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PROCESS OF SIZING TEXTILE YARN AND PRODUCT THEREOF

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FIG. 1

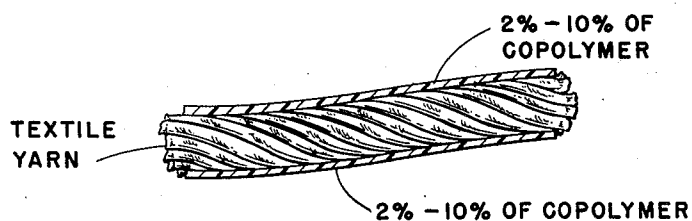
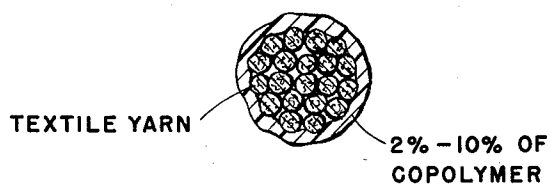


FIG. 2



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1

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PROCESS OF SIZING TEXTILE YARN AND
PRODUCT THEREOF

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The present invention relates to a water-soluble vinyl copolymer containing recurring nitrile and carboxylate groups and especially to the warp sizing of textile yarns therewith.

A wide variety of sizing materials have been proposed and used in protecting yarns during knitting and weaving. Due to the abrasion suffered by warp yarns while being woven on a loom, the chief interest has been in warp sizing materials and particularly those of a removable nature which can be readily scoured off of the woven material. Acceptable results in warp sizing have been obtained on many textile fabrics for many years, but a warp size which works well with one type of fiber seldom produces as good results on others. For example, gelatin is an excellent warp size for viscose fibers; but it is substantially useless for nylon. Nylon is perhaps the most difficult of all yarns to protect with a size; and the predominant commercial warp size for nylon, polyacrylic acid, has a major drawback in its corrosive nature which requires the employment of stainless steel slashers to avoid discoloring the yarn with corrosion products. There is no universal warp size, and a demand has long existed for a product of this type which would be equally effective with cotton, acetate, rayon, and the hydrophobic synthetic textile fibers. For maximum utility, such a size should be of an essentially neutral nature in order to permit the use of conventional mill equipment without introducing any corrosion or staining problems.

An object of the present invention is to provide novel water-dispersible, film-forming copolymers.

Another object of the present invention is to provide an improved warp size for a wide variety of textile materials.

A further object of the invention is to provide an improved warp-sizing process.

Still another object of the invention is to provide improved warp-sized textile yarns.

Other objects and advantages of this invention will be apparent to those skilled in the art, especially upon detailed consideration of the invention disclosed hereinbelow.

The present invention concerns a copolymer having recurring nitrile and —COOX groups in a formula ratio between 1:0.30 and 1:0.75 attached to a long linear carbon chain, wherein X is hydrogen, sodium, potassium or the ammonium radical, which copolymer upon dilution with water to a concentration of 5% by weight has a pH between about 5 and about 9 and a viscosity between about 5 and about 200 centipoises at 140° F. For optimum results, the stated ratio is desirably maintained between 1:0.40 and 1:0.60. Other aspects of the invention include not only the sized textile yarns but also the process of sizing with the above copolymers all types of continuous filament and staple textile yarns including cotton, viscose rayon, cuprammonium rayon, ramie, flax, wool, silk, polyesters such as cellulose acetate, cellulose propionate and polyethyleneglycol terephthalate, nylon of both the adipamide and caprolactam types, polyvinyl

2

compounds such as copolymers of vinyl and vinylidene chlorides and the various homo- and copolymers of acrylonitrile with methyl acrylate, vinyl acetate, vinyl pyridines, etc., as well as blends or mixtures of the aforesaid materials.

One of the monomers employed in the present invention is acrylonitrile; and the other may be acrylic acid, methacrylic acid, maleic acid, maleic anhydride, or the ammonium, potassium or sodium salts thereof. To produce the results obtainable by the present invention, it is essential that the molar ratios of the copolymers be adjusted to provide the proportions of nitrile and carboxylate groups stated above. It is to be noted that the term "carboxylate" is used broadly herein to include —COOH radicals.

