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(71) Applicant: **Kuraray Co., Ltd.**
Kurashiki-shi Okayama-ken (JP)

(72) Inventors:
- **Onishi, Koji**
  Kurashiki-shi, Okayama-ken (JP)
- **Moriguchi, Eriko**
  Kurashiki-shi, Okayama-ken (JP)
- **Katayama, Tetsuya,**
  c/o Kuraray Co., Ltd.
  Kitakanbara-gun, Niigata-ken (JP)
- **Maruyama, Hitoshi**
  Kurashiki-shi, Okayama-ken (JP)

(74) Representative:
VOSSIUS & PARTNER
Siebertstrasse 4
81675 München (DE)

(54) Fiber sizing agent

(57) There is disclosed a fiber sizing agent which comprises a polyvinyl alcohol (A) having a degree of hydrolysis of 60 to 99 mol% and a degree of polymerization of 100 to 5000, and an ammonium salt of a carboxyl group-containing polymer (B) in a blending ratio (A) : (B) of 15 : 85 to 99.9 : 1 by weight. The above fiber sizing agent has excellent adhesivity, cohesion power and abrasion resisance irrespective of a low temperature and low humidity or a high temperature and high humidity and also has such excellent weavability as free from the occurrence of off-sizing, tackiness, fixing, gumming-up or the like in the sized fibers.

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Description

The present invention relates to a fiber sizing agent. More particularly, the present invention pertains to a fiber sizing agent which is industrially useful because it provides such excellent weavability that tackiness or fixing in sized fiber does not occur even at a high temperature and high humidity and that the coherence is not lost even at a low temperature and low humidity. Sizing textile fibers with the inventive sizing agent imparts them with coherence prior to weaving with a loom.

There have heretofore been used starch, polyvinyl alcohol (hereinafter referred to as "PVA"), (meth)acrylic acid ester copolymers and the like as the sizing agent to be applied to the warp of a textile product for the purpose of reinforcement.

Among them, PVA has been widely used as a fiber sizing agent because it forms tough films, has excellent bundling protecting action for textile fibers, non-putrefactiveness, preservability for a long period of time, and the like in comparison with starch. However, in the case of unmodified PVA having water-solubility (a degree of hydrolysis of not less than 88 mol%), it has insufficient adhesivity to hydrophobic fibers at a low temperature and low humidity, thereby frequently causing troubles due to off-sizing or insufficient cohesion power at the time of weaving. In the case of using PVA having an ionic group and a low degree of hydrolysis as the countermeasure against the above-mentioned problems, the PVA causes the sized fibers to unfavorably have tackiness or fixing due to hygroscopic action when being stored under high humidity in summer. As a result, there have been caused such problems in the case of filament yarn as poor rewinding (blocking) from the sized fiber beam (weaver's beam), increase in yarn hairiness, poor shedding property, etc., and such problems in the case of spun yarn as excessively high coefficient of friction due to tackiness of sized fibers such as yarns, poor shedding property, weft stop, occurrence of hairy pills, etc.

In the following, the hitherto problems will be described in detail with reference to filament yarn as an example.

There has heretofore been used an addition product of sodium hydroxide to the copolymer of a (meth)acrylic acid ester and (meth)acrylic acid (hitherto called "acrylic sizing agent") in combination with unmodified PVA having a degree of hydrolysis of 88 mol% for the purpose of improving off-sizing and cohesion power at a low temperature and low humidity. Nevertheless, the problems of off-sizing and insufficient cohesion power still remain unsolved and besides gumming-up problem occurs.

In the case of using a combination of unmodified PVA having a low degree of hydrolysis of less than 88 mol% and the aforesaid acrylic sizing agent treated with sodium hydroxide, the problems of off-sizing and cohesion power are improved at a low temperature and low humidity, but not improved at a high humidity, thus causing sticking because of high hygroscopicity of the combinational sizing agent.

In the case of using a combination of PVA having an ionic group and a low degree of hydrolysis and the aforesaid acrylic sizing agent incorporated with sodium hydroxide, the problems of off-sizing and cohesion power are improved at a low temperature and low humidity, but not improved at a high humidity, thus causing sticking because of high hygroscopicity of the combinational sizing agent as is the case with the unmodified PVA having a low degree of hydrolysis of less than 88 mol%.

The use of an addition product of an ammonium salt to the copolymer of (meth)acrylic acid and a (meth)acrylic acid ester in combination with PVA is disclosed in Japanese Patent Publication Nos. 248/1958 (Sho 33), 12076/1966 (Sho 41), 20436/1966 (Sho 41), 13478/1972 (Sho 47), 8556/1973 (Sho 48) and 29557/1975 (Sho 50). However, the use of the aforementioned addition product in combination with an ordinary PVA has brought about such problems as insufficient adhesivity to hydrophobic fibers and gumming-up.

It is a primary object of the invention to provide, under such circumstances, a fiber sizing agent which has excellent adhesivity, cohesion poker and abrasion resistance irrespective of a low temperature and low humidity or a high temperature and high humidity and also has excellent weavability being free from the occurrence of off-sizing, tackiness, fixing, gumming-up and the like.

