacrylate copolymer (containing from about 3.5 to about 6 mole percent methyl methacrylate) having a viscosity of from about 3 to about 60 mPa·s (measured at 20°C using a 4 percent aqueous solution). Such copolymers can be produced by the alcoholysis of a vinyl acetate/methyl methacrylate copolymer;

30 (b) Partially hydrolyzed polyvinyl alcohol containing from about 4 to about 12 mole percent of vinyl acetate having a viscosity of from about 3 to about 60 mPa·s;

(c) Fully hydrolyzed polyvinyl alcohol 35 having a viscosity of from about 3 to about 70 mPa·s

(d) Polyvinyl alcohol containing "solubilizing comonomers" other than methyl methacrylate (such as methylacrylate, methyl hydrogen maleate);

5 (e) Various mixtures of the above vinyl alcohol polymers.

The nonionic additive of the present invention is a low ethylene oxide adduct (containing an average ethylene oxide content of from about 1 to 10 about 7 units) of a branched alcohol or a mixture of branched alcohols (having an average carbon content of from about 8 to about 18 units). The preferred makeup of this additive is an adduct containing from about 2 to about 5 ethylene oxide units with a branched alcohol containing an average of from about 10 to about 15 carbon atoms. The most preferred is one consisting of an average of about 3 ethylene oxide units with a branched alcohol containing an average of about 13 carbon atoms. "Tergitol" 15-S-3, 20 a product manufactured by Union Carbide, represents this most preferred additive.

The amount of vinyl alcohol polymer in the composition of the present invention is from about 45.5 to about 99.9 percent by weight. The preferred 25 range is from about 63 to about 99.8 percent and the most preferred range is from about 72.7 to about 99.6 percent. In typical polyvinyl alcohol-based size formulations, the higher the polyvinyl alcohol content of the size, the higher will be the weaving 30 efficiency exhibited by the sized yarn. In general size add-on requirements are reduced progressively as the polyvinyl alcohol content of the size is increased.

The amount of the nonionic additive of the 35 present invention is from about 0.1 to about 3

percent by weight. About 0.1 weight percent additive is necessary to give significant drier drum release, while greater than about 3 weight percent may result in reduced weaving efficiencies. A preferred range 5 of additive is from about 0.2 to about 1.5 weight percent with which most of the benefits of the present invention can be achieved. The most preferred concentration range of additive is from about 0.4 to about 0.8 weight percent; compositions 10 containing this level of additive give the best balance of drum deposit performance, abrasion resistance and dye receptivity after desizing.

Optionally, starch can be incorporated in the size compositions of the present invention in an 15 amount of up to about 49.9 weight percent. Up to this level of starch the benefits of the no-wax additive of the present invention are clearly evident. The preferred starch limit is up to about 33 weight percent, while the most preferred starch 20 limit is up to about 25 weight percent. In the most preferred vinyl alcohol polymer/starch blends the effectiveness of the nonionic additive of the present invention approaches that observed with compositions containing vinyl alcohol polymer as the sole 25 polymeric component. A variety of types of starch and derived starch will function as optional additives in the composition of this invention. These include "Kofilm" 50, [an acetylated starch product supplied by National Starch], as well as 30 "Astrogum" 3010 [a medium viscosity sodium carboxymethylated starch] and "Astrogum" 3020 [a low viscosity sodium carboxymethylated starch], which are products supplied by Penick and Ford.

Carboxymethyl cellulose (CMC) can also be 35 used as an optional ingredient in the composition of

the present invention in an amount of up to about 50 wt. %, preferably up to about 33 wt. %, and most preferably up to about 25 wt. %.

5 The combined weight of the starch and CMC ingredients should not exceed the weight of the vinyl alcohol polymer present in the composition.

Another optional additive is a low to medium molecular weight (200-800 number average) oligomer of ethylene oxide often added to vinyl alcohol polymer 10 as a dedusting agent. U.S. Patent No. 4,389,506 describes the use of 3 weight percent of "Carbowax" 600, a product of Union Carbide, as yielding the most preferred dust-free product. Concentrations up to about 5 weight percent "Carbowax" 600 result in only 15 minor reductions in the benefits derived from the presence of the nonionic additive of the present invention and represents the upper additive level recommended. A preferred upper limit is 3 weight percent while the most preferred upper limit of this 20 type of additive is 1.5 weight percent. At the most preferred upper concentration the benefits derived from the nonionic additive of the present invention can be almost fully realized.

Further optional additives can be auxiliary 25 low ethylene oxide adducts (containing an average ethylene oxide content of from about 1 to about 7 units) of a linear alcohol or of a mixture of linear alcohols (having an average carbon content of from about 8 to about 18 units) or medium to high ethylene 30 oxide adducts (containing an average ethylene oxide content of from about 8 to about 40 units) of linear or branched alcohols (having an average carbon content of from about 8 to about 18 units). These additives can be present in the composition of the 35 present invention in low concentrations, i.e. up to about 1 wt. percent.