The monomeric reaction mixture is copolymerized in known manner in either a batch or continuous operation employing conventional vinyl polymerization catalysts which are capable of releasing oxygen but do not necessarily liberate oxygen during the polymerization reaction. Among the many suitable substances are peroxy compounds such as ammonium and alkali metal persulfates which may be used alone or in combination with a reducing component such as sodium sulfite, potassium bisulfite, etc., to form a redox or reduction-oxidation catalyst system. These catalysts form no part of the present invention and therefore need not be described here in complete detail, especially since they are well known in the art. An aqueous medium is preferred for the polymerization reaction, and monomer concentrations of the order of 30% or lower are customarily used. To obtain the desired viscosity of between about 5 and about 200 centipoises in a 5% aqueous dispersion of the copolymer, the molecular weight may be controlled by known expedients such as adding chain-transfer agents, for example, isopropanol or mercaptans to reduce the molecular weight. Another method is to increase the catalyst to monomer ratio to achieve the same purpose. A reduction in molecular weight of course reduces the viscosity of an aqueous solution of any given concentration of the copolymer.

The compositions of the present invention are substantially neutral; that is, they have a pH in a 5% aqueous dispersion of between 5 and 9. To accomplish this, the carboxylate groups of the copolymer contain a major or predominant proportion of sodium or potassium atoms or ammonium radicals, even when the pH of the 5% dispersion is barely on the acid side between 5 and 7. However, under these conditions, an appreciable number of the —COOX groups are —COOH radicals. When the copolymer has a slightly alkaline pH between 7 and 9 upon dilution to 5% in water, —COOH groups are substantially completely absent therefrom. In preparing the copolymers, it is preferred to employ maleic anhydride, methacrylic acid, and especially, acrylic acid to furnish the carboxylate groups, and to substantially neutralize or raise the pH of the material to the desired range with an alkali after copolymerization in order to achieve better control of the pH. However, salts of the aforesaid acids may be substituted as the comonomers, in which case later neutralization is unnecessary unless an acid is introduced to activate the catalyst. Suitable alkaline materials for neutralizing the reaction mixture or to form the salts of the acids listed above include the sodium, potassium, or ammonium hydroxides, carbonates or bicarbonates.

For application to the various textile yarns, dispersions or colloidal solutions of between about 2 and about 10% of the copolymer in water are preferred, as the wet pickup of textile yarns from a sizing or slashing bath is of the order of 100% based on the weight of the dry yarn. Upon drying in a routine manner, this will leave a deposit

of about 2 to 10% size material based on the weight of the yarn. For most purposes, the bath concentration and the deposit on the yarns of about 5% is suggested for optimum results. In addition to the outstanding feature of sizing an extremely wide range of textile yarns, the compositions of the present invention have been found to be outstanding in performance on the commoner yarns of commerce such as viscose, acetate and nylon. Although the film of sizing is readily scourable from the yarns; these films do not become gummy upon exposure to high relative humidities for prolonged periods. In addition, the deposits display no crocking or flaking of the coatings from the yarn; and a high degree of abrasion resistance is displayed by the treated yarns. Besides their utility in the sizing field, the present compositions, by reason of their desirable characteristics in forming tough, dry, translucent films which adhere tenaciously to the substrata, are suitable for many other uses such as adhesives, paper coatings, leather finishes, finishes for knitted and woven textiles, thickening agents, flocculating agents, protective colloids, binders for ceramics, etc.

The numerical or formula ratio of nitrile groups to carboxylate groups in the present invention is very important, as will be apparent from the examples below wherein it is shown that the sizing properties of the compositions fall off markedly when the number of —COOX groups is reduced to 30% or increased to 75% of the number of nitrile groups present. The explanation of these phenomena is not understood at the present time.

For a better understanding of the nature and objects of this invention, reference should be had to the following illustrative examples in which all proportions are given in terms of weight unless otherwise stated therein.