According to the present invention, the object has been solved by the surprising finding that the properties of PVA having a low degree of hydrolysis which include hygroscopicity, tackiness and fixing can dramatically be improved by the use of a specific composition as a fiber sizing agent for sizing textile fibers, which composition comprises PVA having a specific degree of polymerization as well as a specific degree of hydrolysis and an ammonium salt of a carboxyl group-containing polymer in a definite range of proportion, thus adapting itself to the purpose of a fiber sizing agent.

The present invention provides a fiber sizing agent which comprises a polyvinyl alcohol (A) having a degree of hydrolysis of 60 to 99 mol% and a viscosity-average degree of polymerization of 100 to 5000 and an ammonium salt of a carboxyl group-containing polymer (B), the blending ratio (A) : (B) based on weight being 15 : 85 to 99.9 : 0.1; and the present invention also provides a method for weaving fibers such as yarns, particularly polyester filaments, acetate filaments, or nylon filaments sized with the above-mentioned fiber sizing agent through a dry loom such as an air jet loom.

The PVA to be used as the component (A) in the fiber sizing agent according to the present invention, is the PVA having a degree of hydrolysis of 60 to 99 mol% and a viscosity-average degree of polymerization of 100 to 5000. In the case where the degree of hydrolysis of the PVA is less than 60 mol%, the sizing agent is poor in water solubility or water

dispersibility, and thus the desizing property of the textile is worsened. In the case where the degree of hydrolysis is more than 99 mol%, the adhesivity of the sizing agent to hydrophobic fibers is deteriorated. From the viewpoints of water solubility, water dispersibililty, adhesivity to hydrophobic fibers and the like, the degree of hydrolysis thereof is preferably at least 65 mol%, most preferably at least 68 mol%, and is preferably at most 95 mol%, more preferably at most 90 mol%, most preferably at most 85 mol%, furthermost preferably at most 80 mol%.

Moreover, in the case where the viscosity-average degree of polymerization (hereinafter referred to as "degree of polymerization") of the PVA is less than 100, there is a fear of causing insufficiency in the performance as a fiber sizing agent, film strength and adhesivity to fibers. In the case where the degree of polymerization thereof is more than 5000, the viscosity of the sizing agent solution becomes excessively high, and thus is unfavorable from the aspect of sizing workability. From the viewpoints of the performance as a fiber sizing agent, the viscosity of the sizing agent solution and the like, the degree of polymerization is preferably at least 200, more preferably at least 250, and is preferably at most 3000, more preferably at most 2000, most preferably at most 1500.

There may be used in the present invention, an unmodified PVA or an ionic group-containing PVA as the PVA of the component (A). Among them, an ionic group-containing PVA is preferably used, since the use thereof enhances off-sizing resistance as well as water solubility.

The ionic group-containig PVA can be obtained, for example, by hydrolyzing a copolymer of a vinyl ester and an ionic group-containing ethylenically unsaturated monomer which is copolymerizable with the vinyl ester.

The ionic group in the ionic group-containing PVA need only be a group which is water-soluble and exhibits an ionic property, and is preferably exemplified by a carboxylic acid group and a sulfonic acid each of free type or salt type, a carboxylic acid anhydride group and a quaternary ammonium salt. Among them, the carboxylic acid group is most preferable.

The vinyl ester is exemplified by vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl versatate, vinyl caproate, vinyl caprylate, vinyl caprate, vinyl laurate, vinyl palmitate, vinyl stearate, vinyl oleate and vinyl pivalate. Among them, vinyl acetate is preferable from the standpoint of economical efficiency. The vinyl ester may be used alone or in combination with at least one other.

On the other hand, the ionic group-containing ethylenically unsaturated monomer which is copolymerizable with the above-mentioned vinyl ester is exemplified by crotonic acid, (meth)acrylic acid, maleic acid (anhydride), itaconic acid (anhydride), 3-acrylamide-3, 3-dimethylpropyl-trimethyl-ammonium chloride, 3-(meth)acrylamidepropyl-trimethyl-ammonium chloride, (meth)acrylamide-2-methylpropylsulfonic acid, vinylsulfonic acid, allylsulfonic acid and a salt thereof.

In addition, there is usable as the component (A) in the present invention, an end ionic group-modified product which is obtained by polymerizing a vinyl ester monomer such as vinyl ester and then hydrolyzing the resultant polymer in the presence of a thiol compound such as mercaptopropionic acid. In the present invention, the thiol compound such as mercaptopropionic acid is included in the examples of the ionic group-containing monomer.

Moreover, there is also usable as the component (A) in the present invention, a product which is formed by introducing an ionic group through an after-reaction into the PVA obtained by polymerizing a vinyl ester monomer such as vinyl acetate and then hydrolyzing the resultant polymer. In this case, the ionic group-introduced vinyl monomer unit is viewed as an ionic group-containing monomer unit.

