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SIZED SYNTHETIC LINEAR POLYAMIDE YARN

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10 Claims. (Cl. 117—139)

The present invention relates to the sizing treatment of synthetic linear polyamide yarns with an anti-snagging composition so that the said yarns may be flat-knit into a sheer, full-fashioned hosiery fabric.

For a long time silk has dominated the sheer, full-fashioned hosiery field. Relatively recently, a class of synthetic yarns, prepared from a class of materials known as synthetic linear polyamides, has come to be used for sheer, full-fashioned hosiery. The preparation of this type of material and the production of yarn from the material are described in United Ptates Patents Nos. 2,071,250, 2,130,523 and 2,130,948. Generally speaking, these polyamides comprise the reaction product of a polyamide-forming composition in which the molecules are bifunctional and contain two amide-forming groups, each of which is complementary to an amide-forming group in other molecules in said composition. Thus, the polyamides can be prepared by polymerizing a monoaminomonocarboxylic acid or by reacting a diamine with a dibasic carboxylic acid in substantially equimolecular amounts, it being understood that reference herein to amino acids, diamines, and dibasic acids includes also the equivalent amide-forming derivatives thereof.

It will be observed with respect to the structure of the above-said synthetic linear polyamides, that they contain amide groups



where X is oxygen or sulphur and where R is hydrogen or a monovalent hydrocarbon radical) as an integral part of the main chain of atoms in the polymer. It will also be observed that in these polyamides the average number of carbon atoms in the segments of the chain separating the amide groups is at least two. Accordingly, throughout the present specification and claims, the expression, "synthetic linear polyamide," is to be understood as applying to the polyamides described in the aforesaid patents and coming within the limitations set forth in this paragraph.

The preparation of sheer, knit ladies' full-fashioned stockings from this type of yarn is described in United States Patent No. 2,157,116. The knitting of ladies' sheer stockings from yarns of synthetic linear polyamides created new and serious problems in the satisfactory sizing of such yarns. Without any size these yarns, when knitted into sheer, full-fashioned stockings and subsequently handled, developed an undesirably large proportion of pulled threads. For years, the art has been confronted with a similar problem in the knitting of sheer stockings from ingrain silk. The knitting of sheer stockings from ingrain silk produces stockings of which a very large proportion have pulled threads; and because this problem was never solved, ingrain silk stockings are seldom made. There has been no sizing problem for silk in the gum because of the presence of a natural protecting coat of sericin over the silk filaments. The application of sizes to knitting yarns is a relatively new and undeveloped art.

When the word "sizing" is used, it does not refer to the application of oils, finishes, dressings, and the like, but is restricted to the narrower meaning of the word; namely, the application of an adhesive coating to protect the filaments in the knitting operation and in the course of handling the fabric subsequent to the knitting operation.

Sizes have been developed for the warp sizing of artificial silk yarns; e. g., viscose rayon, cellulose acetate, etc. It is also well-known that artificial silks require no size for tricot knitting or circular knitting. Hence, the problem of sizing these yarns has been concerned almost entirely with the preparation of the yarns for weaving. It is, therefore, evident that prior to the introduction of the synthetic linear polyamide yarns into the field of sheer hosiery knitting, there was no problem of sizing knitting yarns. It is equally true that prior to that time, no sizing composition had been developed which was satisfactory for use in knitting sheer hosiery when applied to synthetic linear polyamide yarns.

The requirements for a good warp size for weaving yarns are much less rigorous than the requirements for a good size for yarns to be used in the knitting of sheer, full-fashioned hosiery. Furthermore, the requirements for a satisfactory size for use on yarns composed of synthetic linear polyamides are much more critical than for sizes to be used on previously known artificial filaments or natural fibers. Therefore, a satisfactory size for synthetic linear polyamide yarns for knitting full-fashioned hosiery must possess all of the following characteristics:

1. The size must protect the fabric from snags and pulled threads. A full-fashioned stocking fabric is sheer and delicate. It is subjected to a considerable amount of handling after the knitting operation; for it must be looped, seamed, stitched, inspected, and pre-set before it is dyed. The rough hands of operators cause entirely too

many pulled threads if the size does not give good protection.

