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YARN PREPARATION

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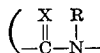
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The present invention relates to the treatment of water-insensitive synthetic linear polymer yarns, of which synthetic linear polyamide yarns are an outstanding example, with a snag-proofing composition so that the said yarns may be flat-knit into 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 States Patents Nos. 2,071,250, 2,130,523, and 2,130,948.

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 Patents Nos. 2,157,116 and 2,157,119. The knitting of ladies' sheer stockings from yarns of synthetic linear polyamides created new and serious problems in the satisfactory treatment of such yarns. Without any treatment 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 problem of treating silk in the gum because of the presence of a natural protecting coat of sericin over the silk filaments.

Flat knit fabrics prepared from untreated nylon yarns exhibit a decided tendency toward edge-rolling which makes the looping and seaming operations very slow and difficult. For this rea-

son, the application of a snag-proofing composition which also improves the edge roll characteristics of the knit fabric is highly desirable.

For reasons of simplicity and economy, it is desirable to apply the snag-proofing composition before knitting. In this case, the treated yarn must not deposit excessive amounts of the snag-proofing composition on the needles and sinkers of the knitting machine since excessive deposition leads to an irregular stitch formation and in extreme cases holes are formed in the fabric. The treated yarn also must not stick to the guides and snappers following a shut-down of the knitting machine, otherwise press-offs will occur when the machine is started again.

Numerous compositions have been, heretofore, applied to textile yarns for a wide variety of purposes, especially to stiffen and to strengthen yarns for the purpose of weaving. Such stiffening action is undesirable in the case of knitting yarn, which must be bent over very sharp angles to form the knit fabric, since resistance to bending would result in uneven stitch formation. For this reason both natural silk yarns and yarns of synthetic linear polyamides are thoroughly wetted before knitting to render them more flexible. Moreover, most of these compositions do not adhere well to synthetic linear polyamides and other synthetic linear polymer yarns in spite of their very good adhesion to other textile fibers. One reason for this lies in the very low moisture absorption and the surface smoothness of the synthetic linear polymer yarns. In addition, the conventional compositions which do adhere to synthetic linear polyamide yarns, in general, give a low degree of snag resistance to the knit fabric and tend to accumulate excessively on the needles and sinkers during the knitting operation.

The number of snag-proofing compositions which may be applied to the yarn before knitting is very limited, and in addition, most of the known compositions tend to deposit excessively on the needles and sinkers and to stick to the needles during knitting. Moreover, the way in which snag-proofing compositions for knitting yarns act is obscure and the necessary characteristics of compositions of this type are not completely understood. In fact, up to the time of the discovery of the present invention no prediction could be made as to the effectiveness of a given composition for the snag-proofing of knitting yarns.

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

A still further object of the invention is to provide a snag-proof, water-insensitive, continuous filament, synthetic linear polyamide yarn capable of being successfully knitted into full-fashioned hosiery.

A specific object of the invention is to obtain snag-resistant, flat-knit fabrics, in the gray, composed of water-insensitive, continuous filament, synthetic linear polymer textile yarns, particularly synthetic linear polyamide yarns, suitable for the production of sheer, full-fashioned hosiery.

Other objects of the invention will become apparent hereinafter.

It has now been found that fabrics in the gray possessing resistance to snagging and suitable for the preparation of sheer, full-fashioned hosiery may be obtained by flat-knitting water-insensitive, continuous filament, synthetic linear polymer yarns, in particular linear polyamide yarns, which have been treated by depositing thereon, as a snag-proofing composition, a film-forming material which is tacky in the air-dried state and which is dispersible in an aqueous liquid. Yarns so treated have good running properties on full-fashioned knitting machines, have excellent protection from snags and runs, and the composition deposited on the yarn prevents serious edge-rolling of the full-fashioned stocking fabric. The snag-proofing composition may be readily removed from the fabric after the completion of the stocking, for example by means of an aqueous boil-off bath.

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 dispersion, or solution, of the material in question.

The term "dispersible," as used in the present specification, is meant to include solubility; that is, a material which is soluble in an aqueous liquid is considered to be dispersible in said liquid.