It is preferable that the content of the ionic group-containing monomer unit in the ionic group-containing PVA be 0.05 to 10 mol%, since with such a content, the PVA can exhibit excellent water solubility and at the same time, excellent off-sizing resistance and sticking resistance. The aforesaid content of the ionic group-containing monomer unit is more preferably 0.05 to 4 mol%, particularly preferably 0.1 to 2 mol%.

In the fiber sizing agent according to the present invention, an ammonium salt of a carboxyl group-containing polymer is used as the component (B). The above-mentioned carboxyl group-containing polymer may be a polymer, that is, a homopolymer or a copolymer, obtained only from at least one carboxyl group-containing ethylenically unsaturated monomer, or a copolymer of a carboxyl group-containing ethylenically unsaturated monomer and a hydrophobic unsaturated monomer which is copolymerizable therewith. Among them, the latter copolymer is preferable from the viewpoint of off-sizing resistance.

The aforesaid ammonium salt of the carboxyl group-containing polymer can be produced by various processes. It is generally produced by polymerizing a carboxyl group-containing ethylenically unsaturated monomer or copolymerizing a carboxyl group-containing ethylenically unsaturated monomer with a hydrophobic unsaturated monomer which is copolymerizable therewith, and then neutralizing the resultant product with ammonia or an amine compound having a boiling point of 100°C or lower. Examples of the amine compound having a boiling point of 100 °C or lower include an aliphatic primary amine such as methylamine (boiling point of -6.3°C) and ethylamine (boiling point of 16.6°C), an aliphatic secondary amine such as dimethylamine (boiling point of 7°C) and diethylamine (boiling point of 56°C) and an aliphatic tertially amine such as triethylamine (boiling point of 89°C). As the ammonium salt of the carboxyl group obtained in such a manner, there is preferably usable a compound represented by the general formula $-COONHR^1R^2R^3$ wherein R^1, R^2 and R^3 are each a hydrogen atom or an aliphatic hydrocarbon group such as an alkyl group having 1 to

5 carbon atoms, at least one of R^1, R^2 and R^3 is preferably a hydrogen atom, and all of them are most preferably hydrogen atoms.

The degree of neutralization of the carboxyl group in the carboxyl group-containing polymer of the component (B) is preferably 0.3 or more, particularly preferably in the range of 0.5 to 0.95.

The above-mentioned carboxyl group-containing ethylenically unsaturated monomer (a) is exemplified by (meth)acrylic acid, crotonic acid, maleic acid (anhydride) and itaconic acid (anhydride). The aforesaid monomer may be used alone or in combination with at least one other.

On the other hand, as the hydrophobic unsaturated monomer to be copolymerized with the foregoing carboxyl group-containing ethylenically unsaturated monomer, there are usable the monomer (b) and/or the monomer (c) as described hereunder. Examples of the hydrophobic unsaturated monomer (b) include an ester of an aliphatic alcohol having 1 to 20 carbon atoms and (meth)acrylic acid such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, stearyl (meth)acrylate and cyclohexyl (meth)acrylate. Examples of the hydrophobic unsaturated monomer (c) other than (b) include an -olefin such as ethylene, propylene, n-butene and isobutene; a diolefin such as butadiene and isoprene; a (meth)acrylamide; a vinyl ester such as vinyl formate, vinyl acetate, vinyl propionate and vinyl pivalate; (meth)acrylonitrile; and an aromatic unsaturated monomer such as styrene and vinyltoluene. Any of the above-mentioned hydrophobic unsaturated monomers (b) and (c) may be used alone or in combination with at least one other.

The above-mentioned component (a) is preferably (meth)acrylic acid; the component (b) is preferably a (meth)acrylic acid ester; and the component (c) is preferably (meth)acrylonitrile or an aromatic unsaturated monomer.

In the case of using, as the component (B), a copolymer of the carboxyl group-containing ethylenically unsaturated monomer (a) and the ethylenically unsaturated monomer copolymerizable therewith [(b) and/or (c)], the content of each of the monomer units in this copolymer is not specifically limited. Usually the content of the monomer (a) unit before neutralization is 5 to 30% by weight, and the contents of the monomer (b) unit and the monomer (c) unit are each 95 to 70% by weight. Preferably said content of the monomer (a) unit is 6 to 20% by weight and said contents of the monomer (b) unit and the monomer (c) unit are each 94 to 80% by weight. More preferably said content of the monomer (a) unit is 8 to 18% by weight and said contents of the monomer (b) unit and the monomer (c) unit are each 92 to 82% by weight. The amount of the monomer (b) unit based on the total amount of the monomer (b) unit and the monomer (C) unit is preferably at least 30% by weight and at most 95% by weight, more preferably at least 50% by weight.

As the process for producing the carboxyl group-containing polymer of the component (B), there are adoptable the publicly known polymerization processes including solution polymerization, suspension polymerization and emulsion polymerization. The molecular weight of the polymer as the component (B) is not specifically limited, but is preferably in the range of 10,000 to 200,000 more preferably in the range of 20,000 to 100,000 expressed in terms of viscosity-average molecular weight.

