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SIZED YARN AND PROCESS OF SIZING

Elmer H. Rossin, Melrose, and Milton J. Scott,
Lexington, Mass., assignors to Monsanto Chem-
ical Company, St. Louis, Mo., a corporation of
Delaware

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The present invention relates to improvements in the art of sizing nylon yarns, particularly polyhexamethylene-adipamide warp yarns, and to novel, sized nylon yarns.

It has been proposed heretofore to size nylon knitting yarns with water solutions of polyvinyl alcohol or mixtures thereof with boric acid or borax. It has also been proposed heretofore to size nylon yarns with alkaline solutions of salts of copolymers of styrene and maleic anhydride in conjunction with agents which render the copolymers insoluble. However, these prior methods have not been entirely satisfactory for various reasons. Thus, the polyvinyl alcohols per se do not give a satisfactory size and mixtures thereof with boric acid and borax soften at high relative humidities and have other disadvantages and have not found acceptance in the trade for the sizing of nylon warp yarns. The alkaline solutions of salts of copolymers of styrene and maleic anhydride which are mentioned above are not considered to be satisfactory sizes for nylon warp yarns, particularly when they are used alone. On the other hand when they are used with insolubilizing agents they cannot be removed from the yarns by normal scouring agents and this is undesirable to the trade for many sizing applications.

It is one object of this invention to provide a relatively inexpensive and suitable sizing composition for sizing nylon yarns, and particularly nylon warp yarns.

It is a further object of this invention to provide an efficient method of sizing nylon yarns, particularly polyhexamethylene-adipamide warp yarns, with a sizing agent which is economical to use, affords excellent protection to such yarns during the weaving operation and is readily removed from the yarns after weaving by a simple scouring operation.

Still further objects and advantages of this invention will appear in the following description and the appended claims.

The methods of this invention are carried out, in general, by treating nylon warp yarns with an aqueous solution having a pH between about 2 and 5 of a water-soluble copolymer of substantially equimolecular proportions of vinyl acetate and maleic anhydride or maleic acid or an alkyl half ester of maleic acid, in which the alkyl group contains from 1 to 4 carbon atoms, or a copolymer of substantially equimolecular proportions of vinyl acetate and mixtures of such anhydride, acid and half ester, and thereafter drying the yarns preparatory to weaving the yarns into a fabric.

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The term "nylon" as used herein is intended to include water-insoluble fiber-forming linear polyamides, particularly the water-insoluble fiber-forming linear polyamides prepared by condensing an aliphatic diamine such as hexamethylene diamine with an aliphatic polybasic acid such as adipic acid or sebacic acid, such as the polyamides described in United States Patents No. 2,071,250, No. 2,130,532 and No. 2,130,948. Of the foregoing linear polyamides, it is preferred to size the water-insoluble, polyhexamethylene-adipamide warp yarns, since they are commercially available and are especially amenable to sizing by the methods of this invention.

It is essential in the practice of this invention that the sizing solution have a pH of at least 2, since solutions having a pH appreciably below 2 are not only harmful to nylon yarns by virtue of hydrolysis, but also are too viscous at a sufficient solids concentration to properly size the yarns. On the other hand, if the pH of the solution is appreciably in excess of 5 the copolymer lacks adhesion to the nylon warp yarns and does not size the yarn satisfactorily.

The aqueous size solutions having a pH of 2 to 3 generally, depending on the molecular weight of the copolymer, can only be obtained with a copolymer of substantially equimolecular proportions of vinyl acetate and maleic anhydride or a copolymer of equimolecular quantities of vinyl acetate and maleic acid or a copolymer of vinyl acetate with an equimolecular quantity of a mixture of maleic components consisting of maleic anhydride and maleic acid or a mixture of such anhydride or acid or both with a minor proportion of methyl acid maleate. Since best results are obtained with a solution of such pH, it is preferred to employ the copolymers described immediately above. Of these copolymers, the copolymer of equimolecular quantities of vinyl acetate and maleic anhydride are preferred.

