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# SIZING AGENT FOR TEXTILE FIBERS DERIVED FROM METHANOLYSIS OF A VINYL ACETATE ACRYLAMIDE COPOLYMER

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## ABSTRACT OF THE DISCLOSURE

A warp sizing agent is prepared by the partial saponification of a vinyl acetate-acrylic amide copolymer. This product is superior to a mixed size including acrylic acid ester and polyvinyl alcohol in terms of such adhesiveness, softness and moisture absorptive property which can be adjusted to suit the particular fibers to be sized by the degree of saponification. In addition, the product is characterized by ease of handling, transporting and weighing because of its powdery state, and is readily dissolved in water.

## BACKGROUND OF THE INVENTION

### Field of the invention

This invention relates to a sizing agent for textile fibers, of all types but especially hydrophobic ones such as polyester and polyamide warp yarns of which are usually sized before weaving.

### Description of the prior art

Hitherto, the particular warp size for this purpose has depended upon the kind of warp thread or yarns to be sized. Thus for hydrophobic fibers such as polyester and polyamide, partially saponified polyvinyl alcohol is not sufficiently adhesive for a satisfactory size.

While acrylic ester possesses better adhesiveness than polyvinyl alcohol, and superior elasticity it has a greater capacity for moisture absorption.

Accordingly the two materials are commonly used conjointly as a more-or-less necessary compromise.

## SUMMARY OF THE INVENTION

The object of this invention is to provide a warp size which is also satisfactory for hydrophobic fiber such as polyester and polyamide, wherein the sizing of which is usually effected by the combined use of partially saponified polyvinyl alcohol and acrylic acid ester size, with the consequent problem of large moisture absorptive property, which causes difficulty in the weaving.

This warp size can be used alone, without another chemical, unlike the conventional size. Having better cohesive force also contributes to the improved quality of the product woven fabrics.

Moreover, the size of this invention is obtained in powdery form with higher purity, is readily transported, weighed and handled and is easily dissolved in water.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

Generally, in the weaving operation, the warp yarn is first reinforced and lubricated by treatment with an appropriate agent called a szie, and such warp size need be selected according to the kind of the wary yarn to be sized.

For example, in the case of hydrophobic fibers such as polyester or polyamine, satisfactory sizing cannot be effected using a partially saponified polyvinyl alcohol



alone, an acrylic acid ester size has greater adhesiveness in comparison with polyvinyl alcohol, but suffers the defect in having a substantial moisture absorptive property. In practice, a mixed size containing saponified polyvinyl alcohol and acrylic acid ester is used.

In our researches on szies for warp yarn, we have found that the sizing agent for textile fibers of this invention can be independently used not only for the hydrophilic fibers but also for said hydrophobic fibers, because its excellent adhesiveness, softness and moisture absorptive property can be adjusted to best suit the kind of fiber to be sized.

Besides, in comparison with the combined use of polyvinyl alcohol and acrylic sizes, which are now popular, the size of this invention had better cohesvie force, and consequently with the use of this size, the weaving process can be smoothly performed. Our tests also indicate that the quality of woven fabrics is improved where the warp yarns have been processed by this size.

The size of this invention is readily soluble in water without the addition of another chemical.

The size of this invention can be obtained by copolymerizing vinyl acetate and acrylic amide, and then partially saponifying the said copolymer.

It is especially important for the product to have an appropriate acrylic amide content and saponification degree, so that the size will have the desired adhesiveness, elasticity, moisture absorptive property, and superior cohesive force in powdery state.

That is, as the acrylic amide content in the acrylic amide copolymer partially saponified part becomes greater, the moisture absorptive property becomes larger, and the sized warp yarns contain too much moisture accordingly. This of course, is undesirable in the weaving process, as tackiness of the yarn increases. On the other hand, as the acrylic amide content becomes smaller, the sizing process becomes more difficult to perform, and simultaneously, the abrasion resistance and softness of the processed warp yarns are reduced.