In the fiber sizing agent according to the present invention, the blending ratio of the PVA (A) to the ammonium salt of the carboxyl group-containing polymer (B) is selected in the range of 15 : 85 to 99.9 : 1 by weight. In the case where the blending proportion of the component (B) is more than the above-prescribed range, gumming-up is prone to be caused during weaving. On the contrary in the case where the blending proportion of the component (B) is less than the above-prescribed range, the working effect on the prevention of tackiness and fixing of the sized fibers is deteriorated. Thus the blending ratio of the component (A) to the component (B) based on weight is preferably 30 : 70 to 99.9 : 0.1, particularly preferably 40 : 60 to 99 : 1 from the aspect of the prevention of gumming-up during weaving and of tackiness and fixing of the sized fibers.

The fiber sizing agent according to the present invention may be used, when desired, in combination with an ordinary PVA, starch, modified starch, an ordinary sizing agent of acrylic type, cellulose-based sizing agent, a lubricant, other auxiliary agents (such as anti-foam agent, mildewproofing agent, antistatic agent, other anionic, nonionic or cationic surfactant, etc.) and the like to the extent that the combinational use does not impair the working effect of the present invention.

In the case where the fiber sizing agent according to the present invention, which is usually in the form of aqueous solution, is used for sizing textile fibers, the aqueous solution is further dilulted with water to form an aqueous solution having a suitable concentration. The concentration of the aqueous solution of the sizing agent is preferably 2 to 20% by weight, more preferably 3 to 18% by weight. In the case of sizing spun yarn, the concentration is particularly preferably 4 to 16% by weight, and in the case of sizing filament yarn, it is particularly preferably 3 to 16% by weight. The amount of the sizing agent expressed in terms of solid content, when added onto warp, is preferably 2 to 25% by weight, more preferably 3 to 20% by weight. The aforesaid amount, when added onto spun yarn, is particularly preferably 5 to 20% by weight, and when added onto filament yarn, is particularly preferably 3 to 16% by weight.

It is preferable that the fiber sizing agent according to the present invention be applied to hydrophobic fibers such as polyester fiber, acetate fiber and nylon fiber, and that aforesaid sizing agent be used for sizing the filaments of the above-mentioned fibers. The sized fibers are weaved through a dry loom such as an air jet loom.

Although the fiber sizing agent according to the present invention has been described hereinbefore especially with

reference to the sizing of warp of filament yarn as an example, it is also useful for sizing warp of spun yarn and resin-finishing of fabric, as a sizing agent for laundry and printing and as a binder for nonwoven fabric.

The fiber sizing agent according to the present invention remarkably improves weavability when used for sizing textile fibers such as filament yarn, finished fabric, twist yarn and spun yarn prior to dry-weaving with a shuttle loom or a shuttleless loom, since the aforesaid fiber sizing agent is excellent in adhesivity and cohesion power to fibers, especially hydrophobic fibers as well as abrasion resistance of the fibers sized with the same. Furthermore, the above-mentioned fiber sizing agent has excellent weaving performance in that tackiness or fixing does not occur in the sized fibers even at a high temperature and high humidity, the weaving efficiency is not lowered even when the sized fiber beam is allowed to stand, by reason of favorable shedding property of said sizing agent, and the cohesion power is not lost even at a low temperature and low humidity.

The present invention will be described in more detail with reference to working examples, which however shall never limit the present invention thereto. In the following examples, comparative examples and preparation examples, part/parts and % shall denote part/parts by weight and % by weight, respectively unless otherwise noted in particular.

Preparation Example 1 (preparation of ionic group-containing PVA)

There was carried out copolymerization of vinyl acetate and each of ionic group-containing ethylenically unsaturated monomers as given in Table 1 in aqueous solution of methanol by a publicly known method. The copolymer thus obtained was hydrolyzed with sodium hydroxide to produce PVA 1 to PVA 14, and PVA 24. In Table 1 are given the viscosity-average degree of polymerization, degree of hydrolysis, water solubility in a concentration of 10 % at 40°C and sizability (whether the sizing was capable or incapable) of each of PVA.

Preparation Example 2 (preparation of PVA)

There was carried out polymerization of vinyl acetate in aqueous solution of methanol by a publicly known method. The polymer thus obtained was hydrolyzed with sodium hydroxide to produce PVA 15 to PVA 23. In Table 1 are given the viscosity-average degree of polymerization, degree of hydrolysis, water solubility in a concentration of 10% at 40°C and sizability (whether the sizing was capable or incapable) of each of the PVA.