2. The size must adhere well and bind the filaments together during twisting, coning and other textile operations and perform well during and following the knitting operation. The action of the knitting needles and sinkers on the sized yarn is so drastic as to cause flaking off of the size with resultant loss of protection if the size does not adhere extremely well. Since synthetic linear polyamide filaments are spun substantially round and smooth and synthetic linear polyamides are markedly insensitive to water, the problem of size adherence is much greater than it is for relatively water-sensitive yarns such as viscose rayon, cotton, etc.

3. The sized yarn must run well on the knitting machine; that is, after passing through the dip trough, it must not stick to the guides and snappers following a shutdown of the machine and size must not accumulate on the needles and sinkers. Sticking on the guides and snappers causes press-offs when the machine is started up again. Accumulation on the needles and sinkers eventually causes holes and runs in the fabric if the accumulation becomes severe.

4. The size must soften sufficiently on passing through the dip trough to enable the formation of regular stitches of uniform size and to cement the loops together when the fabric dries. If the size softens insufficiently, poor stitch formation and poor snag resistance result. On the other hand, if it softens too much, the size accumulates on the needles and sinkers to the point where knitting of hose without holes is impossible even though stitch formation is good and snag resistance is good. Thus a commercial size for full-fashioned hosiery knitting yarns must have an extremely carefully balanced set of properties if good running properties, good stitch formation and good snag resistance are to be developed by the same composition.

5. The size must minimize edge rolling of the knitted fabric to facilitate subsequent seaming. If the full-fashioned stocking fabric rolls at the edges as it comes off the knitting machine, the fabric is difficult to seam and the cost of production increases; also the seams are likely to be bulky and crooked.

6. The size must be readily removable in an aqueous boil-off bath before dyeing. It is generally desirable, though not always necessary, to remove the size before dyeing the fabric. It is much more economical to remove the size with water than with some other solvent.

7. The size should be free from any tendency to cause corrosion or abrasion of the various parts of the knitting machines which the yarn contacts.

The problem of developing a size which will fulfill these rigorous requirements is relatively new in the field of synthetic yarn production. Many different sizing compositions have been developed for use on rayon yarns, and many of these sizes have been tried with synthetic linear polyamide yarns; but all of the many sizing compositions tried have been found to lack one or more of the above requirements to such a great extent as to render impossible their use in sizing synthetic linear polyamide yarns for the knitting of full-fashioned hosiery.

It is, therefore, an object of the present invention to furnish an improved type of textile sizing composition particularly suitable for sizing synthetic linear polyamide knitting yarns to be used in the production of sheer, full-fashioned hosiery.

It is a further object of the present invention to furnish an improved method of sizing textile yarns, particularly synthetic linear polyamide knitting yarns to be used in the production of sheer, full-fashioned hosiery.

A specific object of the invention is to provide a sized, synthetic linear polyamide yarn capable of being successfully knitted into full-fashioned hosiery.

Other objects of the invention will become apparent hereinafter.

It has now been found that excellent sizing compositions, which are suitable for the sizing of synthetic linear polyamide yarns to be used in knitting sheer, full-fashioned hosiery, can be prepared from compostions containing film-forming proteins which are, per se, substantially water-insoluble; i. e., are soluble in water to an extent less than about 5% at 25° C. in the absence of a solubilizing agent.

These new sizing compositions adhere well to the smooth, round, polyamide filaments, bind the filaments together well, impart to the yarn good running properties on full-fashioned knitting machines, protect the full-fashioned stocking fabric well from snags and runs, prevent serious edge rolling of the full-fashioned stocking fabric, and are readily removed by hot water containing small amounts of alkaline agents. By the term "film-forming" is meant the ability to form a substantially coherent film or coating upon evaporation of a thin layer of a solution of the protein in question.

The present invention includes the use of pulasticizing agents for the proteins in the sizing composition. Hardening agents for the proteins which will reder the protein less soluble on application to the yarn, i. e., coating followed by drying, but which will not precipitate the protein from its solution are also contemplated in accordance with the present invention. Typical hardening agents are formaldehyde, tannic acid, aluminum salts, and various other heavy metal salts.