The aqueous size solution of the present invention will generally have a solids content of from about 2 to about 20 weight percent. The preferred size bath solids content is from about 5 to 5 about 15 weight percent while the most preferred formulation contains from about 7 to about 12 weight percent since this level of solids in most cases will provide sufficient size add-on to give the sized yarn adequate abrasion resistance. The aqueous polyvinyl 10 alcohol based size solution is considered to be unique because it does not contain a wax additive which must be present under normal mill conditions.

The aqueous size solution is prepared by slurring polyvinyl alcohol with water at ambient 15 temperature. The nonionic additive along with any optional additives are then introduced. The subsequent mixture is heated with stirring at about 77°C until complete solution has been achieved.

The size solution of the present invention 20 can also be prepared directly from a blend of vinyl alcohol polymer with a low amount of the nonionic additive of the present invention. The polyvinyl alcohol/nonionic additive mixtures of this invention are produced by dry blending a variety of polyvinyl 25 alcohol and the additive(s) under high intensity mixing conditions at a temperature at which the additive component(s) will be liquid(s). Moreover if more than one nonionic additive is used, the latter can be preblended and added as a single component. 30 For example, using a Readco Sigma Blade mixer manufactured by the Read Co., York, PA, polyvinyl alcohol and "Tergitol" 15-S-3 or "Tergitol" 15-S-3/"Carbowax" 600 mixtures were converted into homogeneous blends by mixing for about 30 minutes at 35 a temperature above about 20°C. This mode of

preparation is carried out by slurring in water at ambient temperature the required amount of vinyl alcohol polymer/nonionic additive blend to give the desired size bath solids. The resulting mixture is 5 then heated with stirring at a temperature of about 77°C until complete solution has been achieved.

The size solution of the present invention can also be produced by using a concentrate of the nonionic additive of the present invention in a vinyl 10 alcohol polymer. The concentrate consists essentially of from about 45 to about 90 percent by weight of vinyl alcohol polymer and from about 10 to about 55 percent by weight of the liquid, nonionic low ethylene oxide adduct additive of the present 15 invention. Optionally, the concentrate can contain up to about 45 percent by weight of starch, up to about 45 percent by weight of Carbowax, up to about 45 percent by weight of carboxymethyl cellulose and up to about 45 percent by weight of low ethylene 20 oxide adduct of a linear alcohol or mixture of linear alcohols or medium to high ethylene oxide adduct of linear or branched alcohols. The concentrate is used to produce the size composition of the present 25 invention by adding it in the required amount to a preformed vinyl alcohol polymer solution. Use of such a concentrate can provide a unique and surprising advantage. Normally when vinyl alcohol polymers are added even with vigorous agitation to hot aqueous solutions, the vinyl alcohol component 30 fuses upon contact with the hot water and becomes very difficultly soluble. In contrast the above described concentrate, if it contains at least about 30% by weight of the nonionic additive of this invention, is relatively easy to disperse when added 35 directly to hot water. The most preferred nonionic

additive level is from about 40% to about 50%. Above about 50% the vinyl alcohol polymer tends not to absorb all of the additive. Use of the above described concentrate provides the highly desirable

5 advantage of permitting rapid readjustments in the level of the nonionic additive of the present invention in a given hot size bath to match specific mill requirement.

Preferably, the above referred to
10 concentrate contains from about 45 to about 70 percent by weight of vinyl alcohol polymer, from about 30 to about 55 percent by weight of nonionic additive, up to about 20 percent by weight of starch, up to about 20 percent by weight of Carbowax, and up
15 to about 20 percent by weight of carboxymethyl cellulose. Most preferably the concentrate will contain from about 50 to about 60 percent by weight of vinyl alcohol polymer, from about 40 to about 50 percent by weight of nonionic additive, up to about 5
20 percent by weight of starch, up to about 5 percent by weight of Carbowax and up to about 5 percent by weight of carboxymethyl cellulose.

The size is applied to the yarn web or sley using a slasher. The latter is equipped with a
25 heated size box containing the size formulation. The unsized sley is sized by being drawn through the hot size solution, through squeeze rolls to remove excess size solution, over a series of heated drying drums, through a bust bar assembly to separate the sley into
30 individual warp ends and finally onto a beam for collection. When the required amount of sized sley has been collected on the beam, the latter is installed in a loom where the yarn is woven into greige fabric.

The sized spun yarn produced using the size composition of the present invention has a wax-free protective surface coating and exhibits the unique property of providing excellent weaving performance 5 despite the absence of wax in the vinyl alcohol polymer based size. Moreover the greige fabric produced being wax-free, is readily desizable under mild desize conditions yielding a desized fabric with excellent dye receptivity. Desizing is carried out 10 by passing the sized greige fabric through an alkaline scour bath followed by several hot water (about 65-85°C) rinses. Fabric prepared with conventional wax-containing sizes requires much more stringent scouring and rinse conditions than are 15 required with the size formulations of the present invention. A high level of removal of the size components from the greige fabric is required prior to its processing in the finishing mill so as to permit efficient and reproducible dyeing as well as 20 other finishing operations on the fabric. Both the no-wax sized yarn and the no-wax greige fabric produced from it are thus considered to be unique.

