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3,277,000

LUBRICATING COMPOSITIONS FOR SEGMENTED ELASTOMERIC COPOLYMER FILAMENTS

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No Drawing. Continuation of application Ser. No. 240,713, Nov. 28, 1962. This application May 7, 1965, Ser. No. 454,181

2 Claims. (Cl. 252—8.9)

This application is a continuation of Serial No. 240,713, filed November 28, 1962, and now abandoned.

This invention relates to lubricated elastic structures and in particular to filaments of synthetic segmented elastomeric copolymers having an oil-based lubricant thereon.

It is well known that an elastic filament made of rubber or of a segmented elastomer, e.g., of the spandex type, cannot be processed if free of a lubricating finish. Such elastic fibers have a greater tendency than do relatively inelastic fibers for cohesion of adjacent filaments of the yarn to one another and for sticking of the yarn to other surfaces which causes erratic running tensions. Talc has been the classic lubricant for filaments made of rubber, and it may also be used to lubricate spandex filaments. Talc, however, has many disadvantages as a lubricant. It presents a housekeeping nuisance as well as a dust hazard, since it is spattered around the area in which the yarn is finished and processed. Moreover, a talc-coated filament presents serious abrasion problems both in spinning machines and on processing equipment.

Oils would appear to be attractive substitutes for talc for the purpose of overcoming these disadvantages. However, it has been generally accepted that oils cannot be used to lubricate rubber filaments because of the harmful effect of such oils on physical properties. The problem of using oils with spandex filaments was solved by Yuk in U.S. Patent No. 3,039,895, wherein it is taught that a textile oil, such as mineral oil, makes a satisfactory finish for filaments of synthetic segmented elastomeric copolymers when at least 2% by weight of finely divided particles of certain metal soaps are dispersed therein. Although this represents a great step forward in the art of finishes for spandex-type filaments, the requirement that the finish contain 2% or more by weight of finely divided particles in the Yuk finishes results in certain disadvantages: in particular, a tendency of the dispersed solids to settle in the finish troughs, and the building up of deposits on filament guides and needles in knitting machines and other processing equipment for the elastic filaments.

It is, therefore, an object of this invention to provide an elastic filament having the property of uniform tension in over-end takeoff from a wound bobbin and having thereon an oil-based finish containing less than 2% of dispersed solids. Another object is to provide an elastic filament with a lubricating finish which may be processed without difficulty. Other objects will be apparent from the following detailed description.

The objects of this invention are accomplished by an oiled elastic structure comprising a filament of a synthetic segmented elastomeric copolymer having a substantially anhydrous lubricating finish comprising a mixture of a textile oil and a polyethylene oxide ester of a higher fatty acid, said mixture having dispersed therein finely divided particles of a Group I, II, or III metal salt of a higher fatty acid. I have discovered that incorporation of minor amounts of certain polyethylene oxide esters of the higher fatty acids in the finishes described by Yuk permits use of significantly less than 2% of finely divided particles of the metal soaps without interfering with the frictional properties of the lubricated elastic filament. In addition,

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I have found that the polyethylene oxide esters have a mild plasticizing effect on the elastic filaments, providing processing improvements such as more even lay-down of threads on beams during working and improved stitch formation in the fabrication of bare powernet fabrics.

In preparing the finishes for the elastic structures, a minor amount of a polyethylene oxide monoester of a higher fatty acid is admixed with a textile oil. The polyethylene oxide esters are referred to herein as ethylene oxide adducts. These adducts may be prepared by condensing ethylene oxide with higher fatty acids, i.e., the saturated carboxylic acids containing at least 12 carbon atoms in the molecule. Suitable acids include lauric, myristic, palmitic, margaric, stearic, arachidic, behenic, and cerotic acid. The preferred acids contain no more than 22 carbon atoms. The ethylene oxide adducts useful in the present invention must be soluble in the textile oil at a temperature above the melting point of the adduct. These adducts contain from 2 to about 20 mols of ethylene oxide per mol of acid. Many of these adducts are known in the art and are commercially available. The preferred adducts are waxy solids at room temperature and melt above about 25° C. A preferred group, i.e., those having 6 to 12 mols of ethylene oxide per mol of acid, melt between about 25° C. and 50° C., are self-dispersing in water, and are soluble in mineral oil above their melting points. A preferred adduct is "Myrj 45," a polyethylene oxide ester of stearic acid, sold by Atlas Chemical Industries, which is reported to contain 8 mols of ethylene oxide per mol of stearic acid.