The following examples are given to illustrate preferred sizing compositions and preferred methods of applying the same. The details set forth in the examples are not, however, to be considered as limitative of the invention. The percentages set forth in the examples designate percentages by weight.

Example I

The following example illustrates the preparation of snag-resistant, flat-knit hosiery fabric prepared from a synthetic linear polyamide, utilizing a protein of the salt- and alkali-soluble, or globulin, class and a plasticizing agent as the sizing agent.

A 30-denier, 10-filament, 30-turn Z twist, oriented polyhexamethylene adipamide yarn is sized on a "bobbin-to-bobbin" sizing machine, in which the yarn is taken from a spool through a pre-tension device over a roll dipping in the sizing solution and wound up on a bobbin, with a solution comprising 10 parts of protein obtained from the residues of extracting the oil from soya beans, 1.5 parts of sodium carbonate, 81.5 parts of water, 2 parts of glycerol, and 5 parts of triethanolamine oleate as plasticizing agents. The yarn is passed over the roll at a speed of about 1000 feet per minute. The roll rotates with a circumferential roll speed of 6.3 feet per minute. After drying

and coning, the resulting sized yarn is knit in a wet condition in a Wildman 45-gauge, single-unit, full-fashioned hosiery knitting machine. The knit fabric obtained in this way has an excellent resistance to snagging and good edge rolling properties, i. e., is easily unrolled to a flat fabric.

Example II

The following example typifies the preparation of a flat-knit, full-fashioned stocking fabric from a yarn composed of polyhexamethylene adipamide sized with the phosphoprotein casein.

A sizing solution comprising 5 parts of lactic acid casein, 7.5 parts of commercial 29% ammonium hydroxide solution, 5 parts of ethanolamine as plasticizer, and 100 parts of water is applied to a skein of oriented polyhexamethylene adipamide yarn by immersing in the solution for 5 minutes. The excess solution is removed from the yarn by whirling in a centrifuge for 2 minutes, and the yarn is finally dried at room temperature. After spooling and coning in the known manner, the yarn is flat knit to a fabric which possesses resistance to snagging and good edge rolling properties.

Example III

The following example typifies the production of snag-resistant, flat-knit fabrics from yarns composed of polyhexamethylene adipamide and sized with the typical prolamine zein.

A 30-filament, 10-denier, 30-turn Z twist, oriented polyhexamethylene adipamide yarn is sized on the "bobbin-to-bobbin" type sizing machine of Example I at a yarn speed of 1000 feet per minute and a circumferential roll speed of 4.7 feet per minute. The sizing composition comprises 10 parts of zein, 10 parts of triethanolamine oleate, 2 parts of ethanol formamide, and 78 parts of water. The sized yarn is coned and knit as in the examples above. The resulting flat-knit fabric is resistant to snagging and shows good edge rolling characteristics.

Example IV

The following example illustrates the preparation of a snag-resistant, flat-knit fabric prepared from yarns composed of polyhexamethylene adipamide sized with casein which has been solubilized by heating with an aqueous solution of ethylene imine.

A skein of oriented polyhexamethylene adipamide yarn is dipped in a solution prepared by refluxing 40 parts of casein and 40 parts of ethylene imine in 350 parts of water for 3 hours and diluting with 530 parts of water. The sized yarn is whirled for 2 minutes in a centrifuge and then allowed to dry in the air. After spooling and coning in the known manner, the treated yarn is knit as in the preceding examples to form a flat fabric which possesses snag resistance and good edge rolling qualities.

Example V

The following example illustrates the preparation of flat-knit hosiery fabric from a synthetic linear polyamide yarn sized with a modified casein prepared by milling casein with a weakly alkaline agent.

Commercial hydrochloric acid casein to the extent of 100 parts is milled for 20 minutes with 7 parts of sodium acetate and 15 parts of water until the mixture is homogeneous and plastic. After drying, the resulting product is dissolved in 1095.2 parts of water and 30 parts of isopropanol glycolamide and 2.8 parts of formaldehyde are added. Oriented polyhexamethylene adipamide yarn is sized with this solution on the "bobbin-to-bobbin" type sizing machine of Example I, using a yarn speed of 1000 feet per minute over the roll, which revolves at a circumferential speed of 12.1 feet per minute. The yarn is coned and flat knit to form a hosiery fabric in the known manner. The resulting fabric shows a high degree of snag resistance and possesses good edge rolling properties.