The no-wax size composition of the present invention is especially suited for use with 25 polyester/cotton spun yarn blends. It is particularly useful for 65/35, 50/50 and 40/60 polyester/cotton spun yarn blends. The size composition also has utility for 100% cotton spun yarns.

30 Incorporation of the no-wax additive of the present invention into vinyl alcohol polymer based size formulations permits the elimination of wax as an additive, making feasible the preparation of sized yarn exhibiting excellent slashing and weaving 35 characteristics suitable for producing a variety of

types of fabrics under typical weaving conditions (e.g. involving shuttle, airjet, rapier looms). The derived fabrics, being wax-free, are characterized by easy size removal and the desized fabric exhibits 5 superior dye receptivity.

The following examples are given for the purpose of illustrating the present invention. All parts and percentages are by weight unless otherwise specified.

10 Examples

Sizing solutions were prepared in a steam-jacketed kettle by adding the vinyl alcohol polymer to the requisite amount of ambient temperature water to obtain the desired size bath 15 solids. The temperature of the slurry was brought to 77°C with stirring. Any additives to be tested in the formulation were added at this point.

The resulting size solution was used to size 24 ends of a polyester/cotton spun yarn using a 20 "Callaway Slasher" Model 51 manufactured by West Point Foundry and Machine Co. operated at 10 meters/minute using pressure at the squeeze roll. After the yarn had been sized, the size add-on was measured by weight loss after extraction of the sized 25 yarn with boiling water. Assessment of the performance of the size formulation during slashing as well as characterization of the sized yarn itself was carried out using the following test procedures.

(a) Drum deposits

30 The extent to which deposits form on the No. 1 drying drum in the slasher is related directly to the tendency of a given size formulation to cause sticking of the individual warp ends to the drying drums in the slasher. Thus the effectiveness of a 35 release agent added to the size formulation to

minimize yarn sticking in the drying section of the slasher can be measured accurately. Operating the Callaway slasher under the conditions described above and setting the temperature of the No. 1 drying drum 5 at 190°C and the remaining three drums at 220°C, the amount of deposit accumulating on the No. 1 drum will reach an equilibrium value in about one minute. Once equilibrium is achieved the deposits on this drum are removed quantitatively with a rubber squeegee during 10 one complete revolution of the drum; the deposit is then dried and weighed. The amount of deposit collected provides a direct measure of a size formulation's performance, namely the greater the amount of drum deposit, the greater the tendency the 15 formulation has to cause drying drum sticking. Of the various all vinyl alcohol polymer based size formulations evaluated during the course of this study, the highest drum deposit was observed with unmodified PVA No. 2 (a fully hydrolyzed vinyl 20 alcohol/methyl acrylate copolymer having a 4% solution viscosity of 13.5 mPa.s and a saponification number of 40). In each example cited, the actual drum deposit value observed and a rating proportionated against the PVA No. 2 value (unless 25 noted otherwise) are given. A rating of 0.200 or lower is considered necessary for operability under typical mill conditions of a 100% vinyl alcohol polymer size.

(b) Abrasion resistance of the sized yarn 30 is determined using a laboratory abrasion tester. The test method employed consists of stringing 21 ends of sized yarn through a section of conventional weaving loom reed and applying controlled tension to each individual warp end. The reed is made to 35 oscillate against the warp ends at one cycle/second

and the number of cycles required to cause the breakage of each end is recorded. A second set of 21 ends is next tested in the same manner. The two sets of data obtained are then statistically averaged so 5 as to give the number of cycles required to cause 50% breakage of the warp ends used in the test. This quantity in cycles is referred to as the F_{50} rating for a given size formulation.

Abrasion resistance is highly dependent upon 10 size add-on. For comparative purposes all F_{50} data must be normalized to a given size add-on, namely, 10%. This is preferably done by obtaining F_{50} values at six or more add-ons for a given size 15 formulation and subjecting the resulting data to a linear regression analysis. All F_{50} data reported in the characterization of the various examples cited have been treated in this manner. A maximum F_{50} value was observed for size formulations prepared with PVA No. 1 (a fully hydrolyzed vinyl 20 alcohol/methyl methacrylate copolymer having a 4% solution viscosity of 28 mPa.s and having a saponification number of 30). In all examples cited the actual F_{50} value observed and a comparison rating with the PVA No. 1 size (unless otherwise 25 noted) are given; the latter was calculated by setting at unity the log F_{50} value of the PVA No. 1 size at 10% size add-on and proportionating against it the log F_{50} value observed at 10% size add-on for the size formulation in the example. At 10% 30 add-on a rating of 0.875 or higher is considered to be a requirement for operability under typical mill conditions using a 100% vinyl alcohol polymer size.