Example I

A reduction-oxidation catalyst system in the form of 2.0 parts by weight of ammonium persulfate and 1.0 part of potassium metabisulfite, each dissolved in about 48 parts of water, are added to 1100 parts of water at 60° C. in a reaction vessel equipped with a reflux condenser and agitator through which a stream of carbon dioxide is continuously bubbling. In another vessel 180 parts of 99% acrylonitrile and 226 parts of 53.2% aqueous acrylic acid (1:0.50 acrylonitrile:acrylic acid molar ratio) are mixed and then slowly added to the reactor over a period of 1.5 hours with continual agitation. One hour after introducing the first of the monomer mixture, the redox catalyst system is renewed by the addition of 0.67 part of ammonium persulfate in about 48 parts of water and 0.33 part of potassium metabisulfite in solution in the same amount of water. Another hour is allowed for polymerization after the addition of mixed monomers is completed while continuing to maintain the stirring, inert atmosphere and 60° C. temperature; then the reaction mixture is cooled to room temperature and neutralized with ammonium hydroxide (28% NH_3 by weight) to a pH of 7.7. After dilution with water to 3% solids, a sample of the product is found to have a viscosity of 52 centipoises at 25° C. Another portion of the reaction mixture is diluted to a 5% solids concentration with water and employed as a warp-sizing bath, through which separate continuous filament yarns of cellulose acetate, viscose rayon and the adipamide type of nylon are drawn and found to have a wet pickup of about 100% based on the weight of the untreated yarn. All three of these yarns are found to be well sized for weaving with a stiff resilient finish which displays no tendency toward crocking or becoming gummy when exposed for a prolonged period to an atmosphere having a relative humidity of 80% at 70° F.

Example II

A mixed monomer solution is made by stirring 226 parts of 53.2% aqueous acrylic acid and 180 parts of 99% acrylonitrile together (acrylonitrile:acrylic acid molar ratio=1:0.50). To provide a catalyst, 9 parts of am-

monium persulfate is dissolved in a solution of 74 parts of isopropanol in 300 parts of water. These two solutions are added to 1030 parts of water at 70° C. in a suitable reaction vessel in 7 aliquot portions at 10-minute intervals. A carbon dioxide atmosphere is maintained in the vessel throughout the reaction, and the temperature is held in the range of 64–74° C. Following the addition of the monomer, the polymerization is allowed to continue for two more hours; then the product is neutralized with an aqueous sodium hydroxide solution to a pH of 5.5, and the reaction products are diluted to a 15% solids content with water. A sample of this mixture is dried on a glass plate at room temperature and then is exposed to an atmosphere of 80% relative humidity at 70° F. for one week. Upon examination, it is found that the tough, dry, translucent film adheres tenaciously to the glass. Continuous acetate, viscose and adipamide-type nylon yarns are warp sized with a 5% aqueous dispersion of the reaction product, and excellent results are obtained, especially in respect to stiffness and the absence of crocking.

Example III

A copolymer of equal weights of acrylonitrile and acrylic acid (1:0.74 mol ratio) is prepared and neutralized according to the procedure of Example I. Upon testing a 5% aqueous dispersion of this reaction product for warp sizing continuous filament yarns of acetate, viscous and nylon of the adipamide type, it is found that good results are obtained on the viscose yarn; and the sizing on the acetate and nylon yarns is satisfactory for commercial operations.

Example IV

A copolymer of 70% acrylonitrile and 30% acrylic acid (1:0.316 mol ratio) is formed and neutralized in the same way as in Example II. Upon applying a 5% aqueous dispersion of the product to both continuous filament and staple yarns of unblended viscose, acetate, nylon of the caprolactam type and a copolymer fiber of 95% acrylonitrile with 5% methyl acrylate, the film on the yarn is found to be satisfactory for commercial warp sizing in all cases but not equal to the warp sizing results obtained in Examples I and II.