The term "tacky," as used in the present specification, is defined by the following test: A No. 9 lead shot is dropped from a height of 1 centimeter onto a freshly prepared film of the composition having a thickness of approximately 0.2 millimeter and which has been dried in the atmosphere for 24 hours at a temperature of 25° C. and a relative humidity of 50%. If, upon inverting the film, the lead shot does not fall free within a period of 5 seconds, the composition is considered to be tacky in the air-dried state. If, on the other hand, the shot does not remain in contact with the film for at least 5 seconds, the composition is not tacky and is not suitable for the purposes of this invention. In the cases of the preferred compositions of this invention, the shot will remain in contact with the film for a period as great as 15 seconds or more.

That the physical characteristic described as "tackiness" is an essential feature of the snag-proofing compositions of this invention will no doubt be quite surprising to those skilled in the art. It is known, of course, that tackiness is extremely undesirable in warp sizes or in dressings for finished fabrics, including finished knitted fabrics. The term "finished fabrics" is used here in the sense of contrast with the terms "un-

finished fabrics" or "fabrics in the gray." It was, therefore, contrary to all expectations that materials possessing that characteristic would be adapted to the treatment of knitting yarns and furthermore would be outstanding in the impartation of snag-proof properties to fabrics knit from said yarns. Neither could it have been expected that tacky, film-forming materials would not stick to or deposit excessively on the needles, sinkers and other parts of the knitting machines.

It should be emphasized, in connection with the above, that the tacky snag-proofing compositions operable in the process of this invention are in general not adapted to the problem of dressing finished fabrics, including finished knitted fabrics, since they tend to leave the fabric in a tacky condition. Conversely, agents known to be useful for the treatment of finished fabrics are not in general satisfactory for the treatment of the yarn previous to knitting, in that they do not impart snag resistance to fabrics knitted from the yarn.

Among the various classes of materials which may be used in snag-proofing compositions in accordance with the present invention, alkyd resins, vinyl interpolymers, natural resins, and carbohydrates are particularly suitable, provided, of course, that they are dispersible in an aqueous liquid, that they are film-forming in character and that they are tacky in their air-dried state. Those materials falling within these classes which are not tacky in the air-dried state may often be rendered tacky by the addition of a plasticizer, and thus made suitable for use in accordance with the invention.

The following examples are given to illustrate preferred snag-proofing 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 fabrics prepared from synthetic linear polyamides, utilizing as the snag-proofing composition an alkyd resin which is insoluble in water, but soluble in dilute aqueous alkalies.

A 30-denier, 10-filament 30-turn, "Z" twist, oriented, continuous polyhexamethylene adipamide yarn is treated by passing through a solution comprising 3.3 parts of ethanol, 86.7 parts of water, and 10 parts of the neutral ammonium salt of the alkyd resin of acid number 35, prepared by heating substantially equimolecular quantities of diethylene glycol and the maleic anhydride adduct of a terpene fraction boiling within the range 172° C.-180° C., consisting essentially of alpha-terpinene, and obtained by the rearrangement of alpha-pinene using sulfuric acid as catalyst. Alkyd resins of the above-mentioned general type are marketed by the Hercules Powder Company under the trade-name, "Petrax Resins." The yarn is passed through the bath at a speed of 100 feet a minute and the length of the travel in the bath is 4 inches. The distance from the bath to the wind-up bobbin is 30 feet. After drying and coning, the treated yarn is knit in a wet condition in a Wildman 45-gauge, single-unit, full fashioned hosiery knitting machine. None of the snag-proofing composition is deposited on either the needles or the sinkers, nor

does the newly formed fabric tend to stick to the needles. The resulting fabric is highly resistant to snagging, and consequently receives little damage, due to pulled threads, in the subsequent operations of stocking manufacture.

Example II

This example typifies the preparation of a flat-knit full-fashioned stocking fabric from a yarn composed of polyhexamethylene adipamide treated with a water-insoluble, alkali-soluble, alkyd resin in which a plasticizer is necessary to render the composition tacky in the air-dried state.