The polyethylene oxide esters hereinabove mentioned are used in minor amounts in the finishes of this invention. Mixtures of these esters may be used if desired. Generally, they constitute less than 20% by weight of the finish. Preferably, the finishes do not contain more than about 5% of these esters. Ordinarily, the benefits of the present invention are achieved by the use of as little as about 0.5% by weight of the ester in the finish.

The major ingredient in the lubricating finish is a textile oil. By the term "textile oil" is meant the organic liquids with which textile fibers are normally treated during processing, such liquids being in general oils of low volatility that serve to lubricate the fibers, for instance, tallows, naphthenic oil, sulfated or sulfonated oils, aromatic oils, paraffinic oils, and synthetic oils such as the silicones. The preferred textile oil for the purpose of this invention is a white mineral oil of low to medium viscosity (40 to 100 Saybolt viscosity at about 38° C.). Mixtures of oils may be used if desired.

The soaps used in dispersion in the aforementioned Yuk finishes are suitable for use in the present invention. These are the essentially colorless, finely divided soaps of certain metals of Groups I, II, and III of the Periodic Table. Metals of Group Ia of the well-known Mendeleev's Periodic Table are useful and include those having atomic weights between about 7 and 133, i.e., lithium, sodium, potassium, rubidium, and cesium. Metals of Group II include those having atomic weights between about 24 and 137, i.e., magnesium, calcium, strontium, barium, zinc, and cadmium. From Group III, aluminum which has an atomic weight of about 27 may be used.

The higher fatty acid component of the suitable soaps comprise the C₈ to C₂₂ saturated and unsaturated fatty acids. The soap, which is the salt of these fatty acids, may be prepared, of course, from substituted acids such as keto- and hydroxy-acids, for example, 4-ketostearic acid or 12-hydroxystearic acid, instead of fatty acids, or in admixture therewith, if desired. In all cases, a fatty acid-metal combination is suitable if the resulting soap is essentially colorless and may be obtained in a finely divided state. Thus, with the metals indicated, any of

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the acids described above may be used, since these soaps are obtainable as finely divided particles.

Representative examples of suitable soaps include sodium caprate, sodium laurate, sodium behenate, potassium oleate, potassium myristate, lithium stearate, lithium palmitate, zinc stearate, calcium oleate, magnesium laurate, aluminum trioctoate, and aluminum distearate. The preferred soaps are water-insoluble soaps and are those of the Group II metals, especially those of zinc, calcium and magnesium. Magnesium stearate is particularly preferred.

In the practice of this invention, it is important that the particle size of the dispersed soaps be in a critical range. In particular, the average radius of the dispersed particle as determined by standard light scattering methods should fall in the range 0.05 to 5 microns. Preferably, the dispersed particles fall within the range 0.2 to 1.5 microns.

The finishes of the present invention contain less than about 2% of dispersed soap particles. A minimum amount of dispersed soap, however, is necessary to achieve the benefits of the present invention. It has now been found that as little as about 0.5% by weight of soap may be used in the practice of this invention. Accordingly, the oil finish of this invention contains from about 0.5% to about 2% by weight of dispersed solids.

The finishes are readily prepared by dissolving the ethylene oxide adduct in mineral oil at a temperature above the melting point of the adduct. The soap is then added and a satisfactorily stable dispersion is obtained by heating to about 80°–85° C. with good agitation. The finishes of this invention may also contain color inhibitors, anti-static agents, and other additives as desired.

Ordinarily, a lubricated elastic filament, according to the present invention, will contain at least 3.5% by weight and less than about 25% by weight of the finish. Preferably, the amount of finish on a lubricated elastic filament of this invention is in the range from about 12% to about 15%.

The finishes of this invention may be applied to elastic fibers in any convenient manner. In general, the finish may be applied by any of the standard procedures such as by dipping, padding, or spraying. Running yarns may be treated, for example, by spraying, or by passing them through baths or over wicks or other similar devices from which they pick up the finish. Passing the filaments over a roller which dips into a trough containing the finish is a convenient method of application. When the finish is continuously applied to elastic fibers as they are being spun, the trough-roller apparatus is preferably located at a point on the threadline just beyond the first driven feed roll which the elastic filaments contact after leaving the spinneret.

The segmented copolymer which makes up the elastic filament of this invention consists of segments of a high-melting, crystalline polymer alternating with segments of a low-melting, amorphous polymer. The crystalline, high-melting segment may be derived from, for example, a polyurea, polyurethane, polyamide, bisureylene polymer, or polyester. The low-melting, amorphous segment may be derived from, for example, a polyester, a polyether, or a hydrocarbon polymer. Polymers of the spandex type are illustrative of such a segmented copolymer.