Table 1

PVA	Degree of polymerization	Degree of hydrolysis (mol%)	Ionic group-containing monomer, content		Water-solubility[1)]	Capability or incapability of sizing
PVA- 1	500	73	IA	0.5 mol%	soluble	capable
PVA- 2	500	73	SAS	0.5 mol%	-do-	-do-
PVA- 3	500	73	APTAC	0.5 mol%	-do-	-do-
PVA- 4	500	67	IA	1.0 mol%	-do-	-do-
PVA- 5	500	70	IA	0.5 mol%	-do-	-do-
PVA- 6	500	78	IA	0.5 mol%	-do-	-do-
PVA- 7	500	81	IA	0.5 mol%	-do-	-do-
PVA- 8	500	84	IA	0.5 mol%	-do-	-do-
PVA- 9	500	82	IA	0.5 mol%	-do-	-do-
PVA-10	500	57	IA	0.5 mol%	insoluble	incapable
PVA-11	500	99.5	IA	0.5 mol%	soluble	capable
PVA-12	500	73	IA	3.9 mol%	-do-	-do-
PVA-13	500	73	IA	1.8 mol%	-do-	-do-
PVA-14	500	73	IA	0.1 mol%	dispersed	-do-
PVA-15	500	80	none		soluble	-do-
PVA-16	500	88	none		-do-	-do-
PVA-17	500	76	none		-do-	-do-
PVA-18	500	78	none		-do-	-do-
PVA-19	500	81	none		-do-	-do-
PVA-20	500	84	none		-do-	-do-
PVA-21	500	82	none		-do-	-do-
PVA-22	400	57	none		insoluble	incapable
PVA-23	500	99.5	none		soluble	capable
PVA-24	1400	73	IA	0.1 mol%	-do-	-do-

Remarks
1) Water-solubility of PVA at 40 °C and 10% concentration
IA : itaconic acid
SAS : sodium allylsulfonate
APTAC : 3-acrylamide-3,3-demethylpropyl-trimethyl-ammonium chloride

Preparation Example 3 (preparation of ammonium salt of carboxyl group-containing copolymer (ACR-A))

Solution polymerization was carried out to copolymerize acrylic acid and methacrylic acid as the coponent (a), butyl acrylate, methyl methacrylate and stearyl methacrylate as the component (b) and acrylonitrile and styrene as the component (c) at 78 to 80°C for about 4 hours in isopropyl alcohol by the use of benzoyl peroxide as the polymerization initiator. By neutralizing, with aqueous ammonia, the resultant ammonium salt of carboxyl group-containing copolymer consisting of 17% of the component (a) composed of 5% of acrylic acid and 12% of methacrylic acid; 72% of the component (b) composed of 30% of butyl acrylate, 30% of methyl methacrylate and 12% of stearyl methacrylate; and 11% of the component (c) composed of 10% of acrylonitrile and 1% of styrene, there was prepared a water-soluble ammonium salt of carboxyl group-containing copolymer (ACR-A). The ACR-A thus obtained had a viscosity-average molecu-

lar weight of 50,000 and a degree of neutralization for the carboxyl group of 0.7.

Preparation Example 4 (preparation of sodium salt of carboxyl group-containing copolymer (ACR-B))

The procedure of Preparation Example 3 was repeated to prepare a water-soluble sodium salt of carboxyl group-containing copolymer (ACR-B) except that aqueous solution of sodium hydroxide was used in place of aqueous ammonia. The ACR-B thus obtained had a viscosity-average molecular weight of 50,000 and a degree of neutralization for the carboxyl group of 0.7.

The performance of the fiber sizing agent was evaluated according to the following manner.

(1) Off-sizing resistance

The extent of the sizing agent falling off onto the loom (including a reed, heald, dropper, etc.) at the time of weaving was visually judged according to the following criterion. In this case, it is favorable that the falling off of the sizing agent be not caused. To be less prone to falling off means that the sizing agent is excellent in cohesion property for fibers even at a low temperature and low humidity.

(2) Anti-sticking property

Sized fibers which had been wound on a small bobbin were allowed to stand at 30°C and RH (relative humidity) of 84% for 4 days and thereafter the maximum value of the rewinding tension was determined to judge the anti-sticking property of the sizing agent according to the following criterion. In this case, it is favorable that sticking be not caused, and the lower the rewinding tension, the better the anti-sticking property. The favorable anti-sticking property means that the tackiness and fixing in the sized fibers are less prone to occur even at a high temperature and high humidity.

(3) Desizability of gray fabric

Gray fabric soon after weaving was treated in 0.1% aqueous solution of sodium hydroxide at 90°C for 30 minutes and thereafter the desizability was evaluated by means of iodometric coloration to judge the same according to the folowing criterion. In this case, it is favorable that desizing be as complete as possible.

(4) Anti-gumming up property

The extent of the tacky adhesion of the sizing agent after weaving, onto the respective portions of the loom including a reed and heald was visually judged according to the following criterion. In this case, it is favorable that gumming up be not caused.

(5) Metal-fiber (m-f) friction coefficient

The metal-fiber (m-f) friction coefficient was obtained from the difference between the tension before friction and the tension after friction, when sized fibers were rubbed against a friction block made of chromium-plated steel by the use of a μ meter. (produced by Eiko Sokki Co., Ltd.) In this case, it is favorable that the m-f friction factor be as low as possible.

(6) Shedding property

An observation was made of the shedding property of warp from the opposite direction of the nozzle for the loom during weaving to visually judge the shedding property according to the following criterion. In this case, it is favorable that the shedding be as complete as possible. The favorable shedding means that the slippage is satisfactory at the time of weaving.