A 30-denier, 10-filament, 30-turn, oriented, continuous polyhexamethylene adipamide yarn is handled on a "bobbin-to-bobbin" type machine, in which the yarn is taken from a spool of the yarn through a pre-tension device over a roll dipping in the snag-proofing solution and wound up on a bobbin. The snag-proofing composition comprises 5 parts of ethanol, 3 parts of dibutyl phthalate, 3 parts of a polymerized ethylene oxide with an average molecular weight of approximately 1500, 74 parts of water, and 15 parts of the neutral ammonium salt of the alkyd resin of acid number 35, prepared by heating in substantially equimolecular quantities a mixture comprising 15% glycerol and 85% ethylene glycol and the maleic anhydride adduct of a terpene fraction boiling within the range 172° C.-180° C., consisting essentially of alpha-terpinene, obtained by the rearrangement of alpha-pinene. Alkyd resins of the above-mentioned general type are marketed by the Hercules Powder Company under the trade-name, "Petrex Resins." The yarn is passed over the roll at a speed of 1000 feet per minute, while the roll rotates with a circumferential speed of 12.2 feet per minute. In this manner, 3.2% of the snag-proofing composition is applied to the yarn. After drying, coning and oiling, the yarn is knit as in Example I to form a fabric with excellent resistance to snagging.

In the manufacture of full-fashioned hosiery using yarn treated with the composition of this example only about nine snags were produced per hundred stockings, whereas substantially all the stockings knit from untreated yarn were snagged.

Example III

The following example illustrates the use of a snag-proofing composition based on an acidic, water-soluble alkyd resin derived from a polyhydric alcohol and a dibasic acid, and which is neutralized before application to the yarn.

An oriented, continuous, 10-filament, 30-denier polyhexamethylene adipamide yarn with 30 turns of "Z" twist per inch is treated with a solution comprising 15 parts of a mannitol maleate resin, prepared by heating mannitol and maleic anhydride in the molecular ratio of 10:8 at 150° C., until the acid number of the resulting resin drops to 70, 10.2 parts of 29% ammonium hydroxide solution, and 74.8 parts of water, and dried. This is accomplished using the "bobbin-to-bobbin" type machine of Example II, utilizing a yarn speed of 1000 feet per minute and a circumferential roll speed of 7.2 feet per minute. The treated yarn is found to contain 6.5% mannitol maleate, based on the original weight of the yarn. After coning in the usual manner, the yarn is knit as in the preceding examples to form a highly snag-resistant flat fabric containing

substantially the same amount of snag-proofing composition as the treated yarn.

Example IV

The following example typifies the production of snag-resistant synthetic linear polyamide fabrics from yarns treated with an oil-modified, water-insoluble, alkali-soluble alkyd resin.

A bath is prepared from the oil-modified alkyd resin, with an acid number of 100, prepared by heating 228.2 parts of glycerol, 539.4 parts of phthalic anhydride, and 232.4 parts of castor oil, by dissolving it in 5000 parts of water and 441 parts of commercial concentrated ammonium hydroxide solution. A skein of 45-denier, 20-turn, "Z" twist, oriented, continuous polyhexamethylene adipamide yarn is immersed in this bath at 25° C. 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. The amount of dry material deposited on the yarn is 3.5% of the weight of the dry yarn. After spooling and coning in the known manner, the yarn is flat knit to a fabric which possesses good resistance to snagging.

Example V

The following example is representative of the production of snag-resistant, flat-knit hosiery fabrics prepared from synthetic linear polyamides treated with a tacky vinyl interpolymer composition.

A 10-filament, 30-denier, oriented, continuous polyhexamethylene adipamide yarn with 30 turns of "Z" twist per inch is treated on the "bobbin-to-bobbin" machine mentioned in Example II with a solution of the neutral sodium salt of a hydrolyzed ethylene-maleic anhydride interpolymer. This copolymer is prepared in an autoclave from a solution of 24 parts of maleic anhydride in 140 parts of xylene and 27 parts of ethylene at an initial pressure, at room temperature, of 320 pounds per square inch. One part of benzoyl peroxide is used as catalyst. Exothermic reaction is effected upon heating the mixture to 75° C. The solution is prepared by heating 10 parts of the interpolymer and 5 parts of sodium hydroxide in 85 parts of water at 90° C. for 18 hours.

The yarn is processed at a speed of 1000 feet per minute with a circumferential roll speed of 4.5 feet per minute. The treated yarn is found to have absorbed 5.0% of its weight of the interpolymer salt. After coning in the usual manner, the yarn is knit in the wet state as in the preceding examples to form a fabric containing substantially the same amount of snag-proofing composition as the treated yarn. The resulting flat-knit hosiery fabric is highly resistant to snagging.

Example VI

The following example further illustrates the production of snag-resistant flat-knit fabrics prepared from water-insensitive, synthetic, continuous yarns by the use of a typical tacky vinyl interpolymer composition as the snag-proofing composition.