(c) Dye receptivity

Sized yarn to be used in this test is first 35 heat set by passing it through an oven at 200°C with

a holdup time of 45 seconds. The heat-treated yarn is then desized under mild conditions consisting of soaking the yarn for 15 seconds at 55°C in a 0.5% Alkanol WZN (a modified sodium alkylaryl sulfonate 5 supplied by E. I. du Pont de Nemours and Company) solution followed by rinsing the yarn for 45 seconds at 75°C three times. After passage through a wringer the yarn is dried thoroughly. Using the dried, desized yarn its dye receptivity is determined by 10 measuring the time in seconds for an aqueous solution of Chemurgy green dye to penetrate one inch up a hank of dry yarn. The poorest dye receptivity was observed using PVA No. 1 containing 8% "Synchem" 110 wax (a solid hot water dispersible tallow wax, 15 supplied by Milliken). Setting this value at unity all other dye receptivity values for the examples cited have been proportionated against it. Thus in each example given both the observed dye receptivity as well as a dye receptivity rating are reported. A 20 rating of 3.5 or higher is considered to be necessary to achieve good dye receptivity under normal mill conditions.

Examples 1 and 2 and
Comparative Examples 1 and 2

25 A sizing solution based on PVA No. 2 containing 0.4% "Tergitol" 15-S-3 (Ex. 1) was tested at 12 size add-on levels ranging from 5-15% (based on yarn weight) and compared with similar formulations prepared with PVA No. 2 alone (Ex. C-1), PVA No. 2 30 containing 8% "Synchem" 110 wax (typical mill formulation) (Ex. C-2), and PVA No. 2 containing 0.4% Tergitol 15-S-3 and 1.5% "Carbowax" 600 (Ex. 2). Results are summarized in Table I.

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Table I

Example	Composition	F ₅₀		Abrasion		Dye	
		Drum Deposit Obs'd Rating	Deposit (mg)	Resistance Obs'd (Cycles)	Rating	Receptivity Obs'd (Sec)	Rating
1	PVA No. 2 + 0.4% "Tergitol" 15-S-3	1.1	0.066	1640	0.939	3.5	6.257
C-1	PVA No. 2	16.8	1.000	1845	0.954	4.5	4.867
C-2	PVA No. 2 + 8% "Synchem" 110 wax	0.2	0.006	1185	0.900	20.7	1.058
2	PVA No. 2 + 0.4% "Tergitol" 15-S-3 + 1.5% "Carbowax" 600	1.1	0.066	1115	0.890	3.2	6.844

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As can be seen from the above data, Examples 1 and 2, which represent embodiments of the present invention, provided yarn having acceptable combinations of the three key performance features, 5 comparative Examples 1 and 2 were unacceptable because in C-1 the drum deposit was too high, and in C-2 the dye receptivity was extremely poor.

Examples 3 and 4 and Comparative Examples 3 and 4

A sizing solution based on PVA No. 1 10 containing 0.4% "Tergitol" 15-S-3 (Ex. 3) was evaluated at 12 size add-on levels falling in the range of 5-15% (based on yarn weight) and compared with similar formulations based on PVA No. 1 alone (Ex. C-3), PVA No. 1 + 8% "Synchem" 110 wax (typical 15 mill formulation (Ex. C-4) and PVA No. 1 containing 0.4% "Tergitol" 15-S-3 and 1.5% "Carbowax" 600 (Ex. 4). Results are summarized in Table II.

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Table II

Example	Composition	Drum Deposit Obs'd (mg)	F ₅₀ Resistance Obs'd (Cycles)	Abrasion Rating	Dye	
					Obs'd (Sec)	Receptivity Rating
3	PVA No. 1 + 0.4%	0.5	0.030	1.815	0.952	4.3
	"Tergitol" 15-S-3					5.102
C-3	PVA No. 1	6.6	0.393	2.655	1.000	4.2
C-4	PVA No. 1 + 8%	0.1	0.006	1.060	0.884	21.9
	"Synchem" 110 Wax					1.000
4	PVA No. 1 + 0.4%	0.8	0.048	1.690	0.939	3.8
	"Tergitol" 15-S-3 + 1.5%					5.747
	"Carbowax" 600					

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The above data illustrate that the same advantages reported in Examples 1 and 2 could be realized using the additive of the present invention with an alternative grade of vinyl alcohol polymer.