Example V

A suitable reactor is charged with 200 parts of water at 60° C. and then with 15 parts of water containing 0.56 part of ammonium persulfate and 15 parts of water containing 0.28 part of potassium metabisulfite while constantly stirring the mixture and passing in carbon dioxide slowly during the entire reaction period. Meanwhile, 53.5 parts of 99% acrylonitrile (1.0 mol) is added at a slow and constant rate over a period of 1.5 hours while simultaneously adding an aqueous solution of 30 parts of diammonium maleate (0.2 mol) in 150 parts of water at a constant rate over the same period. One hour after starting to feed in the monomer 0.20 part of ammonium persulfate in solution in 10 parts of water and 0.10 part of potassium bisulfite dissolved in a similar quantity of water are added to restore the activity of the catalyst system. The polymerization is allowed to proceed for a total reaction time of 2.5 hours; then the reaction mixture is cooled to room temperature. Upon dilution to 5% solids concentration with water, the pH is found to be only slightly below 7.0; and, upon sizing continuous filament acetate, viscose, and nylon of the adipamide type with this dispersion, good resistance to abrasion and crocking are obtained.

While there are above disclosed only a limited number of embodiments of the composition, process and product of the invention herein presented, it is possible to produce still other embodiments without departing from the inventive concept herein disclosed; and it is desired that only such limitations be imposed on the appended claims as are stated therein or required by the prior art. In particular, the present compositions may be employed in ad-

mixture with a wide variety of compatible textile-treating agents, including other sizes such as gelatin, starch, etc., lubricants such as sulfonated tallow, etc., and various wetting agents.

Reference is made to the accompanying drawing which illustrates the concept of the present invention. Fig. 1 is a side elevational view, partly in section, of a textile yarn which has been coated with from 2% to about 10% by weight of a copolymer of the class described hereinabove. Fig. 2 is a front elevational view, partly in section, of a textile yarn having coated thereon from about 2% to about 10% by weight of a copolymer such as those described hereinabove.

We claim:

1. A process of warp sizing textile yarns which comprises applying an aqueous solution of pH between about 5 and about 9 of a copolymer having recurring nitrile and —COOX groups in a ratio between 1:0.30 and 1:0.75 attached to a linear carbon chain of substantial length wherein X is of the group consisting of hydrogen, sodium, potassium and the ammonium radical, which copolymer has a viscosity between about 5 and about 200 centipoises when determined at a concentration of 5 percent by weight in water at 140 degrees Fahrenheit, in sufficient quantity to deposit on a textile yarn between about 2 and about 10 percent of copolymer, based on the weight of the untreated dry yarn, and drying the treated yarn to produce a readily-scourable dry protective coating of the copolymer on the yarn.

2. A process according to claim 1 in which said ratio is between 1:0.40 and 1:0.60.

3. A process according to claim 1 in which a major proportion of the nitrile groups is derived from acrylonitrile, a major proportion of the —COOX groups is derived from acrylic acid and X predominantly represents the ammonium radical.

4. A process according to claim 1 in which a major proportion of the nitrile groups is derived from acrylonitrile, a major proportion of the —COOX groups is derived from acrylic acid and X predominantly represents sodium.

5. A process according to claim 1 in which a major proportion of the nitrile groups is derived from acrylonitrile and a major proportion of the —COOX groups is derived from a compound of the group consisting of maleic acid and maleic anhydride.

trile and a major proportion of the —COOX groups is derived from a compound of the group consisting of maleic acid and maleic anhydride.

6. An article which comprises a textile yarn coated with a readily-scourable dry film of a copolymer having recurring nitrile and —COOX groups in a ratio between 1:0.30 and 1:0.75 attached to a linear carbon chain of substantial length wherein X is of the group consisting of hydrogen, sodium, potassium and the ammonium radical, which film is between about 2 and about 10 percent of the weight of the dry untreated yarn.

7. An article according to claim 6 in which said ratio is between 1:0.40 and 1:0.60.

8. An article according to claim 6 in which a major proportion of the nitrile groups is derived from acrylonitrile, a major proportion of the —COOX groups is derived from acrylic acid and X predominantly represents the ammonium radical.

9. An article according to claim 6 in which a major proportion of the nitrile groups is derived from acrylonitrile, a major proportion of the —COOX groups is derived from acrylic acid and X predominantly represents sodium.

10. An article according to claim 6 in which a major proportion of the nitrile groups is derived from acrylonitrile and a major proportion of the —COOX groups is derived from a compound of the group consisting of maleic acid and maleic anhydride.

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