As examples of the various classes of synthetic linear polyamides from which fibers suitable for the purposes of this invention may be prepared, we may cite the polyamides derived from diamines and dibasic acids or their amide-forming derivatives; those derived from polyamide-forming amino acids or their amide-forming derivatives; and interpolyamides prepared from diamines, dibasic acids, and polyamide-forming amino acids. As further examples of polyamides of the diamine-dibasic acid type may be mentioned polytetramethylene sebacamide, polypentamethylene adipamide, polymentamethylene sebacamide, polyhexamethylene sebacamide, polyoctamethylene adipamide, polydecamethylene adipamide, poly-p-xylylene sebacamide, poly-m-phenylene sebacamide, polyhexamethylene hexahydroterephthalamide, polyhexamethylene isophthalamide, poly-3-methyl hexamethylene-2-methyl adipamide, polyhexamethylene-4-keto-pimelamide, the polyamide prepared from hexamethylene diamine and sulfonedibutyric acid, and the polyamide prepared from equimolecular quantities of hexamethylene diamine, decamethylenediamine, adipic acid, and sebacic acid.

Polyamides of the amino acid type, suitable for the purposes of this invention, include polymerized 6-aminocaproic acid, polymerized 9-aminononanoic acid, polymerized 12-aminostearic acid, and the interpolyamide derived from equimolecular quantities of 6-aminocaproic acid and 10-aminodecanoic acid.

Examples of interpolyamides prepared from diamines, dibasic acids, and amide-forming amino acids, include the polymers derived from equimolecular quantities of hexamethylene diamine, adipic acid, and 12-aminostearic acid, and the polyamide derived from hexamethylene diamine, sebacic acid, and 6-aminocaproic acid in which the molecular quantities are in the ratio of 3:3:1.

As examples of the various classes of proteins which may be employed, we may cite the globulins or proteins which are insoluble in water but soluble in dilute salt solutions; the prolamines, or alcohol-soluble proteins; the glutelins, or alkali-soluble proteins; and the phosphoproteins.

Serum globulin from blood, glycinin from soya beans and edestin from hemp seed are representative globulins. Examples of prolamins are gliadin, zein from corn, and hordein, obtained from barley. Oryzenin, obtained from rice, and the maize glutelin of corn are typical glutelins. Examples of phosphoproteins are casein from milk, and vitellin from egg yolk.

Denatured proteins; i. e., those whose solubility is diminished in many of the solvents which ordinarily dissolve them, may also be successfully employed in the preferred procedures, although the number of suitable solvents is lessened and low concentrations must, in many cases, be employed. Edestan, i. e., denatured edestin, is a typical example of a denatured protein.

It is within the scope of this invention to include natural and synthetic resins such as rosin,

vinyl polymers and interpolymers, salicylic acid-formaldehyde resin, in the protein sizing composition.

As mentioned above, it is frequently desirable to add plasticizing agents to the film-forming protein compositions in order to increase their adhesion to the polyamides and to render the sizing coating more flexible. The plasticizing agents may be of the water-soluble or water-insoluble type. Examples of suitable water-soluble plasticizers include glycerol, triethylene glycol, polymerized ethylene oxide, ethanol formamide, triethanolamine, and triethanolamine salts. Typical water-insoluble plasticizers, which may be used in the practice of this invention, include di-(beta-methoxyethyl) adipate, mixed N-ethyl toluenesulfonamides, amyl benzene-sulfonamide, and dibutyl phthalate. The water-soluble plasticizers are preferred in aqueous sizing solutions, while water-insoluble plasticizers may be used when solvents other than water are employed.

In some instances it has been found desirable to use hardening agents for the proteins in the sizing compositions. The hardening agents may also be applied to the yarn either before or after the application of the protein sizing composition. As above set forth, the hardening agent for the protein should be one which renders the protein less soluble, which does not precipitate the protein from its solution, but which exerts its effect upon evaporation of part or all of the solvent. It is possible to obtain a substantially water-insoluble coating of size on yarn even with the use of a water-soluble protein providing the protein is used in conjunction with a hardening agent. Formaldehyde is suitable for use with blood albumin while basic aluminum acetate and ammonium tannate are useful with glue and gelatine compositions.