5 Example 5 and Comparative Examples 5 and 6

This set of examples employed a 75/25 blend of "Vinol" 425/"Vinol" 205 polyvinyl alcohols supplied by Air Products. "Vinol" 425 is an intermediate hydrolyzed (94% by weight hydrolysis) 10 and "Vinol" 205 is a partially hydrolyzed (88% by weight hydrolysis) PVA grade. A sizing solution containing this blend of polyvinyl alcohols with 0.4% "Tergitol" 15-S-3 present (Ex. 5) was evaluated at 12 size add-on levels ranging from 5-15% (based on yarn 15 weight) and compared with similar formulations prepared with the unmodified blend (Ex. C-5) and with the blend containing 8% "Synchem" 110 wax (Ex. C-6). The results are summarized in Table III.

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Table III

Example	Composition	Drum Deposit Obs'd (mg)	F ₅₀ Resistance Obs'd (Cycles)	Abrasion Rating	Dye	
					Receptivity Obs'd (Sec)	Rating
5	75/25 "vinol" 425/ "vinol" 205 + 0.4% "tergitol" 15-S-3	2.8	0.167	1585	0.935	3.8
C-5	75/25 "vinol" 425/ "vinol" 205	22.2	1.000	2415	0.988	4.0
C-6	75/25 "vinol" 425/ "vinol" 205 + 8% "Synchem" 110 Wax	0.5	0.030	975	0.879	20.8
						1.0529

As can be seen from the above data, the additive of the present invention provided the same advantages with compositions based on intermediate and partially hydrolyzed polyvinyl alcohols as was observed with the vinyl alcohol polymer compositions described in Examples 1, 2, 3 and 4.

Example 6 and Comparative Examples 7 and 8

A size formulation containing a 75/25 PVA No. 2/"Kofilm" 50 starch blend, 0.4% "Tergitol" 10 15-S-3 and 1.5% "Carbowax" 600, (Ex. 6) was evaluated at 12 add-on levels ranging from 5-15% (based on the yarn weight) and compared with a similar formulation containing no additives (Ex. C-7) as well as one with 8% "Synchem" 110 wax (Ex. C-8) present. The results 15 are summarized in Table IV.

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Example	Composition	Drum Deposit Obs'd (mg)	F ₅₀ Rating (1)	Abrasione Resistance Obs'd (cycles)	Rating (1) Obs'd (1)	Receptivity	
						Dye Obs'd (Sec)	Rating Obs'd (Sec)
6	75/25 PVA No. 2/ "Kofilm" 50 + 0.4%	2.8	0.163	665	0.953	2.9	7.576
	"Tergitol" 15-S-3 + 1.5%						
	"Carbowax" 600						
C-7	75/25 PVA No. 2/ "Kofilm" 50		17.2	1.000	915	1.000	2.9
C-8	75/25 PVA No. 2/ "Kofilm" 50 + 8% "Synchem" 110 Wax	0.6	0.035	595	0.937	17.7	1.238

Footnotes

(1) Setting the performance observed for Comparative Example 7 at unity.

The above data showed that the additive of the present invention in PVA/starch based systems significantly reduces the drum deposit and increases the dye receptivity of the yarn. The adverse effect 5 of the additive of the present invention on abrasion resistance was observed to be no greater than that of "Synchem" 110 wax.

Example 7 and Comparative Examples 9 and 10

A size formulation derived from a 50/50 PVA 10 No.2/"Kofilm" 50 starch blend and containing 0.4% "Tergitol" 15-S-3 and 1.5% "Carbowax" 600 (Ex. 7) was evaluated at 12 size add-on levels ranging from 5-15% (based on yarn weight) and compared with a similar 15 size formulation containing no additives (Ex. C-9) as well as a formulation with 8% "Synchem" 110 wax (Ex. C-10) present. The results are summarized in Table V.

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Example	Composition	Drum Deposit Obs'd (mg)	Rating (1)	F ₅₀		Abrasion Resistance (Cycles)	Rating (1)	Dye Receptivity Obs'd (Sec)	Rating Obs'd 3.7 5.917
				4.2	0.167				
7	50/50 PVA No. 2/ "Kofilm" 50 + 0.48	4.2	2/						
	"Tergitol" 15-S-3 + 1.58								
	"Carbowax" 600								
C-9	50/50 PVA No. 2/ "Kofilm" 50		25.2	1.000		615	1.000	4.3	5.102
C-10	50/50 PVA No. 2/ "Kofilm" 50 + 8% "Synchem" 110 Wax		0.9	0.036		335	0.905	9.3	2.353

Footnotes

(1) Setting the performance rating of Comparative Example 9 at unity.

As shown by the above data the additive of the present invention provided beneficial effects when used with 50/50 vinyl alcohol polymer/starch blends in both drum deposit performance as well as in 5 dye receptivity. The additive reduced abrasion resistance to approximately the same extent as did the "Synchem" 110 wax additive.

Comparative Examples 11-13

Size formulations based on PVA No. 2 were 10 prepared with several low ethylene oxide adducts of linear alcohols namely "Tergitol" 25-L-3, "Alfonic" 1012-40 and "Alfonic" 1412-40 (Ex. C-11 to 13).

