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Marshall et al.

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[54] **POLYAMIDE YARN**

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[58] **Field of Search**..... 117/139.5 A, 139.5 CQ, 117/76 T, 72, 138.8 N; 252/8.6; 57/140 C; 428/395, 474; 427/385, 416

[56] **References Cited**

UNITED STATES PATENTS

2,693,427	11/1954	Kingsford	117/138.8 N X
2,881,146	4/1959	Remer et al.	117/139.5 A
3,103,448	9/1963	Ross	117/139.5 CQ
3,150,481	9/1964	Bilsky et al.	117/139.5 CQ X
3,442,694	5/1969	Sookne et al.	117/139.5 A X
3,475,207	10/1969	Berch et al.	117/138.8 N X

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[57] **ABSTRACT**

An improved polyamide yarn is prepared by first applying to the yarn an aqueous emulsion of an oxidized polyethylene wax having an average molecular weight between about 1,000 and about 3,000, and containing between about 3 percent and about 9 percent oxygen by weight, thereafter heating said yarn to a temperature between about 100°C. and about 175°C., and then applying to said yarn a composition comprising an aqueous dispersion of colloidal silica and a polyethylene glycol ester of a C_6 to C_{18} aliphatic acid, said polyethylene glycol having a molecular weight of about 200 to 600. The yarn is particularly useful for industrial purposes such as braided hose, rope belts, etc.

3 Claims, No Drawings

POLYAMIDE YARN

BACKGROUND OF THE INVENTION

This invention relates to finished polyamide yarns. More particularly, it relates to multifilament synthetic polyamide yarns having applied finishes which enable the yarns to be satisfactorily processed and utilized in the commercial production of braided hose, rope, drive belts, and other industrial cord applications.

Polyamide yarns, for example polycaproamide yarns, tend to develop high electrostatic charges and excessive tensions when running over guides, tension gates and other objects during processing and subsequent handling so that the utilization of unfinished polyamide yarns in textile production is unsatisfactory. Moreover, polyamide yarns have different physical characteristics than most other filament forming polymers and conventional finishes are not suitable to provide the optimum combination of lubrication and bundle cohesion to overcome processing problems.

U.S. Pat. No. 3,103,448 relates to the treatment of synthetic continuous filament polyamide yarn, and more particularly to a process for rendering such yarns more durable when fabricated into cord or rope, and, in particular, more resistant to wet and dry chafing abrasion when processed into such commodities. Said patent features applying to the yarn a water-resistant coating of an oxidized polyethylene wax having an average molecular weight between about 1,000 and about 3,000 and an oxygen content between about 3 percent and about 9 percent by weight.

Although U.S. Pat. No. 3,103,448 has made a major contribution to this art, polyamide yarn treated in accordance with the process of the patent does not have satisfactory yarn-to-yarn friction properties required for coned package formation. Accordingly, for many industrial uses it would be highly desirable to modify the yarn finish to provide improved balance of yarn-to-yarn friction and cohesion required for good package formation in rewinding the yarn onto cones, without adversely affecting the wet and dry chafing abrasion properties of cord or rope fabricated from the yarn.

SUMMARY OF THE INVENTION

It is an object of this invention to provide an improved finish for polyamide yarn which enables the use of the yarn for industrial purposes such as braided hose, rope belts, etc.

It is still another object of this invention to provide an improved finish for polyamide yarn which provides a balance of yarn to yarn friction and cohesion required for good package formation in rewinding the yarn on cones.

These and other objects are accomplished in accordance with this invention whereby an improved polyamide yarn is prepared by first applying to the yarn an aqueous emulsion of an oxidized polyethylene wax having an average molecular weight between about 1,000 and about 3,000, and containing about 3 to 9 percent, preferably 3 to 6 percent of oxygen, by weight, thereafter heating said yarn to a temperature between about 100°C. and about 175°C. to form a water-resistant coating thereon, and then applying to said yarn a composition consisting essentially of 60 to 90 parts by weight of an aqueous dispersion of colloidal silica, preferably containing about 25 to 50 weight percent silica in the form of a stable silica sol, and 10 to 40 parts by

weight of a polyethylene glycol ester of a C_6–C_{18} aliphatic acid, said polyethylene glycol preferably having a molecular weight of about 200 to 600.