With respect to the degree of hardening, or amount of hardening agent to be used with the protein composition, it is preferred that this be sufficient to give a film which will not dissolve freely in water but which on wetting with water will become definitely tacky, i. e., the yarn will have a slightly sticky feel to the fingers within a period of five minutes. The hardening should preferably be insufficient to give a film which does not become at least faintly tacky on wetting.

Various coning oils may be applied to the yarns sized according to this invention. Examples of such compositions include olive, teaseed, and mineral oils, sulfonated oils, blown castor and linseed oils, and butyl palmitate. Modifying agents such as triethanolamine salts, alkyl or aryl phosphates, dodecylamine salts, and antioxidants such as o-phenyl phenol may also be used.

Lubricants may also be added to the sizing composition or may be included in the wetting trough through which the yarn passes just prior to knitting. Examples of agents of this type include triethanolamine oleate, dodecylamine acetate, glycerol monoricinoleate, and diglycol stearate.

The protein sizing composition is preferably applied to the yarn in the form of an aqueous solution to which solubilizing agents such as dilute alkalies or added acids are added, if necessary. However, nonaqueous solvents may be used within the scope of this invention, e. g., a solution of zein in alcohol.

In general, the protein sizing composition is best applied in the form of its solution, and preferably in the form of its aqueous solution for reasons of economy. Thus, for example, casein and soya bean protein may be rendered soluble in water by milling with small amounts of water and alkalies, salts, metallic oxides or other agents, of the type disclosed in U. S. Patents Nos. 2,005,730 and 2,103,153. The protein may be dissolved in dilute aqueous sodium hydroxide or ammonium hydroxide or by heating with an aqueous solution of ethylene imine. Zein is suitably solubilized by means of a dilute aqueous solution of triethanolamine oleate.

Solutions containing from 4% to 20% protein are suitable for use as sizing compositions in accordance with the present invention; preferably, however, the solutions will contain from 5% to 15% of the protein. The sizing composition may be applied to the yarn in any desired manner, for example, by means of a "bobbin-to-bobbin" type machine in which the yarn passes over a rotating roll dipping in a solution of the sizing composition. In this type of machine the yarn is drawn from the end of a stationary bobbin, passed over a size applying roll and wound with a suitable traverse motion on a take-up bobbin. The speed at which the size applying roll rotates is determined by the rate at which the yarn passes over the said roll, and will usually vary between 0.1% and 1.0% of the speed of the yarn. Thus, for example, at a yarn speed of 1,000 feet per minute and a roll 3 inches in diameter, a suitable range of roll speeds lies between 2 and 10 R. P. M.

Alternatively, the sizing composition may be applied to the yarn by passing the yarn in a continuous manner through a solution of the composition, or by dipping loosely wound skeins into the solution. A solution of the sizing composition may be applied to a moving yarn by spraying or the like.

The conditions of applying the sizing composition are preferably regulated so that the quantity of solid sizing composition deposited on the yarn will comprise from 1% to 20% of the weight of the dry yarn. The amount of sizing composition on the yarn may be simply determined by boiling a weighed sample of the sized yarn in a dilute alkaline solution, or other material which is inert to the yarn but will dissolve the size, and reweighing the yarn after drying.

The viscosity of the solution of sizing composition may vary within wide limits; however, a 4% solution of the sizing composition should have a viscosity of less than 12 poises at the temperature of application. The temperature of application may vary between the freezing point and the boiling point of the solution.

Drying of the sized yarn may be effected at normal temperatures or under the influence of heat, as by means of a radiant heater or by a current of heated air. When the yarn is sized by a continuous process involving passing the yarn from the original package to a wind-up bobbin, drying may be effected before collecting on the bobbin, as by increasing the length of yarn travel from the point of sizing to the bobbin, or it may be allowed to dry on the bobbin by suitable combination of the two methods.