Data characterizing the low ethylene oxide adducts is summarized in the Table below.

15	<u>Product</u>	<u>Hydrophobic Mol Wt.</u>	<u>No Carbons</u>	<u>Ethylene Oxide Moles</u>	<u>Wt. %</u>
	"Alfonic" 1012-40	170	C 10.9	2.5	40
20	"Alfonic" 1412-40	206	C 13.4	3.0	40
	"Tergitol" 15-S-3	200	C 13	3.0	37
	"Tergitol" 25-L-3	200	C 13	3.0	37

25 The hydrophobe is a linear alcohol in the "Alfonic" products and in "Tergitol" 25-L-3 but is secondary alcohol in "Tergitol" 15-S-3. The above Table shows that "Alfonic" 1412-40 and "Tergitol" 25-L-3 are an almost exact linear counterparts of
30 "Tergitol" 15-S-3. The "Alfonic" products are supplied by Conoco and the "Tergitol" products are supplied by Union Carbide.

Table VI shows the composition and properties of size formulations prepared with the 35 above linear alcohol derived ethylene oxide adducts as well as with the additive of the present invention (Ex. 1).

Example	Composition	F 50 Abrasion			Dye Receptivity	
		Drum Deposit Obs'd (mg)	Deposit Rating	Resistance Obs'd (Cycles)	Obs'd (Sec)	Rating
C-11	PVA No. 2 + 0.4% "Tergitol" 25-L-3 + 3.0% "CARBOWAX" 600	4.6	0.274	635	0.819	3.5 6.217
C-12	PVA No. 2 + 0.4% "Alfonic" 1012-40 + 3.0% "CARBOWAX" 600	4.9	0.292	485	0.784	3.6 6.086
C-13	PVA No. 2 + 0.4% "Alfonic" 1412-40 + 3.0% "CARBOWAX" 600	6.7	0.400	455	0.776	3.5 6.257
1	PVA No. 2 + 0.4% "Tergitol" 15-S-3 + 3.0% "CARBOWAX" 600	1.1	0.066	1070	0.885	3.5 6.257

As can be seen from the above data, the formulations (Ex. C-11 to 13) containing a linear alcohol-based additive gave significantly inferior drum deposit and abrasion resistance performance than 5 were observed when the additive of the present invention was used.

Examples 8-10 and Comparative Examples 14-20

Size formulations were prepared with PVA No. 2 modified with a range of "Tergitol" 15-S 10 products containing from 3 to 40 ethylene oxide units (i.e. "Tergitol" 15-S-3 to "Tergitol" 15-S-40). The level of the "Tergitol" additive was 0.4 wt. %, and 3.0% "Carbowax" 600 was also present in the formulation. Included in Table VII are 15 characterization data for these formulations and a formulation containing only the "Carbowax" 600 additive.

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TABLE VII

Example	Composition			F ₅₀			Abrasion			Dye		
	"Tergitol" "Carbowax"			Drum	Deposit	Resistance	Obs'd	Rating	Obs'd	Receptivity	Rating	
	PVA	Grade	Grade (8)	Obs'd	Rating	(Cycles)	Obs'd	Rating	(Sec)	Obs'd	Rating	
C-14	PVA	—	—	3.0	9.0	0.536	1400	0.912	3.7	5.919		
8	PVA	15-S-3	(0.4) —	3.0	0.2	0.012	1070	0.885	3.5	6.257		
9	PVA	15-S-5	(0.4) —	3.0	1.5	0.089	850	0.856	3.6	6.083		
10	PVA	15-S-7	(0.4) —	3.0	1.3	0.077	670	0.825	3.8	5.763		
11	PVA	15-S-9	(0.4)	3.0	3.2	0.190	550	0.800	3.5	6.257		
C-15	PVA	15-S-12	(0.4)	3.0	4.3	0.256	415	0.765	3.6	6.083		
C-16	PVA	15-S-15	(0.4)	3.0	3.6	0.214	345	0.741	3.7	5.919		
C-17	PVA	15-S-20	(0.4)	3.0	3.6	0.214	330	0.735	3.5	6.257		
C-18	PVA	15-S-30	(0.4)	3.0	5.3	0.315	440	0.772	3.7	5.919		
C-19	PVA	15-S-40	(0.4)	3.0	4.7	0.292	315	0.730	3.6	6.083		
C-20	PVA	15-S-40	(0.4)	3.0								
	No.	2										

As shown by the data in Table VII, the additives of the present invention ("Tergitol" 15-S-3, 15-S-5 and 15-S-7) gave improved results (Ex. 8-10). "Tergitols" 15-S-9 to 40 (Ex. C-15 to 20) 5 gave significantly inferior drum deposit performances. Moreover, the abrasion resistance values observed became increasingly lower as the number of ethylene oxide units in the "Tergitol" additive was increased.