An oriented 10-filament, 30-denier, continuous polyhexamethylene adipamide yarn having 30 turns of "Z" twist per inch is treated on the "bobbin-to-bobbin" type machine of Example II with a solution of a sodium salt of a hydrolyzed propylene-maleic anhydride copolymer.

The copolymer is prepared in an autoclave from 30 parts of maleic anhydride dissolved in

200 parts of toluene and 35 parts of propylene, using 1.5 parts of benzoyl peroxide as catalyst. The initial pressure, at room temperature, is 280 pounds per square inch. Upon heating the mixture to 100 C. an exothermic reaction occurs.

The snag-proofing composition is prepared by heating 10 parts of the interpolymer and 5 parts of sodium hydroxide in 85 parts of water at 90° C. The yarn is treated at a speed of 1000 feet per minute and a circumferential roll speed of 4.5 feet per minute. After coning in the usual manner, the yarn is knit as in the preceding examples to form a snag-resistant flat fabric suitable for further processing in the preparation of sheer, full-fashioned hosiery.

Example VII

The following example illustrates the treatment of a polyamide yarn with a composition of a methacrylate polymer which is not tacky of itself, but is rendered tacky by the addition of suitable plasticizing agents.

An oriented, continuous, 10-filament polyhexamethylene adipamide yarn is impregnated on the "bobbin-to-bobbin" type machine of Example II with a solution comprising 325 parts of di-beta-methoxyethyl adipate, 325 parts of a polymerized ethylene oxide of an average molecular weight of approximately 1500, 8500 parts of water, and an interpolymer prepared by emulsion type polymerization from 640 parts of beta-methoxyethyl methacrylate and 110 parts of methacrylic acid, using 7.5 parts of benzoyl peroxide as the catalyst and 7.5 parts of methylated starch as the emulsifying agent. A circumferential roll speed of 9.4 feet per minute and a yarn speed of 1000 feet per minute is used. A highly snag-resistant fabric results upon flat knitting the yarn according to the procedure of the previous examples.

Example VIII

The following example is illustrative of the use of a natural resinous material of the terpene type to produce highly snag-resistant, flat-knit, synthetic linear polyamide hosiery fabrics.

Oriented, continuous polyhexamethylene adipamide yarn is impregnated in a continuous manner by passing it through a 10% aqueous solution of the sodium salt of rosin at a rate of 100 feet per minute. The length of the path of the yarn through the bath is 4 inches, and the distance between the bath and the wind-up bobbin is 30 feet. After coning in the usual manner, the yarn is flat knit as in the previous examples to give a hosiery fabric with a very high degree of resistance to snagging.

Example IX

The following example illustrates the production of snag-resistant synthetic linear polyamide hosiery fabric by the use, as a snag-proofing composition for the yarn, of a typical tacky carboxylate composition.

Oriented, continuous multifilament polyhexamethylene adipamide yarn is passed through a 20% solution of honey, using a circumferential roll speed of 7.2 feet per minute and a yarn speed of 1000 feet per minute on the "bobbin-to-bobbin" type machine of Example II. Coning and flat knitting, according to the procedure of the preceding examples, results in a hosiery fabric showing resistance to snagging.

The process of this invention is particularly applicable to any synthetic linear polymer,

water-insensitive, continuous yarn since the snag-proofing compositions employed in this invention adhere well to these yarns, in contrast to the more well-known compositions. By the term "water-insensitive" it is meant that the individual filaments of the yarn absorb less than 10% of their weight of water at 25° C. and 100% relative humidity. Examples of such yarns are the synthetic material made of a vinyl chloride-vinyl acetate interpolymer marketed by the Carbide and Carbon Corporation under the name "Vinyon"; yarns composed of polymerized methyl methacrylate or polymerized ethyl methacrylate; polyvinyl chloride yarns; chlorinated polyvinyl chloride yarns; and yarns composed of high molecular weight ethylene polymers.

Of particular interest in this invention are the synthetic linear polyamide materials generically known as nylon.

While the process has been described as applied to yarn, i. e., multiple filaments, it is obviously equally applicable to single filaments (monofil) of any desired denier.