The segmented copolymers described in several patents are useful in the practice of this invention. Among these are U.S. Patents 2,929,801, 2,929,802, 2,929,803, 2,929,804, 2,957,852, 2,962,470, 3,009,901, 3,023,192, 3,037,960, 3,040,003, 3,044,987, 3,044,989, and 3,044,990. As disclosed in these references, such segmented copolymers when in filament form display elongations at the break in excess of 200%, elastic recovery (or tensile recovery) above about 90%, and stress de-

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cays below about 20%. The terms "elastic recovery" and "stress decay" are defined in U.S. 2,957,852.

This invention will be further illustrated, but is not intended to be limited by, the following examples in which parts and percentages are by weight unless otherwise specified.

Example I

Polytetramethylene ether glycol and p,p'-methylene-diphenyl diisocyanate are intimately mixed in the ratio of 2 mols of diisocyanate per mol of polyether glycol and are reacted at about 96° C. for 90–100 minutes to yield an isocyanate-terminated polyether. The isocyanate-terminated polyether, cooled to below 45° C., is conducted at a rate of 9.2 pounds per hour into a high-shear mixer containing a rotating disc, and a stream of N,N-dimethylacetamide is added at 6.8 pounds per hour. The mixture (57.5% solids) is thoroughly agitated for 15 minutes and then passes to a chamber in which a mixture of hydrazine (35% in water) and diethylamine (5% in dimethylacetamide), in the ratio of 4.2 parts of hydrazine to 1 part of diethylamine, together with additional dimethylacetamide is added as a single stream at a rate of 16.5 pounds per hour with strong agitation. The mixture passes to a reaction chamber held at a temperature of 20° to 70° C., the contents having a residence time of about 2–3 minutes. The emerging polymer solution contains approximately 30.0% solids and has a viscosity of 1400 poises at 30° C. The polymer has an intrinsic viscosity of 1.2. To the polymer solution are added a slurry of titanium dioxide in dimethylacetamide and a solution of poly-(N,N-diethyl-beta-aminoethyl methacrylate) in dimethylacetamide such that the final mixture contains 5% of each additive, based on the elastomeric solids.

The foregoing mixture is heated to a temperature of 70° C. and spun into a dry spinning column in the conventional manner. The individual filaments are brought into contact within the column and adhere to one another to give a coalesced multifilament of about 280 denier. Upon emergence from the column, the coalesced multifilament is treated with a finish having the following composition:

	Percent
Mineral oil (No. 50) -----	95.5
"Myrj 45" ¹ -----	3.0
Magnesium stearate -----	1.5

¹ Polyethylene oxide ester of stearic acid sold by Atlas Chemical Industries (adduct of 8 mols of ethylene oxide per mol of stearic acid).

When unwound from a bobbin, the spandex filament so treated shows substantially no tendency to stick to adjacent filaments.

Example II

A finish having the following composition is applied to the as-spun, untreated spandex yarn of Example I:

	Percent
Mineral oil (No. 50) -----	99
"Myrj 45" -----	0.5
Magnesium stearate -----	0.5

Results with the finished yarn are similar to those from Example I.

Example III

A finish having the following composition is applied to the as-spun, untreated spandex yarn of Example I:

	Percent
Mineral oil (No. 50) -----	95
"Myrj 45" -----	3
Magnesium stearate -----	2

Results with the finished yarn are similar to those from Example I.

Example IV

A finish having the following composition is applied to a sample of the polyester-based spandex fiber described in U.S. Patent 2,953,839:

	Percent
Mineral oil (No. 50) -----	95
"Myrj 45" -----	4
Magnesium stearate -----	1

With only 3.5% by weight of this finish on the yarn, very acceptable frictional properties and uniform takeoff tension are found on unwinding the treated yarn.

Example V

Finishes having the compositions indicated in the table below are applied to separate samples of the as-spun, untreated spandex yarn of Example I.

TABLE

Finish			Finish on Yarn (Percent)	Average Frictional Force (grams)	Maximum Deviation in Observed Frictional Measurements (grams)
Mineral No. 50 (Percent)	Magnesium Stearate (Percent)	Polyethylene Oxide Ester			
95-----	1.0	4.0% "Myrj 45"-----	15.2	7.5	0.5
95-----	0.5	4.5% "Myrj 45"-----	13.3	7.5	0.5
95-----	0.5	4.5% Atlas Compound TL-142 *	17.5	7.5	0.6
95-----	1.0	4.0% Atlas Compound TL-143 **	12.0	8.0	0.6
95-----	0.5	4.5% Atlas Compound TL-143	11.7	7.5	0.6
100-----	0	0-----	15.1	7.5	2.0

* Adduct of 10 mols of ethylene oxide per mol of behenic acid.