Preferably, the polyamide yarn is coated with sufficient aqueous emulsion of the oxidized polyethylene wax to provide a water-resistant wax coating thereon of between 0.05 percent and about 2 percent by weight of the yarn. Preferably, the second finish composition is applied to the yarn in an amount sufficient to supply between about 0.1 percent and about 5 percent of silica based on the weight of the yarn. The finish compositions may be diluted with water to a water content up to about 80 weight percent of the diluted composition. The finish compositions are applied to the polyamide yarn by any known means, including bath, spray, padding, kiss roll application or the like.

Oxidized polyethylene wax materials suitable for use in the present invention are described in U.S. Pat. No. 3,060,163 according to which normally solid, hard, waxy polymers of ethylene, which are saturated aliphatic compounds characterized by a recurring —CH_2— group and which have average molecular weights between about 1,000 and about 3,000, especially polyethylene/alkanol telomers of this character, are subjected, in the liquid phase, to the action of an oxygen-containing gas to cause reaction of at least about 5 pounds of oxygen per 100 pounds of wax, desirably between about 5 pounds and about 17 pounds of oxygen, per 100 pounds of wax, i.e., to provide an oxidized polyethylene wax containing at least about 3 percent, desirably between about 3 percent and about 9 percent of oxygen by weight, based on the weight of the oxidized wax, and acid numbers of not more than about 50, preferably between about 10 and about 45. The oxidized polyethylene/isopropanol telomer waxes prepared according to the above method containing between about 3 percent and about 6 percent oxygen and having average molecular weights between about 1,000 and about 3,000, melting points between about 90°C. and about 110°C., acid numbers between about 10 and about 20, are especially preferred. The preferred oxidized wax products are characterized by an extremely low incidence of, or in many cases, substantially complete absence of ester groups. Thus, the saponification number (which measures both acid and ester groups) is substantially identical to or only slightly greater than the acid number (which measures only acid groups) so that these products all have an extremely low or zero ester number (saponification number minus acid number) and have ratios of saponification number to acid number of about 1 to about 1.2 and not more than about 1.5.

The waxy ethylene polymers which are oxidized as above described, may themselves be prepared by any suitable known methods, for example by subjecting ethylene, either alone, or in the presence of a co-reactant to temperatures between about 150°C. and about 300°C. and pressures ranging from about 500 p.s.i. to about 7,000 p.s.i. as disclosed in U.S. Pat. Nos. 2,683,141 and 2,504,400.

In carrying out the process according to the present invention, the oxidized polyethylene wax as described, is emulsified in water by known methods using any suitable emulsifying agent. In general, we prefer to melt the polyethylene wax together with the emulsifying agent and then pour the melted wax gradually with stirring into hot water at a temperature slightly below the boiling temperature. Concentration of the wax component

in the emulsion is not critical, and will be adjusted to provide the desired coat weight on the yarn under the particular application conditions employed.

The colloidal silica dispersions or sols used in accordance with the present invention may be prepared by reacting an acid, such as a mineral acid capable of forming salts by reaction with silicates, with a water-soluble silicate in the manner customarily employed to form silica gel, and washing the resulting gel with water to remove electrolytes. The gel is then treated with a weak aqueous solution of a substance capable of forming hydroxyl ions and, after removing the gel from solution, heating the gel while avoiding evaporation of water until the gel is converted to a sol.

Aqueous dispersions of colloidal silica prepared in the above manner are particularly adapted for the purposes of the invention. It is possible, however, to prepare the colloidal dispersions or sols as described above, then to acidify them and use them in a slightly acid condition, when desired. Other types of colloidal solutions or sols of silica may also be used. For example, the sols may be prepared by reacting water-soluble silicates with an acid and subjecting the acidified silicate to treatment with alcohol and/or cooling to remove the electrolyte, as described in U.S. Pat. No. 2,285,449 and U.S. Pat. No. 2,285,477. It is also possible to use sols prepared by treatment of an alkali silicate with an ion-exchange material as described in U.S. Pat. No. 2,244,325.

The concentration of the colloidal dispersion of silica used is relatively unimportant, as it is possible to employ a wide variety of solution strengths depending on the type of apparatus used or the degree of pick-up which is possible in the particular apparatus employed. Normally, commercially available aqueous dispersions of colloidal silica are employed, preferably containing 25% to 50% silica. As indicated above, such dispersions of colloidal silica may be diluted with water if desired.

