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3,296,063

SYNTHETIC ELASTOMERIC LUBRICATED  
FILAMENT

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This invention relates to lubricated elastic structures and in particular to filaments of synthetic, segmented, elastomeric copolymers having thereon a lubricating finish containing polyamylsiloxane.

It is well known that elastic filaments made of rubber or of a segmented elastomer, e.g., of the spandex type, generally require 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 problem in tidiness as well as a dust hazard, since it is scattered around the area in which the yarn is finished and processed. Moreover, a talc-coated filament presents serious abrasion problems both on 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 3,039,895, wherein it is taught that a textile oil, such as mineral oil, may be used as a finish for filaments of synthetic, segmented, elastomeric copolymers when 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 requisite presence of the finely divided soap 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 in filament guides and needles in knitting machines and other processing equipment for the elastic filaments. Other disadvantages of known liquid finishes for spandex filaments are as follows: they tend to foster discoloration of the filaments, they are seriously deficient in providing antistatic protection, or they have an objectionable odor.

This invention provides elastic filaments with a lubricating finish which may be processed without difficulty. More particularly, this invention provides elastic filaments with a stable finish which need not contain any particulate solid material and yet furnishes adequate frictional properties on the filaments. Furthermore, the elastic filaments of this invention are provided with a lubricating finish that (1) may be used in lesser amounts on the filaments than has heretofore been required, (2) plasticizes the filaments, and (3) affords antistatic protection without promoting discoloration. Other advantages will be apparent from the following detailed description.

The advantages of this invention are attained by providing an elastic structure comprising a filament of a synthetic, segmented, elastomeric copolymer having a lubricating finish thereon, with the finish having as essential ingredients a minor proportion of a polyamylsiloxane component having a viscosity of from about 8,000 to about 20,000 centistokes and a major proportion of a polydi-

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methylsiloxane component having a viscosity from about 5 to about 100 centistokes. Surprisingly, I have discovered that when the polyamylsiloxane is used with the polydimethylsiloxane not only is superior lubricity provided for the elastic filament without the need for solid particles being dispersed in the finish but also a substantial degree of antistatic protection is provided. I have also discovered that the polyamylsiloxane has a beneficial plasticizing effect on the filament, rendering it more supple and thereby more readily processable. When reference is made herein to the presence of the polyamylsiloxane on the elastic filament, it is not intended that the total amount of the ingredient be on the surface of the filament since a portion of it may be absorbed.

The polyamylsiloxane which in combination with the polydimethylsiloxane provides the advantages of this invention is a liquid, trifunctional polyamylsiloxane having unique properties. It is prepared by the hydrolysis and condensation of n-amytrichlorosilane, which may be obtained as described in U.S. Patent 2,632,013 by the reaction of trichlorosilane and 1-pentene. The hydrolysis of the amytrichlorosilane is carried out in a medium comprised of isopropyl ether and water. Several washing steps are carried out, and the hydrolyzate is neutralized by refluxing with a mixture of sodium bicarbonate and water. The ether and water are removed, and the hydrolysis product is dissolved in toluene and refluxed with sodium hydroxide to effect a further condensation-equilibration reaction. During this reaction, residual water is removed as an azeotrope with toluene. The product is then filtered and is obtained as a liquid having a viscosity in the range of 8,000 to 20,000 centistokes. A polyamylsiloxane having a viscosity in the range of 13,000 to 17,000 centistokes is preferred for this invention.

The trifunctional polyamylsiloxane prepared as described above is quite different from the conventional, trifunctional siloxane resins in that care is taken to reduce residual chloride and hydroxyl contents to a minimum. As is well known, the conventional, trifunctional siloxane resin systems are generally prepared with the express purpose of providing sufficient hydroxyl and/or alkoxy content to insure proper curing. Moreover, conventional resin systems contain difunctional units to provide property improvements and to insure lower viscosity characteristics. Why the polyamylsiloxane resin behaves so differently from closely related materials is not precisely known. One possible explanation of its behavior is that the siloxane polymer is produced in the form of cyclic chains rather than in a highly cross-linked form. One outstanding property of the polyamylsiloxane is its compatibility with conventional dimethyl silicones and with mineral oil.

The polydimethylsiloxanes which are combined with the polyamylsiloxanes in preparing the finishes for use in this invention are well-known silicone oils. Those having viscosities from about 5 to about 100 centistokes at 25° C. are solvents for the polyamylsiloxanes and the two form a homogeneous mixture at 25° C. Mixtures of each component may be employed.

The segmented copolymers from which the elastic filaments of this invention may be prepared consist 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. As is known (see vol. 740, Official Gazette, p. 2, March 3, 1959) spandex is a generic term for a manu-

factured fiber in which the fiber forming substance is a long chain synthetic polymer comprised of at least 85% of a segmented polyurethane. The segmented copolymers may have either a linear or cross-linked structure.

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, 3,044,990, 3,071,557, and 3,097,192. 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 decays below about 20%. The terms "elastic recovery" and "stress decay" are defined in U.S. Patent 2,957,852.

The finishes of this invention are applied to the filaments of the segmented elastomers in any conventional manner. Generally, sufficient finish to provide at least about 0.025% of the polyamylsiloxane, based on the weight of the untreated elastic filament, is required before beneficial antistatic properties are evident. However, no absolute minimum of the polyamylsiloxane can be specified for all situations. Obviously, minimum static on a running yarn line is desirable. For the usual spandex filaments, a maximum level of acceptable static is  $\pm 1,000$  volts, measured at a yarn speed of 20 yards (18.3 meters) per minute as described hereinafter.