As examples of the various classes of synthetic linear polyamides from which fibers suitable for the purposes of this invention may be prepared may be cited the polyamides derived from diamines and dibasic acids or their amide-forming derivatives; those derived from polyamide-forming amino acids; 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 subacamide, polypentamethylene adipamide, polypentamethylene sebacamide, polyhexamethylene sebacamide, polyoctamethylene adipamide, polydecamethylene adipamide, poly-p-xylylene sebacamide, polyhexamethylene hexahydroterephthalamide, polyhexamethylene isophthalamide, poly-3-methyl hexamethylene-2-methyl adipamide, polyhexamethylene-4-ketopimelamide, the polyamide prepared from hexamethylenediamine and sulfonedibutyric acid, the polyamide derived from hexamethylenediamine and piperazine diacetic acid, and the interpolyamide prepared from equimolecular quantities of hexamethylenediamine, 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 hexamethylenediamine, adipic acid, and 12-aminostearic acid, and the polyamide derived from hexamethylenediamine, sebacic acid, and 6-aminocaproic acid in which the molecular quantities are in the ratio of 3:3:1.

The process is of particular utility with yarns of denier of 90 or less since it is with fabrics knit from these yarns that snag resistance is most needed. Higher denier yarns tend to give more snag-resistant fabrics without a snag-proofing treatment. Likewise the process is also of greatest advantage with yarns of smoother contour which are especially prone to give easily snagged

fabrics. Such a contour is typical of the synthetic polymer yarns.

A wide variety of compositions is suitable for use as snag-proofing compositions in accordance with the present invention. Chemically, these compositions are quite unrelated and they comprise a variety of diverse materials. It is through their physical characteristics that they form a unitary, generic group, within which any composition is applicable to this process. As already indicated, these physical characteristics are (a) film-forming ability, (b) tackiness in the air-dried state, (c) dispersibility in an aqueous liquid.

As above indicated, tacky compositions comprising alkyd resins, vinyl interpolymers, methacrylate polymers, natural resins, and carbohydrates have been found to be particularly suitable. A preferred embodiment of this invention comprises the use of tacky compositions based on alkyd resins as a class. Especially suitable examples of alkyd resins are those of relatively high acid number derived from polyhydric alcohols and di- and polybasic acids, such as the mannitol maleates, sorbitol phthalates, mannitol phthalates and sorbitol citrates with acid numbers of 30 to 150. Among other alkyd resins which have been found suitable for use in the process of this invention, those based on compounds of the terpene group are unusually effective. Thus, alkyd type resins based on terpene acids, such as the adduct between rosin and maleic anhydride, or the terpene-maleic anhydride adduct known as "Petrex" acid, marketed by the Hercules Powder Company, are especially effective snag-proofing compositions.

Another preferred embodiment of this invention comprises the use of tacky compositions based on vinyl polymers. Completely or partially hydrolyzed copolymers of olefin hydrocarbons and maleic anhydride such as an ethylene-maleic anhydride interpolymers, are examples of tacky vinyl polymers which are especially preferred for the purposes of this invention.

A typical natural resin is represented by pine rosin, preferably in the form of its emulsion or water-soluble salts. Non-crystallizing sugar syrups such as honey or corn syrup are typical tacky carbohydrates.

Further species of tacky compositions of the classes mentioned in the examples above include highly plasticized glycerol phthalates with acid numbers of 60 or above, plasticized oil-modified alkyd resins obtained from terpene-maleic anhydride condensates and di- or polyhydric alcohols, and plasticized compositions containing the resin prepared from 75% methyl methacrylate and 25% of methacrylic acid under the influence of peroxide catalysts.

Other classes of tacky, film-forming materials suitable for use in snag-proofing compositions according to this invention are urea-formaldehyde resins, phenol-formaldehyde type resins, resinous terpene derivatives, synthetic linear polyamides, synthetic linear polyamides, and synthetic linear polyquaternary ammonium salts. An example of a urea-formaldehyde resin suitable for use in snag-proofing compositions, according to this invention, is a reaction product of urea and formaldehyde which has been condensed only to the water-soluble syrupy state. Compositions containing resorcinol-formaldehyde, or salicylic acid-formaldehyde resins and a plasticizing agent are suitable snag-proofing compositions for the purposes of this invention.