An appropriate acrylic amide content in the saponified copolymer is 0.2–17 mol. percent, and by converting about 75–95 mol. percent of residual acetic acid radical contained in the partially saponified copolymer to the hydroxylic group, the size can be obtained in powder state with ease.

If the conversion is less than 75 mol. percent obtaining the size in powder state becomes increasingly difficult.

When the residual acetic acid radical converted to hydroxyl radical exceeds 95 mol. percent, then desizing becomes almost impossible to effect.

In the copolymerization of vinyl acetate ($M_1$) and acrylic amide ($M_2$) the monomer reactivity ratio is $r_1$–0.07, $r_2$–7.5 respectively and therefore in order to obtain uniform copolymer it is better to copolymerize in unison with each other by adding the acrylic amide (having faster reaction velocity) gradually, in proportion to the polymerizing degree of vinyl acetate (having slow reaction velocity).

The invention is hereinafter explained in detail, referring to the following examples. However, it should be understood that these examples are not intended to restrict this invention but are given merely by way of illustration. In the examples, the terms "part" or "percent" mean *by weight,* unless otherwise specified.

## EXAMPLE 1

By adding continuously a total of 0.10 part of acrylic amide to copolymerized liquid composed of 0.0053 part of azobisisobutyronitrile as against 1 part of vinyl-acetate, and 1.13 parts of methanol, polymerization proceeds for about 12 hours at a temperature of 65° C. and vinyl ace-

tate and acrylic amide copolymer in the yield of more than 99% is produced.

In the next step, to a solution composed of 30 parts of the said copolymer and 70 parts of methanol, 1/75 mole of sodium methylate per one mole of vinyl acetate is added and the saponifying reaction is performed at a temperature of 40° C. The product is a partially saponified vinyl acetate and acrylic amide copolymer having polymerization degree 500 with 85 mol. percent saponification degree of acetic acid radicals (the product is Item No. 1 of this invention as indicated in Table 1).

Other copolymers are prepared and then saponified as previously described but starting with 0.024 and 0.002 parts of acrylic amide instead of 0.10 part. These products are designated Item 2 and Item 3, respectively in Table 1.

After dissolving these three products, polyester warp yarns were sized with them having use of a two-step roller type sizing machine and the fundamental property as of each of the thus sized warp yarns were determined.

The sizing conditions and the test results are shown in Table 1. Also, for purpose of comparison the same data were determined for the same kind of yarns sized in the same way but using 4.2 parts of partially saponified (saponification degree 88 mol. percent) polyvinyl alcohol alone, (designated in Table I as comparative size No. 1), and the combined use of 4.2 parts as above-stated, of this partially saponified polyvinyl alcohol, and 1.8 parts Marposol S-50 (trademark: Acrylic warp size, manufactured by Matsumoto Oil and Fat Co., Ltd.) (designated in Table 1 as size No. 2).

As indicated in Table 1, Item No. 2 of this invention is superior in terms of pliability and cohesive force, to comparative size No. 2.

Even though the size takeup is less than that of comparative size No. 2, Item No. 2 of this invention size results in a higher value for the cohesive force.

Besides, it is recognized that relating to moisture absorptive property in the case of Item No. 1 of this invention size, it is limited by the extent of increase in acrylic amide content, while in the case of Item No. 3 of this invention size, its friction resistance is limited also by the extent of decrease in acrylic amide content.

TABLE 1

| | Item of this invention | | | Comparative size | Comparative size |
|---|---|---|---|---|---|
| | No. 1 | No. 2 | No. 3 | No. 1 | No. 2 |
| Acrylic amide content (mol percent) | 11 | 2 | 0.3 | ---------- | |
| Size takeup (percent) | 5.5 | 5.1 | 5.0 | 4.9 | 5.7 |
| Cohesive force (times) | 32 | 28 | 23 | 15 | 19 |
| Pliability | 108 | 138 | 165 | 180 | 175 |

The above table was obtained under the following conditions.