The aqueous solutions having a pH between about 3 and 5 are generally prepared by dissolving copolymers of vinyl acetate and an equimolecular quantity of an alkyl half ester of maleic acid or mixtures of such half esters with maleic anhydride and/or maleic acid in water with the aid of sufficient alkali, which is considerably less than the stoichiometrical proportion required to neutralize the copolymer, until the copolymer dissolves within the desired pH value of 3 to 5. In general an aqueous solution having a pH of about 3 is readily obtained with a copolymer of 50 mol per cent of vinyl acetate, 40 mol per cent of methyl acid maleate and 10 mol per cent of

maleic anhydride, whereas a copolymer of 50 mol per cent of vinyl acetate, 40 mol per cent of secondary butyl half ester of maleic acid and 10 mol per cent of maleic anhydride will usually only dissolve in water at a pH between about 4.5 and 5. It is to be understood, of course, that these examples are dependent on the molecular weight of the copolymer, since high molecular weight copolymers will generally require a higher pH for dissolution in water, whereas low molecular weight copolymers will dissolve in water at lower pH values than those illustrated above. It is also to be understood that aqueous solutions having a pH between about 3 and 5 are readily prepared by adding small amounts of alkali to the water solutions of copolymers of vinyl acetate and maleic anhydride or maleic acid or mixtures of such anhydride and acid previously described herein.

It is necessary, in order to obtain satisfactory results, to use an aqueous solution containing from 2 to 15% by weight, of the copolymers hereinbefore described. Such solutions are suitably prepared by dissolving the copolymer in water using small amounts of alkali, if required, but not sufficient to raise the pH of the solution above 5. The copolymer should also have a molecular weight such that it can be dissolved in water at a pH between about 2 and 5.

The size solution may contain, in addition, to the copolymer, small amounts, say 0.01 to 5% of sizing adjuncts such as, humectants, oils, wetting agents and the like. As examples of humectants may be mentioned glycerine, ethylene glycol, sorbitol, propylene glycol, polyethylene glycols, polyglycerols, polypropylene oxides and the like. Oils which may be used include the sulfonated animal, mineral and vegetable oils or mixtures thereof, water-emulsifiable mixtures of such oils with animal oils, mineral oils, vegetable oils, Twitchell oil and the like. As examples of wetting agents may be mentioned acid-stable anionic wetting agents such as alkyl substituted benzene sodium sulfonates, in which the alkyl group contains from about 10 to 20 carbon atoms, alkali metal or ammonium monoalkyl sulfosuccinates, in which the alkyl group contains from about 10 to 20 carbon atoms, and the like; and acid-stable non-ionic wetting agents such as the surface active condensation products of ethylene oxide with an alkylated phenol having from 8 to 20 carbon atoms in the alkyl group or an alkyl mercaptan having from 8 to 20 carbon atoms.

For best results the size solution should be used or applied to the nylon yarn at a temperature between about 100 and 200° F. At these temperatures the size solution is less viscous and penetrates into the yarn more readily and uniformly.

The size solution is supplied to the yarn in an amount sufficient to apply between about 0.5 and 5% by weight of the copolymer based on the dry weight of the nylon yarn. This may be accomplished in various ways, for example, by passing the yarns through the size solution and beneath the surface thereof or by spraying the yarns with the size solution, and thereafter passing the yarns between squeeze rolls to remove excess solution and to deposit the required amount of the copolymer. The size solution may also be applied in other ways, as, for example, by dipping the yarns in the solution of the copolymer. In any event the solution should contain between 2 and 15% by weight of the copolymer, and if squeeze rolls are used the amount of pressure

exerted on the squeeze rolls should be adjusted to remove sufficient excess solution to deposit the required amount of copolymer within the range of 0.5 to 5%, based on the weight of the dry yarn.

The treated nylon yarns may be dried in various ways. Thus, they may be air-dried at normal room temperatures, that is, between about 65 and 85° F. However, it is preferred to dry the treated yarns at elevated temperatures of about 140 to 250° F. This may be accomplished by passing the treated yarns through an oven in which the circulating air is at a temperature of 140 to 250° F. or the treated yarns may be passed over one or more drying cans, which are heated at a temperature of 140 to 250° F., until the yarns are dry or contain less than 10% moisture.

The sized yarns are now ready for the weaving operation and may be woven in a loom at a relative humidity between about 40 and 80%. Any suitable yarn may be used as the filling in the weaving operation. The size adheres to the nylon yarns during the weaving operation without splitting or dusting off and protects the yarns from the mechanically moving parts of a loom. This excellent adhesion of the size to the nylon yarns is particularly unexpected in view of the fact that alkali metal salts of the same copolymers lack adhesion to nylon yarns during the weaving operation, and especially when it is considered that nylon yarns undergo considerable stretching and contraction in the loom and thus subject the size to considerable stretching and contraction. The copolymer sizes disclosed herein are also sufficiently hard so that they dry on drying cans without sticking to the cans.

The size, which consists essentially of the copolymers hereinbefore described, is readily removed from the warp yarns in the woven fabric by a simple scouring or soaping in a mild soap solution. This means that the fabric can be treated with any suitable finishing agent to produce the desired finish on the fabric.