A plasticized sodium salt of a sulfonated resin obtained by the condensation of pinene and phenol in the presence of dihydroxy-fluoboric acid is representative of suitable compositions based on resinous terpene derivatives. Polytriglycol adipamide, and polyamide prepared from sebaconitrile and decamethylenediamine, and the polyquaternary ammonium salts prepared from 4,4'-tetramethyl diaminodiphenylmethane and decamethylene dibromide are typical examples of synthetic linear polyamides, polyamides, and polyquaternary ammonium salts suitable for the purposes of this invention, but which require a plasticizing agent to be rendered tacky. In addition, mixtures of one or more resinous film-forming materials may be used according to this invention.

As has been mentioned above, it is often necessary to add plasticizing agents to the film-forming compositions to render them tacky, and so useful according to the purpose of this invention. Both water-soluble and water-insoluble plasticizing agents may be used for this purpose. Examples of suitable water-soluble plasticizing agents include glycerol, triethylene glycol, polymerized ethylene oxide, sorbitol, diacetin, triethanolamine oleate, and N-(beta-hydroxyethyl)formamide. Suitable water-insoluble plasticizers include di(beta-methoxyethyl) adipate, dibutyl phthalate, and tributyl phosphate. It has been found that most satisfactory results are usually obtained by use of a water-soluble material. Such plasticizers are compatible with the treating solutions and in many cases reduce the tackiness of the treated yarn upon wetting, which in turn improves the knitting characteristics of the yarn under wet conditions.

The snag-proofing compositions are preferably applied in the form of their solutions in water or in aqueous liquids. In the case of acidic resinous materials which are insoluble in water, dilute alkalies, such as sodium hydroxide, ammonium hydroxide or triethanolamine, may be used to effect solution. In some cases it may be desirable to add a certain proportion of a water-miscible organic solvent to aid solubility and accelerate drying. Quantities up to 50% have been found useful. It is often desirable to neutralize either acidic or basic water-soluble snag-proofing compositions by suitable means. Thus, for example, an ethylene-maleic anhydride interpolymers may be solubilized in water by refluxing with 50%-70% of its weight of sodium hydroxide in dilute aqueous solution. In the case of water-soluble alkyd resins of strongly acid reaction, such as mannitol maleates, the aqueous solution may be neutralized with dilute ammonium hydroxide before use.

Suitable concentrations of the film-forming materials in the snag-proofing compositions lie in the range of about 2% to about 35%, based on the total solids concentration of the solution. Concentrations of 4% to 25% have been found most useful.

The viscosity of the snag-proofing composition may vary within wide limits, but a 4% aqueous dispersion of the film-forming material should have a viscosity of less than 12 poises at the temperature of application; otherwise the yarn may stick on the cones or other supply packages and can be removed only with difficulty.

The snag-proofing composition is conveniently applied to the yarn by means of a "bobbin-to-bobbin" type machine in which the yarn passes over a rotating cylindrical roll dipping in the

solution of the composition. The speed at which the roll rotates will vary with the speed of the yarn and will depend upon the amount of composition which it is desired to apply to the yarn. Thus, for example, at a yarn speed of 1000 feet per minute and with a roll 3 inches in diameter, a suitable range of roll speeds lies between 2 and 16 revolutions per minute.

It is also suitable to apply the composition by passing the yarn in a continuous fashion through a solution or dispersion thereof, or by dipping loosely wound skeins into the solution, followed by wringing to remove excess liquor. Any other suitable method may be employed. For example, the snag-proofing composition may be sprayed on a moving strand of yarn.

The amount of residual, air-dried film-forming material applied to the yarn may vary within wide limits but the preferred amount will lie within the range of 1% to 20% of film-forming material, based on the weight of the dry yarn. The amount of the material on the yarn may in most cases be simply determined by boiling a weighed sample of the treated yarn in a dilute alkaline solution and re-weighing the yarn after drying. The quantity of snag-proofing composition to be applied to the yarn will depend upon the degree of snag protection required and the method to be employed in handling the yarn during knitting. In general, snag protection is increased as the quantity of composition is increased, but with excessive quantities the yarn may stick in the supply package, or undesirable friction may be set up between the yarn and the knitting machine parts. Some experiment is usually necessary to determine the quantity of snag-proofing composition which can be applied to give good protection without excessive sticking or friction. The quantity of composition to be applied will also vary, depending upon the denier of the yarn, the firmness of the yarn package, and the speed of knitting.