** Adduct of 20 mols of ethylene oxide per mol of behenic acid.

The average frictional force in the table above refers to the average force required to overcome the friction between yarn and guide in measurements on a running end of lubricated yarn and is measured at a 70° angle on a dual strain gauge recording yarn frictometer at 100 yards per minute with a 10 gram input load using a dull Cr₂O₃ pin. Where the maximum deviation from the average frictional measurement exceeds 0.75 gram, it is found that the unwinding tension in over-end takeoff is unacceptably erratic. From these data, it is evident that acceptable over-end takeoff tensions are obtainable with dispersed soap contents of less than 2% by weight, when the polyethylene oxide esters of the higher fatty acids are present in the finish.

In the above examples, the physical properties of the elastomeric yarn are not adversely affected by the finish used. Tenacity, elongation, modulus, stress decay, and tensile recovery are measured and found to be essentially equal to the same properties of the identical elastic filament having no finish.

As noted in the examples, the finishes of this invention contain a substantially lower content of dispersed soap than do the aforementioned finishes described in Yuk in U.S. 3,039,895. The advantages of lower soap content are many. In addition to economy of materials, reduction in soap content provides improved stability of the dispersion of the soap particles in the textile oil. This results in less settling of solids in the finish troughs with attendant advantages of less frequent need for cleaning the troughs and/or an easier trough-cleaning operation. Moreover, the lubricated elastic filaments of this invention essentially eliminate the problem of solid deposits building up on yarn guides and knitting needles, which problem has been associated with the use of the Yuk finishes.

Furthermore, the finishes of this invention are generally self-emulsifying in water. Emulsification, together with the low soap content, eliminates an objectionable scum which forms during boil-off on fabrics containing the Yuk finishes. Also, the mild plasticizing effect of the polyethylene oxide esters gives improved processing properties to spandex yarns finished in accordance with this invention. More even lay-down of threads on beams during warping is obtained, knots are more easily tied,

and improved stitch formation is obtained in bare power-net fabrics.

In the above examples the finish is applied to continuous filament elastomeric yarns. Alternatively, individual fine denier filaments, for example, 6 denier or less, may first be treated with the finish of this invention, then collected into a continuous filament tow, which may be cut into staple. The lubricated elastic filaments of staple length may be blended with inelastic staple as taught in U.S. 3,007,227, which blends are useful in the formation of elastic yarn. Staple blends may also be formed by proper blending of the lubricated continuous filament tow with a tow of inelastic continuous filaments and then cutting the blend of tows to staple length.

The lubricated elastic filaments of this invention are useful in a wide variety of products in both the covered and uncovered states. The continuous filaments find

particular utility in foundation garments, girdles, corsets, surgical hosiery, woven or knitted swimwear, socks, and sock tops. The staple blends are useful for making a wide variety of elastic or stretchy products including woven, knitted and non-woven fabrics for use in universal fitting apparel, form-fitting upholstery, surgical stockings, and splint tapes.

As many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not to be limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A lubricant composition for application to a filament of a synthetic segmented elastomeric copolymer, the composition consisting essentially of a textile oil; at least about 0.5% by weight of a normally solid polyethylene oxide monoester of a higher fatty acid having 6 to 12 mols of ethylene oxide per mol of fatty acid containing 12 to 22 carbon atoms, said ester being soluble in said textile oil at a temperature above its melting point of at least 25° C.; and from about 0.5% to less than about 2% by weight of finely divided particles of a metal salt of a fatty acid containing from about 8 to 22 carbon atoms dispersed in the ester-oil solution, said metal being selected from the class consisting of Group Ia metals having an atomic weight between about 7 and 133, Group II metals having an atomic weight between about 24 and 137, and a Group III metal having an atomic weight of about 27, said particles having an average radius in the range between 0.05 to 5 microns.

2. The composition of claim 1 wherein said fatty acid is stearic acid and said ester contains 8 mols of ethylene oxide per mol of acid.

References Cited by the Examiner

UNITED STATES PATENTS

2,025,435	12/1935	Bouhuys.	
2,682,486	6/1954	Humphreys	117—139.5
2,690,426	9/1954	Jefferson et al.	117—139.5 XR
3,039,895	6/1962	Yuk	117—138.8

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