A further understanding of the sizing process and sized yarns of this invention will be obtained from the following specific examples which are intended to illustrate the present invention, but not to limit the scope thereof, parts and percentages being by weight unless otherwise specified.

Example I

An aqueous solution having a pH of about 2.0 was first prepared by dissolving 8 parts of a copolymer of equimolecular proportions of vinyl acetate and maleic anhydride in 92 parts of water, after which it was heated to a temperature of 140° F. The molecular weight of the copolymer was such that a 2% solution thereof in cyclohexanone has a viscosity of 5 centipoises. Nylon (polyhexamethylene - adipamide) warp yarns having 70 filaments, a denier of 34 and 7 Z twist were passed through the solution of the copolymer at a rate of 10 to 20 yards per minute and then passed between squeeze rolls which were set to exert a pressure of 10 to 20 pounds per linear inch. The wet yarns were then passed over five drying cans in tandem arrangement, which cans were heated to temperatures of 180° F., 200° F., 200° F., 200° F., and 160° F., respectively. After leaving the drying cans the sized yarns were substantially dry. No sticking of the copolymer size on the drying cans was noted.

The above sizing process was carried out without stretching the yarns.

The nylon yarns were thus covered with about 4% by weight, based on the dry yarn, of a con-

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tinuous, flexible and tough coating which did not dust or shed to any appreciable extent when the yarns were stretched and allowed to contract. The weaving efficiency of the sized nylon yarns was excellent at a relative humidity of 60%. The fabrics prepared from such sized yarns were readily desized by a simple scouring with warm water.

Example II

An aqueous solution was first prepared by dissolving 8 parts of a copolymer of 50 mol per cent of vinyl acetate, 40 mol per cent of methyl acid maleate and 10 mol per cent of maleic anhydride in 92 parts of water using only sufficient sodium hydroxide to dissolve the copolymer. The resulting solution, which had a pH of 3, was then heated to a temperature of 140–150° F. Nylon (polyhexamethylene-adipamide) warp yarns containing 70 filaments, having a denier of 34 and 7 Z twist were passed through the solution at a rate of 10 to 20 yards per minute and then passed between squeeze rolls which were adjusted to exert a pressure of 10 to 20 pounds per linear inch. The wet yarns were then passed over five drying cans arranged in series, which cans were heated to temperatures of 180° F., 200° F., 200° F., 200° F., and 160° F., respectively. After leaving the drying cans the yarns were substantially dry. The drying cans were observed after a considerable number of sizing operations as described above and no sticking of the copolymer size on the drying cans was noted.

The above sizing process was carried out without stretching the yarns.

The nylon yarns which were sized as described above were covered with about 4% by weight, based on the dry yarns, of a continuous, flexible and tough coating which did not dust or shed to any appreciable extent when the yarns were stretched and allowed to contract a considerable number of times. The weaving efficiency of the sized nylon yarns was excellent at a relative humidity of 60%.

The fabrics prepared from the sized yarns were readily desized by a simple scouring with warm water.

Example III

Nylon (polyhexamethylene-adipamide) warp yarns were sized in accordance with the procedure described in Example II with the exception that the sizing solution was prepared by dissolving 8 parts of a copolymer of 50 mol per cent of vinyl acetate, 40 mol per cent of secondary butyl half ester of maleic acid and 10 mol per cent of maleic anhydride using an amount of sodium hydroxide sufficient to form a solution having a pH of about 4.5. The sized yarns thus produced had substantially the same characteristics and weaving efficiency as the sized yarns produced in accordance with the procedure of Example II. Moreover, the size on the warp yarns was readily removed by a simple scouring with warm water.

The copolymers described herein and in the foregoing examples may be prepared in various ways. For example, they are suitably prepared by heating a mass consisting essentially of vinyl acetate and the maleic component in equimolecular proportions in the presence of a peroxide catalyst such as benzoyl peroxide at temperatures between about 30 and 125° C., the temperature being maintained between 60 and 125° C. by cooling if necessary. They may also be prepared by heating the vinyl acetate and the maleic component in a liquid which is a solvent for the

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monomers but a non-solvent for the copolymer, for example, a liquid such as toluene, in the presence of a peroxide catalyst such as benzoyl peroxide.

It is essential in preparing such copolymers, however, that the vinyl acetate is used in amounts of 50 mol per cent and that the maleic components total substantially 50 mol per cent in the copolymer.

Various modifications may be made in the methods and sized yarns described herein as will be apparent to those skilled in the art to which this invention appertains without departing from the spirit an intent of this invention. Accordingly, it is to be understood that it is not intended to limit this invention except by the scope of the appended claims.