As an alternative method, the snag-proofing composition may be applied to the unseamed and unlooped fabric in the gray as obtained from the knitting machine. Although this process results in a high degree of resistance to snagging, it is inconvenient and expensive and, in addition, offers the danger of excessive snag production before treatment can be effected. The residual film-forming material is subsequently removed before or during the final finishing treatment.

The temperature of application of the snag-proofing composition may vary between just above the freezing point and just below the boiling point of the solution.

Drying of the treated yarn may be effected at normal temperature or under the influence of heat, as by means of a radiant heater or by a current of heated air. When the yarn is impregnated 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 treatment to the bobbin, or it may be allowed to dry on the bobbin during winding, or by any suitable combination of these two methods.

The concentration of the snag-proofing composition, 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 consequent uneven distribution of the film-forming material does not occur. Since the

migration will be toward the edges of the package, analyses for the amount of the material on yarn cut from the center and edge portions of the bobbin will show whether excessive migration has occurred.

The knitting of the yarn to form a hosiery fabric may be effected on any suitable hosiery knitting 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 knit preferably in the wet condition and may suitably be moistened in a wetting trough just before entering the needles.

The products prepared according to the process of this invention may be described as snag-resistant, flat-knit fabrics in the gray, suitable for the preparation of sheer, full-fashioned hosiery comprising synthetic polymer yarns in combination with at least 1% of a dry film-forming composition, based on the dry fabric, which is tacky in the air-dried state and which is dispersible in an aqueous liquid.

The amount of snag-proofing composition in combination with the knit fabric may be determined by the boil-off procedure outlined above for the estimation of the tacky film-forming material on the treated yarn, and will be substantially the same as for the yarn from which the fabric was knit.

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 not to be limited to the details described herein except as set forth in the appended claims.

I claim:

1. The method of producing sheer knit goods, substantially free from snags and pulled threads, from water-insensitive synthetic linear polymer yarn, which comprises applying to said yarn, as a snag-proofing composition, a solution comprising a film-forming material which is tacky in the air-dried state, and which is dispersible in an aqueous liquid, whereby to produce a yarn having a tacky coating of said film-forming material, and knitting said yarn to form sheer knit goods.

2. The method of producing sheer knit goods, substantially free from snags and pulled threads, from water-insensitive synthetic linear polymer yarn, which comprises applying to said yarn, as a snag-proofing composition, an aqueous solution comprising a film-forming material which is tacky in the air-dried state, and which is dispersible in an aqueous liquid, whereby to produce a yarn having a tacky coating of said film-forming material, and knitting said yarn to form sheer knit goods.

3. The method of producing sheer knit goods, substantially free from snags and pulled threads, from water-insensitive synthetic linear polymer yarn, which comprises applying to said yarn, as a snag-proofing composition, an aqueous solution comprising between 2% and 35% of a film-forming material which is tacky in the air-dried state, and which is dispersible in an aqueous liquid, whereby to produce a yarn having a tacky coating of said film-forming material, and knitting said yarn to form sheer knit goods.

4. The method of producing sheer knit goods, substantially free from snags and pulled threads, from water-insensitive synthetic linear polymer yarn, which comprises applying to said yarn, as a snag-proofing composition, a solution compris-

ing a resinous film-forming material which is tacky in the air-dried state, and which is dispersible in an aqueous liquid, whereby to produce a yarn having a tacky coating of said film-forming material, and knitting said yarn to form sheer knit goods.

5. The method of producing sheer knit goods, substantially free from snags and pulled threads, from water-insensitive synthetic linear polymer yarn, which comprises applying to said yarn, as a snag-proofing composition, an aqueous solution comprising a resinous film-forming material which is tacky in the air-dried state, and which is dispersible in an aqueous liquid, whereby to produce a yarn having a tacky coating of said film-forming material, and knitting said yarn to form sheer knit goods.

6. The method of producing sheer knit goods, substantially free from snags and pulled threads, from water-insensitive synthetic linear polymer yarn, which comprises applying to said yarn, as a snag-proofing composition, an aqueous solution comprising between 2% and 35% of a resinous film-forming material which is tacky in the air-dried state, and which is dispersible in an aqueous liquid, whereby to produce a yarn having a tacky coating of said film-forming material, and knitting said yarn to form sheer knit goods.