〈Judgement Criterion〉

◎ : excellent
○ : fairly good
△ : somewhat poor
X : poor
XX : extremely poor

Examples 1 to 25 and Comparative Examples 1 to 11

There were prepared aqueous solutions of fiber sizing agents each having a concentration of 10.5%, comprising PVA, a salt of a carboxyl group-containing copolymer and a lubricant, the kind and amount of each of the aforesaid three components being given in Table 2. By using each of the aqueoues solutions of the fiber sizing agents, sizing and weaving were carried out under the operating conditions described hereunder, and evaluations were made of the performance of the fiber sizing agent. The results are given in Tables 2 to 7.

(1) Weaving standard

Warp:	polyester filament, 「SD 75d/36f」(grade number) (produced by Kuraray Co., Ltd.)
Weft:	ditto
Texture:	plain weave (taffeta)
Loom:	air-jet loom, 540 rpm {produced by Tsudakoma Corporation, under "ZA-203" (grade number)}

(2) Sizing

Type of sizing machine:	warping sizer (produced by Tsudakoma Corporation)
Sizing agent solution temperature:	45°C
Width of squeezing roll:	1800 mm
Squeezing load:	200 kg/width of 1800 m
Thread speed:	140 m/min
Drying temperature:	130°C
Length of sized threads:	5600 m

Table 2

		Example		Comparative Example				
		1	2	1	2	3	4	5
Aqueous solution of sizing agent	PVA(A) (%)	PVA-16	PVA-156	PVA-166	PVA-16	-	PVA-1710	PVA-110
	Salt of copolymer (B)[1] (%)	ACR-A 4	ACR-A 4	ACR-B 4	ACR-B 4	ACR-B 10	-	-
	Lubricant[2] (%)	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	Lubricant[3] (%)	0.2	0.2	0.2	0.2	0.2	0.2	0.2
	(A)/(B)[4]	60/40	60/40	60/40	60/40	0/100	100/0	100/0
	Concentration of sizing agent solution (%)	10.5	10.5	10.5	10.5	10.5	10.5	10.5
Evaluation result	Off-sizing resistance	◎	○	X	◎	◎	△	△
	Anti-sticking property	◎	◎	○	X	△	X	XX
	Desizability for gray fabric	◎	◎	◎	◎	◎	◎	◎
	Anti-gumming property	◎	◎	◎	◎	X	◎	◎
(Remarks) Raw Yarns: polyester filament, SD 75d/36f (Kuraray Co., Ltd) Texture: plain weave (taffeta)								

1) Salt of carboxyl group-containing copolymer
2) Sitex T-190 (produced by Goo Chemical Co., Ltd.)
3) Sitex Silicone 53 (produced by Goo Chemical Co., Ltd.)
4) Content ratio by weight of PVA/salt of carboxyl group-containing copolymer

Table 3

		Example	
		3	4
Aqueous solution of sizing agent	PVA(A) (%)	PVA-2 7	PVA-3 7
	Salt of copolymer (B)[1] (%)	ACR-A 3	ACR-A 3
	Lubricant[2] (%) Lubricant[3] (%)	0.3 0.2	0.3 0.2
	(A)/(B)[4]	70/30	70/30
	Concentration of sizing agent solution (%)	10.5	10.5
Evaluation result	Off-sizing resistance	◎	◎
	Anti-sticking property	◎	◎
	Desizability for gray fabric	◎	◎
	Anti-gumming up property	◎	◎
(Remarks) Raw yarns: polyester filament, SD 75d/36f (Kuraray Co., Ltd.) Texture: plain weave (taffeta)			

1) Salt of carboxyl group-containing copolymer
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4) Content ratio by weight of PVA/salt of carboxyl group-containing copolymer

Table 4

		Example				Comparative Example	
		5	6	7	8	6	7
Aqueous solution of sizing agent	PVA(A) (%)	PVA-18 7	PVA-19 7	PVA-20 7	PVA-21 7	PVA-22 7	PVA-23 7
	Salt of copolymer (B)[1] (%)	ACR-A 3	ACR-A 3	ACR-A 3	ACR-A 3	ACR-A 3	ACR-A 3
	Lubricant[2] (%)	0.3	0.3	0.3	0.3	0.3	0.3
	Lubricant[3] (%)	0.2	0.2	0.2	0.2	0.2	0.2
	(A)/(B)[4]	70/30	70/30	70/30	70/30	70/30	70/30
	Concentration of sizing agent solution (%)	10.5	10.5	10.5	10.5	10.5	10.5
Evaluation result	Off-sizing resistance	○~◎	○	○	○	insoluble in water incapable of sizing	X
	Anti-sticking property	○~◎	○~◎	○~◎	○~◎		◎
	Desizability for gray fabric	○	○	○	○		△
	Anti-gumming up property	◎	◎	◎	◎		◎
(Remarks) Raw yarns: polyester filament, SD 75d/36f (Kuraray Co., Ltd) Texture: plain weave (taffeta)							

1) Salt of carboxyl group-containing copolymer
2) Sitex T-190 (produced by Goo Chemical Co., Ltd.)
3) Sitex Silicone 53 (produced by Coo Chemical Co., Ltd.)
4) Content ratio by weight of PVA/salt of carboxyl group-containing copolymer