Sizing condition:
- Roller rotation times—4.5 times/minutes
- Roller contact length—one-step roller 1.4–1.6 cm.; two-step roller 1.2–1.4 cm.
- Sizing speed—118 m./minutes
- Sizing liquid temperature—20±1° C.
- Relative humidity—58±1%.

Warp filament, polyester 50 d., 24 F. twist 300 times/m.

Property test (temperature and humidity 20° C. RH 65%).

The composition of sizing bath: Percent
- Items of the invention or comparative sizes — 6
- Saitex T-190 [1] — 0.4
- Scourol 100 [2] — 0.5

[1] Saitex T-190, manufactured by Goo Chemical Co., Flux.
[2] Scourol 100, manufactured by Kao Soap Co., Flux.

*Cohesive force.*—Tested by use of Friction & Rubbing tester, TM-type. After setting sized yarns at a bending angle of 130° by use of three pieces of steel pin, one end of the yarns is fixed, with the other end burdened with tension of 10 g./one piece.

On exerting friction on the sized yarns by moving three pins in parallel with the filaments, the times needed for moving the pins until the filaments are separated were measured.

*Pliability.*—Tested by stiffness tester, twisting type. One end of sized filament (3 cm.) in length fixed to a movable pulley, while attaching a magnetic substance to the other end in such manner of the substance may hang down vertically and settle in a less powerful magnetic field.

When the movable pulley rotates at a velocity of 1 r.p.m., if the rotation angle of the pulley needed until a magnetic substance revolves at a certain angle ($\varphi$) is set at $\theta$, pliability is given as follows.

$$\text{Pliability} = \varphi/\theta \times 100$$

The lower this value the greater is the softness of the material.

Acrylic amide content—computed out by nitrogen analysis. As indicated in Table 1, Item No. 2 of this invention is superior in terms of pliability to comparative size No. 2.

Even when the size takeup is lower than that of comparative size No. 2, Item No. 2 of this invention still shows a higher value for the cohesive force.

Besides, it is recognized that relating to moisture absorptive property of Item No. 1 of this invention, it is limited by the extent of increase in acrylic amide content, while in the case of Item No. 3 of this invention, its elasticity is limited also by the extent of decrease in acrylic amide content.

## EXAMPLE 2

Comparison was made between the following cases. That is, the case of employing Item No. 2 of this invention as warp size as indicated in Example 1, and the case of partially saponified polyvinyl alcohol and acrylic acid ester size as now used commonly (comparative size No. 2 as indicated in Table 1).

By using a total of 4600 sized warp yarns on automatic loom, on the right side of which invention Item No. 2 sized warps numbering 2300 were set, and 2300 comparative goods No. 2 sized warp on the left side respectively, the weaving test was conducted.

The result is that the warp sized with the invention size which were cut during the weaving averaged one per 36 yards of cloth while, on the side having the warp yarns sized within the comparative size the yarn was cut at the rate of one yarn per 7.7 yards woven fabric. That is, the ratio of cut yarns during weaving between the two sizes is 1:5.

The sizing conditions were as shown in Example 1, while the weaving conditions were as follows:

Temperature and humidity during the weaving—24–28° C., 74–82% RH.
Loom rotation times—150 r.p.m.
Warp yarn tension—50–55 g.

## EXAMPLE 3

By dropping continuously a solution of 0.1 part acrylic amide and 0.009 part of methanol to copolymerized liquid composed of 1 part of vinyl acetate, 0.155 part methanol, 0.0005 part azobisisobutyronitrile, and 0.0006 acetic acid, polymerization was conducted for about 5 hours at a temperature of 62–64° C.

A copolymer of vinyl acetate and acrylic amide in the yield of about 70% was obtained. After separation of the product from vinyl acetate monomer which has not been polymerized then the said copolymer was dissolved in methanol to a concentration of 3 parts of said copolymer to 7 parts of methanol.