The concentration of the sizing composition solution, the temperature of application and the drying temperature are so chosen in cases of continuous application that appreciable migration of the solution on the wind-up bobbin, and the consequent uneven distribution of the sizing agent, does not occur. Since the migration will be toward the edges of the package, analyses for the amount of sizing agent on yarn cut from the

center and edge portions of the bobbin will show whether excessive migration has occurred.

The flat knitting of the sized yarn to form a sheer, full-fashioned hosiery fabric may be effected on any suitable machine designed for flat knitting. For example, a Wildman, 54-gauge, single-unit, full-fashioned hosiery knitting machine is satisfactory for the purposes of this invention. The yarn is preferably knit in the wet condition and the preferred procedure involves the wetting of the yarn just before it passes through the needles to form the fabric; the wetting of the yarn causing the coating to become at least slightly tacky.

Although the sizing compositions of this invention are most advantageously applied to synthetic linear polyamide yarns which are to be used in the knitting of sheer hosiery, they can also be used for the sizing of knitting yarns made from other synthetic polymers, e. g., polyesters, polyacetals, polymerized ethylene, polyvinyl compounds, and unsymmetrical dichloroethylene polymers and interpolymers.

The sizes of this invention present the distinct advantage over the prior art sizes of adhering well to synthetic linear polyamide yarn while possessing other qualities desired in a size for yarn to be used in the knitting of sheer hosiery or other sheer knit goods of the order of sheer knit hosiery. Yarns sized with the sizes of this invention and in accordance with the process of this invention knit very well, and produce sheer, full-fashioned stocking fabrics which are relatively free of snags and pulled threads. These sizes minimize edge rolling and thus assist in the more economical production of sheer, knit, full-fashioned hosiery. The sizes of this invention cause very little wear and corrosion of the needles and sinkers of the knitting machines. In knitting yarn sized in accordance with this invention, the stitch formation is very good and may be maintained uniform over long periods of time.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to the details described herein except as set forth in the appended claims.

I claim:

1. A synthetic linear polyamide yarn containing, as an adherent coating, a sufficient quantity of a protein size to render the yarn snag-resistant in the production of sheer knit goods, said protein being one which is per se substantially water-insoluble.

2. A synthetic linear polyamide yarn containing, as an adherent coating, a sufficient quantity of a protein size to render the yarn snag-resistant in the production of sheer knit goods, said size containing a plasticizer for said protein, and being substantially insoluble in water, but becoming tacky on application of water.

3. A synthetic linear polyamide yarn containing, as an adherent coating, a sufficient quantity of a substantially water-insoluble protein size to render the yarn snag-resistant in the production of sheer knit goods, said size containing a hardening agent for said protein.

4. A synthetic linear polyamide yarn containing, as an adherent coating, a sufficient quantity of a substantially water-insoluble protein size to render the yarn snag-resistant in the production of sheer knit goods, said size containing a plasticizing agent and a hardening agent for said protein.

5. A synthetic linear polyamide yarn containing, as an adherent coating, a sufficient quantity of a protein size to render the yarn snag-resistant in the production of sheer knit goods, said size containing a resin and being substantially water-insoluble.

6. A synthetic linear polyamide yarn containing, as an adherent coating, a sufficient quantity of a protein size to render the yarn snag-resistant in the production of sheer knit goods, said size constituting between 1% and 20% of the dry weight of the yarn and being substantially water-insoluble.

7. A synthetic linear polyamide yarn as defined in claim 1 in which said protein is casein.

8. A synthetic linear polyamide yarn as defined in claim 3 in which said hardening agent is formaldehyde.

9. A synthetic linear polyamide yarn as defined in claim 1 in which said polyamide is polyhexamethylene adipamide.

10. A synthetic linear polyamide yarn as defined in claim 6 in which said polyamide is polyhexamethylene adipamide.

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CERTIFICATE OF CORRECTION.

Patent No. 2,312,469. March 2, 1943.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 13, for "Ptates" read --States--; page 2, second column, line 37, for "pulasticizing" read --plasticizing--; and line 39, for "reder" read --render--; page 3, second column, line 24, for "polymentamethylene" read --polypentamethylene--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 13th day of April, A. D. 1943.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.