Table 5

		Example						Comparative Example	
		9	10	11	12	13	14	11	12
Aqueous solution of sizing agent	PVA(A) (%)	PVA-4 7	PVA-5 7	PVA-6 7	PVA-7 7	PVA-8 7	PVA-9 7	PVA-10 7	PVA-11 7
	Salt of copolymer (B)[1] (%)	ACR-A 3	ACR-A 3	ACR-A 3	ACR-A 3	ACR-A 3	ACR-A 3	ACR-A 3	ACR-A 3
	Lubricant[2] (%)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	Lubricant[3] (%)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
	(A)/(B)[4]	70/30	70/30	70/30	70/30	70/30	70/30	70/30	70/30
	Concentration of sizing agent solution (%)	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5
Evaluation result	Off-sizing resistance	◎	◎	◎	○~◎	○~◎	○~◎	◎	X
	Anti-sticking property	○	◎	◎	◎	○~◎	◎	○	◎
	Desizability for gray fabric	○	◎	◎	◎	◎	○	X	△
	Anti-gumming up property	◎	◎	◎	◎	◎	◎	◎	◎
(Remarks) Raw yarns: polyester filament, SD 75d/36f (Kuraray Co., Ltd.) Texture: plain weave (taffeta)									

1) Salt of carboxyl group-containing copolymer
2) Sitex T-190 (produced by Goo Chemical Co., Ltd.)
3) Sitex Silicone 53 (produced by Goo Chemical Co., Ltd.)
4) Content ratio by weight of PVA/salt of carboxyl group-containing copolymer

Table 6

		Example			
		15	16	17	18
Aqueous solution of sizing agent	PVA(A) (%)	PVA-12 7	PVA-3 7	PVA-1 7	PVA-14 7
	Salt of copolymer (B)[1] (%)	ACR-A 3	ACR-A 3	ACR-A 3	ACR-A 3
	Lubricant[2] (%)	0.3	0.3	0.3	0.3
	Lubricant[3] (%)	0.2	0.2	0.2	0.2
	(A)/(B)[4]	70/30	70/30	70/30	70/30
	Concentration of sizing agent solution (%)	10.5	10.5	10.5	10.5
Evaluation result	Off-sizing resistance	◎	◎	◎	○
	Anti-sticking property	○~◎	◎	◎	◎
	Desizability for gray fabric	◎	◎	◎	◎
	Anti-gumming up property	◎	◎	◎	◎
(Remarks) Raw yarns: polyester filament, SD 75d/36f (Kuraray Co., Ltd.) Texture: plain weave (taffeta)					

1) Salt of carboxyl group-containing copolymer
2) Sitex T-190 (produced by Goo Chemical Co., Ltd.)
3) Sitex Silicone 53 (produced by Goo Chemical Co., Ltd.)
4) Content ratio by weight of PVA/salt of carboxyl group-containing copolymer

Table 7

		Example							Comparative Example	
		19	20	21	22	23	24	25	10	11
Aqueous solution of sizing agent	PVA(A) (%)	PVA-1 1.6	PVA-1 3	PVA-1 4	PVA-1 5	PVA-1 7	PVA-1 8	PVA-1 9	PVA-1 1	PVA-1 9.995
	Salt of copolymer (B)[1] (%)	ACR-A 8.4	ACR-A 7	ACR-A 6	ACR-A 5	ACR-A 3	ACR-A 2	ACR-A 1	ACR-A 9	ACR-A 0.005
	Lubricant[2] (%)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	Lubricant[3] (%)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
	(A)/(B)[4]	16/84	30/70	40/60	50/50	60/40	80/20	90/10	10/90	99.95/0.05
	Concentration of sizing agent solution (%)	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5
Evaluation result	Off-sizing resistance	◎	◎	◎	◎	◎	◎	○~◎	◎	△
	Anti-sticking property	◎	◎	◎	◎	◎	◎	○	◎	×
	Desizability for gray fabric	○	○~◎	○~◎	◎~○	◎	◎	◎	○	◎
	Anti-gumming up property	○	○	○	○~◎	◎	◎	◎	×	◎

(Remarks)

Raw yarns: polyester filament, SD 75d/36f (Kuraray Co., Ltd.)
Texture: plain weave (taffeta)
1) Salt of carboxyl group-containing copolymer
2) Sitex T-190 (produced by Goo Chemical Co., Ltd.)
3) Sitex Silicone 53 (produced by Goo Chemical Co., Ltd.)
4) Content ratio by weight of PVA/salt of carboxyl group-containing copolymer

Example 26 and Comparative Example 12

There were prepared aqueous solutions of fiber sizing agents each having a concentration of 11.3%, comprising PVA, a salt of a carboxyl group-containing copolymer and a lubricant, the kind and amount of each of the aforesaid three components being given in Table 8. By using each of the aqueoues solutions of the fiber sizing agents, sizing and weaving were carried out under the operating conditions described hereunder, and evaluations were made of the performance of the fiber sizing agent. The results are given in Table 8.