After adding 1/200 mole of sodium methylate per one mole of vinyl acetate in the said copolymer, saponification at a temperature of 30° C. was conducted. Thus, vinyl acetate and acrylic amide copolymer having a saponification degree 88 mol. percent and polymerization degree 1800 was obtained. (Item No. 4 of this invention size).

And then by adjusting the above to an aqueous solution composed of the following compositions and then sizing polyester and cotton blend yarn the property test on the yarns and the weaving test were conducted by use of a slasher sizing machine.

Then for purposes of comparison like yarns were sized using a mixture of 4.5 parts of partially saponified polyvinyl alcohol having polymerization degree 1800 and saponification degree 8 mol. percent and 0.24 part of Marposol S–80 partially saponified polyacrylic acid ester (manufactured by Matsumoto Fat and Oil Co., Ltd. in the same manner as indicated in the foregoing and the similar sized product was tested.

The results are set forth in Table 2.

TABLE 2.—SIZE YARN PROPERTY AND THE RESULT OF WEAVING TEST

| | Invention item No. 4 | Comparative size No. 3 |
|---|---|---|
| Acrylic amide content (mol. percent) | 1.1 | ---------- |
| Size, take up (percent) | 10.7 | 11.5 |
| Strength (g.) | 186 | 187 |
| Stretching degree (percent) | 10.1 | 9.0 |
| Friction resistance (times) | 2,219 | 1,870 |
| Numbers of sized yarn being cut in weaving (nos./hr.) | 0.2-0 | 0.5 |

The sizing condition:

Composing of sizing bath—

In case of this invention Item No. 4, 4.45%, comparative size No. 3, 4.78%

CMC—0.42%

Corn starch—1.82%

Maconol TS–222 (manufactured by Matsumoto Fat and Oil Co., Flux)—0.42%

Kawamoto type 15D sizer was used in the sizing.

Sizing bath temperature—80° C.

Squeeze pressure—0.75 kg./cm.$^2$

Sizing velocity—25 m./min.

Drying temperature—90–95° C.

Weaving conditions:

Used yarn—blend yarn of polyester 65 and cotton 35 45/S

Total number of warp yarns—5054

Fabric density—126 x 72/inch

Automatic loom rotation times—185 times/min.

Temperature and humidity in weaving operation—6–11° C., 55–73% RH

Strength: tested by Shimazu Autograph Model P–110

Abrasion resistance: By the time when all 10 sized spun yarns are cut out by use of TM type Friction & Rubbing tester, the times of friction were examined. Tension 400 g./10 sized yarns, at a bending angle of 115° was employed.

Acrylic amide content was calculated from the nitrogen analysis. According to the test result (1), invention item sized yarns are superior to those sized by comparative goods in respect of abrasion resistance, the number of warp yarn being cut out in weaving operation was fewer than those sized by comparative goods, and so it showed higher efficiency in weaving.

## EXAMPLE 4

After mixing starch, and flux with an aqueous solution of invention Item No. 4 indicated in Example 3 in accordance with the following compositions, and then sizing polyester/cotton blend yarn, the weaving test was conducted.

For comparison purposes, as stated above, after mixing the following compound with an aqueous solution composed of 3.47 parts partially saponified polyvinyl alcohol (polymerization degree 1800, saponification degree 88 mol. percent) 3.47 parts, and 0.35 part of Primal P–6N (manufactured by Nippon Acrylic Co., Ltd. Partially saponified copolymer, comparative goods No. 4), the weaving test was conducted by use of sized yarn.

The test result showed that with said Invention Item No. 4 sized yarns which have been cut in weaving process slightly numbered below 0.2 yarn per hour, and operation efficiency was nearly 100%, whereas with the comparative size No. 4 this figure was 0.6 yarn per hour and the operation efficiency was 95%.