7. The method of producing sheer knit goods, substantially free from snags and pulled threads, from water-insensitive synthetic linear polyamide yarn, which comprises applying to said yarn, as a snag-proofing composition, a solution comprising a film-forming material which is tacky in the air-dried state, and which is dispersible in an aqueous liquid, whereby to produce a yarn having a tacky coating of said film-forming material, and knitting said yarn to form sheer knit goods.

8. The method of producing sheer knit goods, substantially free from snags and pulled threads, from water-insensitive synthetic linear polyamide yarn, which comprises applying to said yarn, as a snag-proofing composition, an aqueous solution comprising a film-forming material which is tacky in the air-dried state, and which is dispersible in an aqueous liquid, whereby to produce a yarn having a tacky coating of said film-forming material, and knitting said yarn to form sheer knit goods.

9. The method of producing sheer knit goods, substantially free from snags and pulled threads, from water-insensitive synthetic linear polyamide yarn, which comprises applying to said yarn, as a snag-proofing composition, an aqueous solution comprising between 2% and 35% of a film-forming material which is tacky in the air-dried state, and which is dispersible in an aqueous liquid, whereby to produce a yarn having a tacky coating of said film-forming material, and knitting said yarn to form sheer knit goods.

10. The method of producing sheer knit goods, substantially free from snags and pulled threads, from water-insensitive synthetic linear polyamide yarn, which comprises applying to said yarn, as a snag-proofing composition, a solution comprising a resinous film-forming material which is tacky in the air-dried state, and which is dispersible in an aqueous liquid, whereby to produce a yarn having a tacky coating of said film-forming material, and knitting said yarn to form sheer knit goods.

11. The method of producing sheer knit goods, substantially free from snags and pulled threads, from water-insensitive synthetic linear polyamide yarn which comprises applying to said yarn,

as a snag-proofing composition, an aqueous solution comprising a resinous film-forming material which is tacky in the air-dried state, and which is dispersible in an aqueous liquid, whereby to produce a yarn having a tacky coating of said film-forming material, and knitting said yarn to form sheer knit goods.

12. The method of producing sheer knit goods, substantially free from snags and pulled threads, from water-insensitive synthetic linear polyamide yarn which comprises applying to said yarn, as a snag-proofing composition, an aqueous solution comprising between 2% and 35% of a resinous film-forming material which is tacky in the air-dried state, and which is dispersible in an aqueous liquid, whereby to produce a yarn having a tacky coating of said film-forming material, and knitting said yarn to form sheer knit goods.

13. The method of producing sheer knit goods, as defined in claim 1, in which the viscosity of the solution of film-forming material is such that a 4% aqueous dispersion of said material has a viscosity of less than 12 poises at the temperature of application.

14. The method of producing sheer knit goods, as defined in claim 2, in which the viscosity of the solution of film-forming material is such that a 4% aqueous dispersion of said material has a viscosity of less than 12 poises at the temperature of application.

15. The method of producing sheer knit goods, as defined in claim 3, in which the viscosity of the solution of film-forming material is such that a 4% aqueous dispersion of said material has a viscosity of less than 12 poises at the temperature of application.

16. A synthetic linear polymer yarn containing, as a snag-proofing composition, a sufficient quantity of a film-forming material to render the yarn snag resistant in the production of sheer knit goods, said film-forming material being tacky in the air-dried state, and being dispersible in an aqueous liquid.

17. A synthetic linear polymer yarn containing, as a snag-proofing composition, 1% to 20% (based on the weight of the dry yarn) of a film-forming material to render the yarn snag resistant in the production of sheer knit goods, said film-forming material being tacky in the air-dried state, and being dispersible in an aqueous liquid.

18. A synthetic linear polyamide yarn containing, as a snag-proofing composition, a sufficient quantity of a film-forming material to render the yarn snag resistant in the production of sheer knit goods, said film-forming material being tacky in the air-dried state, and being dispersible in an aqueous liquid.

19. A synthetic linear polyamide yarn containing, as a snag-proofing composition, 1% to 20% (based on the weight of the dry yarn) of a film-forming material to render the yarn snag resistant in the production of sheer knit goods, said film-forming material being tacky in the air-dried state, and being dispersible in an aqueous liquid.

20. The method of producing sheer knit goods, as defined in claim 1, said film-forming material comprising a castor oil modified phthalic anhydride-glycerol resin.

21. A synthetic linear polymer yarn, as defined in claim 16, in which said film-forming material is a castor oil modified phthalic anhydride-glycerol resin.

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