The ethylene glycols having average molecular weights above about 200 are usually classified as polyethylene glycols, $HO(CH_2CH_2O)_nH$, where n is equal to or greater than 4. They are water-white liquids at ambient temperature up to molecular weights of about 700. Polyethylene glycols having molecular weights of about 200–600 are preferred for use in the present invention. The commercially available polyethylene glycols are actually mixtures of many polyethylene glycols. The polyethylene glycols are prepared commercially by the addition of ethylene oxide to either water, ethylene glycol, or diethylene glycol containing a small amount of sodium hydroxide catalyst. The principal derivatives of the polyethylene glycols are the mono- and diesters, especially the aliphatic acid esters. These esters are manufactured by typical esterification techniques with esterification temperatures often reaching **150°–200°C**. The esters of the invention are preferably monoesters of aliphatic acids having 6–18 carbon atoms. Preferred aliphatic acids of the invention include, for example, stearic acid, palmitic acid, lauric acid, pelargonic acid and capric acid.

DESCRIPTION OF THE PREFERRED EMBODIMENT

As indicated hereinabove, the present invention is an improvement over U.S. Pat. No. 3,103,448, which patent is incorporated herein by reference.

In accordance with the present invention, the oxidized polyethylene wax emulsion may be applied to the yarn either alone, or together with other additives commonly applied to yarns as yarn finishes to improve their processability, for example, antistatic agents, mineral oil, silicones, etc. The instant coating differs from the usual spin finish additives, however, in that it produces a permanent finish rather than being washed out and removed as are the usual spin finishes applied for improving processability. In general, we prefer to apply the oxidized polyethylene wax emulsion as a spin finish, and find it especially adapted for treatment of polyamide filaments including nylon 6, polycaprolactam, filaments.

Any suitable emulsifying agent may be used in preparing the oxidized polyethylene wax emulsions used in the process of our invention. Mixtures of higher fatty acids, for example C_{12} to C_{20} saturated aliphatic acids with volatile amines such as morpholine, methoxy propylamine, 2-amino-2-methyl-1-propanol. etc. may be used as emulsifiers as may also the long chain alkyl aryl sulfonates such as keryl benzene sodium sulfonate, dodecyl benzene sodium sulfonate, alkyl aryl polyether alcohols. Also useful are the general class of non-ionic emulsifiers especially the condensation products of ethylene oxide with hydrophobic material such as a long chain aliphatic alcohol, acid, ester, ether or alkyl phenol. These products are characterized by containing as the hydrophilic portion of the molecule, a plurality of oxyethylene moieties as illustrated in the formulae below.

1.

$$R—O—(CH_2—CH_2O)_x—CH_2—CH_2OH$$

wherein R is an alkyl group having from 12 to 22 carbon atoms or an alkyl phenol residue wherein the alkyl group contains from 6 to 13 carbon atoms inclusive and wherein x is at least 4 especially between about 6 and about 40.

Commercial examples of products in this group include "Triton X-100" wherein R is an alkyl phenol residue wherein the alkyl group is isooctyl and wherein x is 7 to 9; "Triton X-102" wherein R is an isooctyl phenol residue and x is 11; "Tergitol NPX" wherein R is ethylhexyl phenol residue and x is 8 to 9, "Neutronic 600" wherein R is nonyl phenol residue and x is 9; "Emulphor ELN" wherein R is dodecyl phenol residue and x is 19.

2. Condensation products of fatty acids and polyethylene glycols having the general formula

$$RCOO—(CH_2CH_2O)_xCH_2CH_2OH$$

wherein R is a long chain alkyl group having from 12 to 18 carbon atoms inclusive and x is an integer from 8 to 40 inclusive.

3. Polyoxyethylene derivatives of hexitol anhydride or sorbitol fatty acid esters such as "Tween 80".

4. Polyoxyethylene ethers

$$R—O(CH_2CH_2O)_xCH_2CH_2OH$$

wherein R is an alkyl group having from 6 to 18 carbon atoms and x is an integer from 4 to 40 inclusive, or the corresponding phosphated derivatives.