The sizing conditions and weaving conditions are as follows:

| Sizing conditions: | Percent |
|---|---|
| Invention Item No. 4 or comparative size No. 4 | 3.80 |
| Snow Tex (colloidal silica, manufactured by Nissan Chemical) | 0.38 |
| Corn starch | 4.86 |
| Biscon HHK (Flux, manufactured by Kyoto Gosei) | 0.15 |
| MYC #100 (Flux, manufactured by Nippon Fat & Oil Co.) | 0.23 |
| Miracon 102 (Flux, manufactured by Daido Kogyo Co.) | 0.04 |

Sizing conditions:

Sizing machine—Suzuki type hot air sizer

Temperature of sizing bath—94° C.

Sizing velocity—30–32 m./min.

Drying temperature—90–95° C.

For after-waxing, MYC#5000A (manufactured by Nippon Fat & Oil Co.( was employed.

After-waxing at a temperature of 85° C. was conducted.

Kind of used yarn: Polyester/cotton blend yarn 65/35 34/S

Weaving condition:

Weaving machine—Toyoda Automatic Loom

Total warp yarn—3874 33/S

Fabric density—85 x 60 yarns/inch

Loom rotating times—170 times/min.

Temperature and humidity in weaving—21° C., 78% RH

## EXAMPLE 5

After preparing aqueous solutions having the following compositions set forth below, and then sizing wool yarn by use of said sizing liquids in a roller sizing machine, the desizing test on the sized yarns was conducted as indicated. One of these size solutions was made from Invention Item No. 4, and the comparative one from a mixture of 5.5 parts of partially saponified polyvinyl alcohol (polymerization degree 1800, saponification degree 88 mol. percent), Tamanori Super-4000 0.5 part vinyl acetate and maleic anhydride copolymer (manufactured by Hayashiya firm in Arakawa Ward, Tokyo, (comparative size No. 5). These size solutions had the following compositions.

The composition of the size used was as follows:

| | Percent |
|---|---|
| Invention Item No. 4 or No. 5 | 6.0 |
| Corn starch | 3.0 |
| Marpolin #1 (Flux, manufactured by Watanabe Chemical Co.) | 1.0 |
| Bisco HHK (Flux, manufactured by Kyoto Gosei Co.) | 0.2 |

The sizing condition was as follows:

Sizing machine—Kakimoto type two steps Roller

Size solution temperature—60–70° C.

Sizing velocity—107 m./min.

Roller rotation times (r.p.m.)—No. 1, 4; No. 2, 2.2

Contact angle (mm.)—No. 1, 15; No. 2, 14

Thereafter the sized yarns were desized using the following desizing bath:

| | |
|---|---|
| Lactogen (manufactured by Rakuto Kasei Co.) | 2.0 |
| Bisconol W (manufacture by Nippon Fat & Oil Co.) | 0.5 |

After the yarns to be desized have been dipped for about 24 hours, in the said desizing bath at a temperature of 60°–80° C. and rinsing with luke warm water and then water washing were conducted.

According to the above test, the yarns sized with invention item No. 4 were easily desized by the foregoing method with almost 100% completeness, while in the case of the yarns sized by comparative size No. 5, about 3% of size takeup was observed even after having conducted desizing. In other words, the desizing process was only partially effective in the latter case.

We claim:

**1.** A sizing agent for textile yarns and threads consisting essentially of a copolymer of acrylic amide and partially saponified vinyl acetate, said copolymer containing from 0.2 to 17 mol percent acrylic amide and from 75 to 95% of the acetic acid radicals replaced by hydroxy radicals.

**2.** A sizing agent according to claim **1** wherein the acrylic amide is 11 mol percent, the saponification is 85 mol percent, and the polymerization degree is 500.

**3.** A sizing agent according to claim **1** wherein the acrylic amide content is 2 mol percent and the saponification degree is 85 mol percent.



**4.** A sizing agent according to claim **1** wherein the acrylic amide content is 0.3 mol percent and the saponification degree is 85 mol percent.

**5.** A sizing agent according to claim **1** wherein the acrylic amide content is 1.1 mol percent and the saponification degree is 88 mol percent.

**6.** A sizing agent according to claim **5** wherein the polymerization degree is 1800.


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