What is claimed is:

1. A method of sizing water-insoluble nylon warp yarns to prepare them for weaving which comprises treating said yarns with an aqueous solution having a pH between 2 and 5 and comprising from about 2 to 15% by weight of a water-soluble copolymer of substantially 50 mol per cent of vinyl acetate and substantially 50 mol per cent of maleic components selected from the group consisting of maleic anhydride, maleic acid, alkyl half esters of maleic acid, in which the alkyl group contains from 1 to 4 carbon atoms, and mixtures thereof, said solution being supplied in an amount sufficient to deposit from about 0.5 to 5% by weight, based on the dry yarns, of said copolymer, and then drying said yarns.

2. A method of sizing water-insoluble nylon warp yarns to prepare them for weaving which comprises treating said yarns with an aqueous solution having a pH between 2 and 5 and comprising from about 2 to 15% by weight of a water-soluble copolymer of 50 mol per cent of vinyl acetate and 50 mol per cent of maleic anhydride, said solution being supplied in an amount sufficient to deposit from about 0.5 to 5% of said copolymer, based on the dry yarns, and then drying said yarns.

3. A method according to claim 2, but further characterized in that the nylon warp yarns are prepared from polyhexamethylene-adipamide.

4. A method of sizing water-insoluble nylon warp yarns to prepare them for weaving which comprises treating said yarns with an aqueous solution having a pH between 2 and 5 and comprising from about 2 to 15% by weight of a water-soluble copolymer of 50 mol per cent of vinyl acetate and 50 mol per cent of maleic anhydride together with methyl acid maleate, said solution being supplied in an amount sufficient to deposit from about 0.5 to 5% by weight, based on the dry yarns, of said copolymer, and then drying said yarns.

5. A method according to claim 4, but further characterized in that the nylon warp yarns are prepared from polyhexamethylene-adipamide.

6. A method of sizing water-insoluble nylon warp yarns to prepare them for weaving which comprises treating said yarns with an aqueous solution having a pH between 2 and 5 and comprising from about 2 to 15% by weight of a water-soluble copolymer of 50 mol per cent of vinyl acetate and 50 mol per cent of an alkyl half ester of maleic acid, in which the alkyl group contains from 1 to 4 carbon atoms, said solution being supplied in an amount sufficient to deposit from about 0.5 to 5% by weight of said

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copolymer, based on the dry yarns, and then drying said yarns.

7. A method of sizing water-insoluble polyhexamethylenedipamide warp yarns to prepare them for weaving which comprises treating said yarns with an aqueous solution which has a pH between 2 and 5, a temperature of about 100 to 200° F. and comprises from about 2 to 15% by weight of a water-soluble copolymer of equimolecular proportions of vinyl acetate and maleic anhydride, squeezing the yarns sufficiently to deposit about 0.5 to 5% by weight of said copolymer, based on the dry yarns, from said solution, and thereafter drying said yarns at temperatures between about 140 and 250° F.

8. A nylon warp yarn sized with a continuous, flexible and tough film of a water-soluble copolymer of substantially 50 mol per cent of vinyl acetate and substantially 50 mol per cent of vinyl acetate and substantially 50 mol per cent of maleic components selected from the group consisting of maleic anhydride, maleic acid, alkyl half esters of maleic acid, in which the alkyl group contains 1 to 4 carbon atoms, and mixtures thereof, said film comprising from about 0.5 to 5% by weight of said copolymer based on the dry yarn.

9. A warp yarn according to claim 8, but further characterized in that the yarn is composed of polyhexamethylenedipamide.

10. A method of sizing water-insoluble nylon warp yarns to prepare them for weaving which comprises treating said yarns with an aqueous

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solution having a pH between 2 and 5 and comprising from 0.01 to 5% of glycerine and from about 2 to 15% by weight of a water-soluble copolymer of substantially 50 mol per cent of vinyl acetate and substantially 50 mol per cent of maleic anhydride together with methyl acid maleate, said solution being supplied in an amount sufficient to deposit from about 0.5 to 5% by weight, based on the dry yarns, of said copolymer and then drying said yarns.

11. A method of sizing water-insoluble nylon warp yarns to prepare them for weaving which comprises treating said yarns with an aqueous solution having a pH between 2 and 5 and comprising from 0.01 to 5% of polyethylene glycol and from about 2 to 15% by weight of a water-soluble copolymer of substantially 50 mol per cent of vinyl acetate and substantially 50 mol per cent of maleic anhydride together with methyl acid maleate, said solution being supplied in an amount sufficient to deposit from about 0.5 to 5% by weight, based on the dry yarns, of said copolymer and then drying said yarns.

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