In accordance with one preferred embodiment of the invention, an improved polyamide is prepared by first applying to the yarn an aqueous emulsion of a composition consisting essentially of 30 to 60 parts, desirably 40 to 50 parts, by weight, of white mineral oil having a

boiling point of between 265°C. and 330°C., 25 to 50 parts, desirably 30 to 40 parts, by weight, of an ethoxylated phosphated oleyl alcohol, 2 to 10 parts, desirably 4 to 8 parts, by weight, of a sulfonated succinic acid ester of oleyl alcohol, and 5 to 10 parts, desirably 4 to 8 parts, by weight, of an oxidized polyethylene wax having an average molecular weight between about 1,000 and about 3,000, and containing about 3 to 6 percent of oxygen by weight, thereafter heating the yarn to a temperature of about 100°C. to 135°C. to form a water-resistant coating thereon, and then applying to said yarn a composition consisting essentially of 60 to 90 parts by weight of an aqueous dispersion of colloidal silica containing about 25 to 50 weight percent silica in the form of a stable silica sol, and 10 to 40 parts by weight of a polyethylene glycol ester of a C_6–C_{18} aliphatic acid, said polyethylene glycol having a molecular weight of about 200 to 600.

In order to demonstrate the invention, the following examples are given. They are provided for illustrative purposes only and are not to be construed as limiting the scope of the invention, which is defined by the appended claims. In these examples, parts and percentages are by weight.

EXAMPLE 1

A reactor equipped with a heater and stirrer was charged with a mixture of 1,520 parts of e-caprolactam and 80 parts of aminocaproic acid. The mixture was then flushed with nitrogen and was stirred and heated to 255°C. over a 1 hour period at atmospheric pressure to produce a polymerization reaction. The heating and stirring was continued at atmospheric pressure under a nitrogen sweep for an additional 4 hours in order to complete the polymerization. Nitrogen was then admitted to the reactor and a small pressure was maintained while the polymer was extruded from the reactor in the form of a polymer ribbon. The polymer ribbon was subsequently cooled, pelletized, washed and then dried. The polymer was a white solid having a relative viscosity of about 55 to 60 as determined by a concentration of 11 grams of polymer to 100 milliliters of 90 percent formic acid at 25°C. (ASTMD-789-62T).

The polycaproamide pellets were melted at about 285°C. and then melt-extruded under a pressure of about 1,500 p.s.i.g. through a 204-orifice spinnerette, to produce a 6,300-denier yarn. The yarn was passed over a spin-finish roll to apply a spin finish, then collected at about 5,000 feet per minute and then drawn over a heated pin at 100°–135°C. to about 5 times its extruded length to produce a 1,260-denier yarn. The spin finish thus applied was prepared by mixing 4 parts of water with a composition consisting of 48.2 percent of white mineral oil having a boiling point between 265°C. and 330°C., 38.4 percent of phosphated oleyl alcohol ethoxylated with about 7 mols of ethylene oxide, 6.6 percent of sulfonated succinic acid ester of oleyl alcohol, and 6.8 percent of oxidized polyethylene wax consisting of a polyethylene/alkanol telomer wax having an average molecular weight between about 1,000 and about 2,000, an oxygen content of about 3 percent, melting point 213°–221°F. and acid number 14–17. Wet pick up of the water-diluted composition on the fiber was 5 percent based on the weight of fiber; this finish, after heating and drawing the fiber as described above, provided a water-resistant coating on the yarn. Then, the yarn was further treated with an over-finish composition, as described below.

The silica sol used in preparing the overfinish was a commercially available colloidal aqueous silica dispersion having the following analysis:

Solids, weight percent 30
Water, weight percent 70
Specific gravity at 25°C. 1.2
pH at 25°C. 9.9
Mol ratio SiO_2/Na_2O 90

A mixed over-finish composition of 70 parts of the above-described aqueous dispersion of silica and 30 parts of a monopelargonate ester of 400 molecular weight (9–10 ethylene oxide units) polyethylene glycol was prepared, and this composition was applied as an overfinish to the above-described yarn by means of a kiss roll prior to coning. Sufficient finish was applied to provide about 0.3% of silica based on the weight of the yarn. The finish was found to be a significant aid in processing the yarn through the coning operation. The condition of the coned package was excellent. The finished yarn gave excellent performance in braiding and winding operations during manufacture of industrial rope.