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Example 11 and Comparative Example 21

Fabric samples which have been prepared from yarn sized with the size solution of the present invention have been compared with fabric samples identical in every respect except that the latter 15 were prepared with yarn sized with a commercial PVA/tallow wax formulation. Both sets of samples were desized under mild conditions (e.g. 15 seconds soak at 55°C followed by three water rinses at 65°C). The dye receptivity of the fabrics obtained 20 with the size of the present invention exhibited eight times the dye receptivity of those obtained using the conventional wax-containing size. Moreover dye absorption by the former was regular and uniform whereas that exhibited by the latter was highly 25 irregular and nonuniform.

The fabric used in Examples 11 and 21 consisted of a 65/35 polyester/cotton warp having a 36 singles cotton count, and filled with a 100% polyester weft so as to produce a 92/83 construction 30 (ratio of warp threads to weft threads). The warp yarn was sized with a size formulation containing 12.5% solids and contained a size add-on of 15.0%. The size solution used in Example 11 corresponded exactly to that used in Example 2. The size solution 35 used in Comparative Example 21 was the same as that

used in Comparative Example 2 except that it contained 10%. "Synchem" 110 wax instead of 8%.

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Claims:

1. A composition consisting essentially of
 - (a) from about 45.5 to about 99.9% by weight of vinyl alcohol polymer selected from the group consisting of
 - 5 polyvinyl alcohol, vinyl alcohol/methyl methacrylate copolymer, and polyvinyl alcohol containing solubilizing comonomers other than methyl methacrylate, said vinyl alcohol polymer having a saponification number of from about 1 to about 160
 - 10 and a 4 percent solution viscosity of from about 3 to about 70 mPa·s at 20°C:
 - (b) from about 0.1 to about 3 percent by weight of liquid nonionic low ethylene oxide adduct of branched alcohol or mixture of branched alcohols
 - 15 wherein the average ethylene oxide content is from about 1 to about 7 units and the alcohol has an average carbon content of from about 8 to about 18 carbon atoms;
 - (c) from 0 to 49.9 percent by weight of
 - 20 starch;
 - (d) from 0 to about 5 percent by weight of ethylene oxide oligomer having a molecular weight (number average) of from about 200 to about 800 and
 - (e) from 0 to about 49.9 percent by weight
 - 25 of carboxymethyl cellulose,
 - (f) from 0 to about 1 percent by weight of at least one auxiliary ethylene oxide adduct selected from the group consisting of low ethylene oxide adduct (containing an average ethylene oxide content of from about 1 to about 7 units) of a linear alcohol or of a mixture of linear alcohols (having an average carbon content of from about 8 to about 18 units) and medium to high ethylene oxide adduct (containing an average ethylene oxide content of from about 3 to
 - 30 about 40 units) of linear or branched alcohols

(having an average carbon content of from about 8 to about 18 units) provided that the combined weight of starch and carboxymethyl cellulose does not exceed the weight of vinyl alcohol polymer.

5 2. The composition of Claim 1 wherein the vinyl alcohol polymer is selected from the group consisting of fully hydrolyzed polyvinyl alcohol having a viscosity of from about 3 to about 70 mPa·s, fully hydrolyzed vinyl alcohol/methyl methacrylate 10 copolymer which contains from about 3.5 to about 6 weight % of copolymerized methyl methacrylate comonomer having a viscosity of from about 3 to about 60 mPa·s, partially hydrolyzed polyvinyl alcohol containing from about 4 to about 12 mole % of vinyl acetate 15 having a viscosity of from about 3 to about 60 mPa·s, polyvinyl alcohol containing solubilizing comonomers selected from the group consisting of methylacrylate and methyl hydrogen maleate having a viscosity of from about 3 to about 70 mPa·s and mixtures of said 20 vinyl alcohol polymers.

or Claim 2

3. The composition of Claim 1/wherein the amount of vinyl alcohol polymer is from about 63 to about 99.8 % by weight, the amount of ethylene oxide adduct is from about 0.2 to about 1% by weight, the 25 amount of starch is from 0 to about 33% by weight, the amount of ethylene oxide oligomer is from 0 to about 3% by weight, the amount of carboxymethyl cellulose is from 0 to about 33% by weight and wherein said ethylene oxide adduct has an average 30 ethylene oxide content of from about 2 to about 5 and the alcohol has an average carbon content of from about 10 to about 15 carbon atoms.

or Claim 2

4. The composition of Claim 1/wherein the amount of vinyl alcohol polymer is from about 72.7 to 35 about 99.6 % by weight, the amount of ethylene oxide

adduct is from about 0.4 to about 0.8% by weight, the amount of starch is from 0 to about 25% by weight, the amount of ethylene oxide oligomer is from 0 to about 1.5% by weight, the amount of carboxymethyl cellulose is from 0 to about 25% by weight and wherein said ethylene oxide adduct has an average ethylene oxide content of about 3 and the alcohol has an average carbon content of about 13 carbon atoms.