(1) Weaving standard

Warp:	polyester spun yarn 40/1 {produced by Kuraray Co., Ltd. under 「1013 S 40/1」 (grade number)}
Weft:	ditto
Warp density:	136 ends/inch
Weft density:	72 ends/inch
Weaving width:	47 inches
Loom:	air-jet loom, 540 rpm {produced by Tsudakoma Corporation, under "ZA-203" (grade number)}

(2) Sizing

Type of sizing machine:	two-box two-sheet type (produced by Tsudakoma Corporation)
Sizing agent solution temperature:	92°C
Width of squeezing roll:	1800 mm
Squeezing load:	800 kg/width of 1800 m
Thread speed:	65 m/min.
Drying temperature:	100 to 130°C
Length of sized threads:	5600 yards

Table 8

		Example	Comparative Example
		26	12
Aqueous solution of sizing agent	PVA(A) (%)	PVA-1 2.2	PVA-1 2.2
		PVA-24 6.6	PVA-24 6.6
	Salt of copolymer (B)[1)] (%)	ACR-A 2.2	ACR-B 2.2
	Lubricant[2)] (%)	0.3	0.3
	(A)/(B)[3)]	80/20	80/20
	Concentration of sizing agent solution (%)	11.3	11.3
Evaluation result	m-f friction coefficient	0.201	0.221
	Shedding property	◎	X
	Off-sizing resistance	◎	◎
	Anti-gumming up property	◎	○
	Desizability for gray fabric	◎	◎
[Remarks] Raw yarns: polyester filament, 40/1 {Kuraray Co., Ltd. 1013 s 40/1 (grade number)} Texture: plain weave			

1) Salt of carboxyl group-containing copolymer
2) 「Warpset 100 」(trade name) (produced by Takemoto Oil & Fat Co., Ltd.)
3) Content ratio by weight of PVA/salt of carboxyl group-containing copolymer

Claims

1. A fiber sizing agent which comprises a polyvinyl alcohol (A) having a degree of hydrolysis of 60 to 99 mol% and a viscosity-average degree of polymerisation of 100 to 5000 and an ammonium salt of a carboxyl group-containing polymer (B), the blending ratio (A) : (B) based on weight being 15 : 85 to 99.9 : 0.1.

2. The fiber sizing agent according to Claim 1, wherein the polyvinyl alcohol (A) has a degree of hydrolysis of 60 to 85 mol% and a viscosity-average degree of polymerization of 100 to 5000.

3. The fiber sizing agent according to Claim 1, wherein the polyvinyl alcohol (A) has a degree of hydrolysis of 60 to 85 mol% and a viscosity-average degree of polymerization of 200 to 1500.

4. The fiber sizing agent according to any of claims 1 to 3, wherein the polyvinyl alcohol (A) further contains 0.05 to 10 mol% of an ionic group-containing monomer unit.

5. The fiber sizing agent according to Claim 4, wherein the polyvinyl alcohol (A) has a degree of hydrolysis of 60 to 85 mol% and a viscosity-average degree of polymerization of 200 to 1500 and further contains 0.05 to 4 mol% of an ionic group-containing monomer unit.

6. The fiber sizing agent according to any one of Claims 1 to 5, wherein the ammonium salt of a carboxyl group-containing polymer (B) has a degree of neutralization of at least 0.3.

7. The fiber sizing agent according to any one of Claims 1 to 6, wherein the ammonium salt of a carboxyl group-containing polymer (B) is the ammonium salt of the copolymer of (meth)acrylic acid and a hydrophobic unsaturated monomer.

8. The fiber sizing agent according to Claim 7, wherein the hydrophobic unsaturated monomer is at least one member selected from the group consisting of (meth)acrylic acid esters, (meth)acrylonitrile and aromatic unsaturated monomers.

9. Use of the fiber sizing agent according to any one of claims 1 to 8, for sizing polyester fibers acetate fibers or nylon fibers.

10. A method for weaving fibers sized with the fiber sizing agent as set forth in any one of the Claims 1 to 9 through a dry-loom.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 11 0625

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DATABASE WPI Section Ch, Week 9041 Derwent Publications Ltd., London, GB; Class A14, AN 90-307932 XP002044127 & JP 02 216 239 A (ASAHI CHEM IND CO LTD) , 29 August 1990 * abstract * ---	1-10	D06M15/333 D06M15/263
A	EP 0 450 437 A (BASF AG) 9 October 1991 * page 2, line 1 - page 4, line 49 * * claims; examples 1-11 * ---	1-10	
A	GB 880 980 A (REVERTEX LIMITED) 25 October 1961 * page 1, line 24 - page 2, line 122 * ---	1-7,9,10	
A	US 4 172 930 A (KAJITANI KOICHI ET AL.) 30 October 1979 * column 3, line 12 - column 5, line 52 * * table 1 * ---	1-10	
A	DATABASE WPI Section Ch, Derwent Publications Ltd., London, GB; Class A00, AN 68-64459P XP002044128 & JP 41 012 076 B (GO-OU CHEMICAL INDUSTRY) * abstract * -----	1-10	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
D06M
C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 October 1997	Herrmann, J

CATEGORY OF CITED DOCUMENTS

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