In a comparative test wherein the above-described spin finish composition was applied to the yarn but the over-finish composition was not applied, the condition of the coned package was relatively poor.

In the following examples, the procedure of Example 1 was followed except that application of the silica-containing over-finish composition was modified to determine optimum concentrations, components, component ratios, etc.

EXAMPLE 2

In accordance with the procedure of Example 1, an over-finish composition was prepared and applied to the polyamide yarn as described in Example 1 except that the over-finish composition was diluted with an equal weight of water. The yarn was found to have only slightly better coning properties than the overfinished yarn of Example 1.

EXAMPLE 3

An over-finish composition was prepared and applied to the polyamide as described in Example 1 except that 20 parts of the polyethylene glycol monopelargonate was combined with 80 parts of the silica dispersion. The yarn was found to have relatively poor coning properties as compared to the overfinished yarn of Example 1.

EXAMPLE 4

An over-finish composition was prepared and applied to the polyamide yarn as described in Example 1 except that 40 parts of the polyethylene glycol monopelargonate was combined with 60 parts of the silica dispersion. This fiber was found to have relatively good coning properties but not equal to the overfinished yarn of Example 1.

EXAMPLE 5

An over-finish composition was prepared and applied to the polyamide yarn as described in Example 1 except that 30 parts of a monolaurate ester of 400 molecular weight polyethylene glycol was substituted for the monopelargonate ester used in Example 1. The yarn was found to have coning properties slightly inferior to those of the overfinished yarn of Example 1.

EXAMPLE 6

An over-finish composition was prepared and applied to the polyamide yarn as described in Example 1 except that the composition was applied to the yarn in amount sufficient to provide 0.28% to 0.6% silica based on the weight of the yarn. In each case, the condition of the coned package was excellent, and the finished yarn gave excellent performance in braiding and winding operations during manufacture of industrial rope.

Discussion

The above examples demonstrate that the instant finish system provides a water-resistant finish combined with a finish having exceptional filament cohesive properties. The over-finish enables the use of these yarns for industrial purposes such as braided hose, rope belts, etc. without need of twisting to control loose filaments. In addition, it provides the proper balance of yarn to yarn friction and cohesion required for good package formation in rewinding yarn on cones. Particularly preferred results were obtained when the over-finish was incorporated on the yarn in an amount to supply about 0.1% to 0.6% silica based on the weight of the yarn. The examples show that for optimum coning properties, the weight ratio of said silica to polyethylene glycol ester on the yarn should be between about 0.45 and 0.7. Particularly preferred results were obtained with use of the monopelargonate ester of 400 molecular weight polyethylene glycol.

We claim:

1. A continuous filament polyamide yarn which is first coated with a first finish composition consisting essentially of 30 to 60 parts by weight of white mineral oil having a boiling point of between 265°C. and 330°C., 25 to 50 parts by weight of an ethoxylated phosphated oleyl alcohol, 2 to 10 parts by weight of a sulfonated succinic acid ester of oleyl alcohol, and 5 to 10 parts by weight of an oxidized polyethylene wax having an average molecular weight between about 1,000 and about 3,000 and containing 3 to 6 percent of oxygen by weight; then coated with a second finish composition consisting essentially of 60 to 70 parts by weight of an aqueous dispersion of colloidal silica containing about 25 to 50 weight percent silica in the form of a stable silica sol, and 30 to 40 parts by weight of a polyethylene glycol ester of a C_6–C_{18} aliphatic acid, said polyethylene glycol having a molecular weight of about 200 to 600, and the weight ratio of said silica to said polyethylene glycol ester being between 0.45 and 0.70; said yarn being coated with an effective amount of said first finish composition to provide a water-resistant oxidized polyethylene wax coating thereon of between 0.05 and about 2 percent by weight of the yarn, and said second finish composition being applied to the yarn in an amount sufficient to supply between about 0.1 percent and about 0.6 percent of silica based on the weight of the yarn, whereby processing of said yarn through coning operations is improved.

2. The yarn of claim **1** wherein the polyethylene glycol ester is the monopelargonate ester of polyethylene glycol having a molecular weight of about 200 to 600.

3. The yarn of claim **1** wherein the polyamide is polycaproamide.

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