5 5. A composition consisting essentially of

10 (a) from about 45 to about 90% by weight of vinyl alcohol polymer selected from the group consisting of polyvinyl alcohol and vinyl alcohol/methyl methacrylate copolymer, and polyvinyl alcohol containing solubilizing comonomers other than methyl

15 methacrylate, said vinyl alcohol polymer having a saponification number of from about 1 to about 160 and a 4 percent solution viscosity of from about 3 to about 70 mPa·s at 20°C:

20 (b) from about 10 to about 55% by weight of liquid nonionic low ethylene oxide adduct of branched alcohol or mixture of branched alcohols wherein the average ethylene oxide content is from about 2 to about 7 units and the alcohol has an average carbon content of from about 8 to about 18 carbon atoms;

25 (c) from about 0 to 45 percent by weight of starch;

30 (d) from 0 to about 45 percent by weight of ethylene oxide oligomer having a molecular weight (number average) of from about 200 to about 800 and

35 (e) from 0 to about 45 percent by weight of carboxymethyl cellulose,

 (f) from 0 to about 45 percent by weight of an auxiliary ethylene oxide adduct selected from the group consisting of low ethylene oxide adduct containing an average ethylene oxide content of from

about 1 to about 7 units) of a linear alcohol or of a mixture of linear alcohols (having an average carbon content of from about 8 to about 18 units) and medium to high ethylene oxide adduct (containing an average

5 ethylene oxide content of from about 8 to about 40 units) of linear or branched alcohols (having an average carbon content of from about 8 to about 18 units).

6. The composition of Claim 5 wherein the
10 vinyl alcohol polymer is selected from the group
consisting of fully hydrolyzed polyvinyl alcohol
having a viscosity of from about 3 to about 70 mPa·s,
fully hydrolyzed vinyl alcohol/methyl methacrylate
copolymer, which contains from about 3.5 to about 6
15 weight % of copolymerized methyl methacrylate
comonomer having a viscosity of from about 3 to about
60 mPa s, partially hydrolyzed polyvinyl alcohol
containing from about 4 to about 12 mole % of vinyl
acetate having a viscosity of from about 3 to about
20 60 mPa s, polyvinyl alcohol containing solubilizing
comonomers selected from the group consisting of
methylacrylate and methyl hydrogen maleate having a
viscosity of from about 3 to about 70 mPa.s and
mixtures of said vinyl alcohol polymers and mixtures
25 of said vinyl alcohol polymers. or Claim 6

7. The composition of Claim 5 /wherein the
amount of vinyl alcohol polymer is from about 45 to
about 70% by weight, the amount of ethylene oxide
adduct is from about 30 to about 55% by weight, the
30 amount of starch is from 0 to about 25% by weight,
the amount of ethylene oxide oligomer is from 0 to
about 25% by weight, the amount of carboxymethyl
cellulose is from 0 to about 25% by weight and
wherein said ethylene oxide adduct has an average
35 ethylene oxide content of from about 3 to about 5 and

the alcohol has an average carbon content of from about 10 to about 19 carbon atoms. or Claim 6

8. The composition of Claim 5/wherein the amount of vinyl alcohol polymer is from about 50 to 5 about 60% by weight, the amount of ethylene oxide adduct is from about 40 to about 50% by weight, the amount of starch is from 0 to about 5% by weight, the amount of ethylene oxide oligomer is from 0 to about 5% by weight, the amount of carboxymethyl cellulose 10 is from 0 to about 5% by weight and wherein said ethylene oxide adduct has an average ethylene oxide content of about 3 and the alcohol has an average carbon content of about 13 carbon atoms.

9. A wax-free aqueous size solution 15 comprising the composition of any one of Claims 1 to 8 having a solids content of from about 2 to about 20% by weight.

10. A wax-free aqueous size solution comprising the composition of any one of Claims 1 to 8 20 having a solids content of from about 5 to about 15% by weight.

11. A wax-free aqueous size solution comprising the composition of any one of Claims 1 to 8 25 having a solids content of from about 7 to about 12% by weight.

12. A process for sizing spun yarn with a wax-free aqueous solution according to Claim 9, Claim 10, or Claim 11.

13. Sized yarn comprising spun yarn having a
wax-free protective surface coating of the
5 composition of any one of Claims 1 to 8.

14. Sized yarn comprising spun yarn having a
wax-free protective surface coating of the
composition of any one of Claims 1 to 8, wherein said yarn
is selected from the group consisting of cotton and
10 polyester/cotton spun yarns.

15. Sized yarn comprising spun yarn having a
wax-free protective surface coating of the
composition of any one of Claims 1 to 8, wherein said yarn
is selected from the group consisting of 65/35, 50/50
15 and 40/60 polyester/cotton spun yarn.

16. Fabric prepared from sized yarn according
to Claim 13, Claim 14, or Claim 15.

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