The maximum amount of the polyamylsiloxane that may be used is not critical; however, amounts in excess of about 2% are generally not required. Practical considerations of viscosity and ease of application also govern the amount of the different components to be used in the finish. Those skilled in the art can readily adjust the proportions to provide the required percentage of polyamylsiloxane on the filaments. For general use, a finish viscosity of about 100 centistokes at 25° C. is a practical upper limit. A mixture of about 50% polyamylsiloxane, having a viscosity of from about 8,000 to about 20,000 centistokes, and 50% polydimethylsiloxane, having a viscosity of 20 centistokes, will provide this maximum viscosity.

The total amount of finish to be applied to the filaments is not critical and is limited by practical considerations. Since amounts as great as 12% may result in the finish dripping from the filaments, in most instances lesser amounts should be used.

The finish may be applied to elastic filaments 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 spandex fibers as they are being spun, the trough-roller apparatus is preferably located at a point just beyond the first driven feed roll which the spandex filaments contact after leaving the spinneret.

The addition of a finish containing polyamylsiloxane to the spinning solution, i.e., cospinning, is a convenient and advantageous method of application. The finish ingredients are added to the spinning solution and extruded simultaneously with the fiber-forming materials. This is particularly advantageous in spinning fine-denier, elastic threads, e.g., 20-denier spandex. This method requires no finish roll and permits a lower spinning tension, which is especially important in producing fine deniers.

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. In Examples III, IV, and V, static generation of the yarn samples is determined with a Keithley Electrostatic Voltmeter by measuring the charge built up on a Cr<sub>2</sub>O<sub>3</sub> pin having a matté finish when the yarn sample is

being passed over the pin at a 70° angle and with a 10-gram load at 60–62% relative humidity and at a temperature of 22–23° C. Except for Example III, the yarn passes over the pin at a speed of 20 yards (18.3 meters) per minute.

#### EXAMPLE I

Polytetramethylene ether glycol of molecular weight about 2000 and p,p'-methylenediphenyl 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 90–150 minutes to yield an isocyanate-terminated polyether, cooled to below 45° C., is conducted at a rate of 17.5 parts per hour into a mixer, and a stream of N,N-dimethylacetamide is added at 27.6 parts per hour. The mixture (39% solids) is discharged continuously into a pipeline and conducted to a second mixer, in which it is intimately mixed with a stream of dimethylacetamide containing 9.1 per cent metaxylylenediamine and 0.6 percent diethylamine, added at a total rate of 10.3 parts per hour. The residence time is 3–4 minutes, and the temperature rises from about 40° C. to 90° C. The emerging polymer solution contains approximately 33.7% solids and has a viscosity of 1450 poises at 40° C. The polymer has an inherent viscosity of 1.27, measured at 25° C. in hexamethylphosphoramide at a concentration of 0.5 gram per 100 ml. of solution. To the polymer solution are added a slurry of titanium dioxide in dimethylacetamide, a solution of poly-(N,N-diethyl-beta-aminoethyl methacrylate) in dimethylacetamide and a solution of 4,4'-butylidene bis-(6-t-butyl-m-cresol) in dimethylacetamide such that the final mixture contains 5%, 5% and 1% respectively, 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 yarn of about 420 denier (46 Tex). Upon emergence from the column, the coalesced multifilament yarn is treated with a finish having the following composition:

10% polyamylsiloxane (viscosity 10,000 centistokes)  
90% polydimethylsiloxane (viscosity 20 centistokes)

The above-described finish is applied to the spandex filaments at levels of about 1.5% and 3.8%, based on the weight of the spandex. When unwound from a bobbin, the spandex filament so treated shows substantially no tendency to stick to adjacent filaments and may be unwound under very low tension. In a comparative test it is found that in order to provide an equally low tension in unwinding the filaments from a wound package, about 12% to 15% by weight of the mineral oil-based finishes of the prior art (e.g., containing 5% dispersed magnesium stearate, as described in U.S. 3,039,895) is required. At finish levels of only 1% to 4%, such prior art finishes fail to prevent breaks during unwinding of the spandex yarn.

The plasticizing action of the polyamylsiloxane is seen in the following data. A typical circular-knit girdle fabric is made on a 13-inch, 36-gauge Scott & Williams DRC rib-knitting machine, using two ends of the above-described spandex and four ends of 100-denier, bulked nylon. Samples are made using spandex having different finishes as indicated in the table below. The number of breaks during the knitting of comparable amounts of fabric are indicated.

Finish	Percent Finish on Yarn	Number of Breaks
10% Polyamylsiloxane.....	1.5	0
90% Polydimethylsiloxane.....		
10% Polyamylsiloxane.....	3.8	0
90% Polydimethylsiloxane.....		
100% Polydimethylsiloxane.....	3.4	4

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The benefit of the polyamylsiloxane in providing a more supple yarn is seen by comparison with the finish without this ingredient which shows a relatively high number of breaks as the thread enters the knitting needles. To achieve knitting performance equivalent to the finishes of this invention, about 12% of a mineral oil-based finish containing magnesium stearate is required.

## EXAMPLE II

Finishes having the following compositions are applied in the amounts indicated to coalesced spandex multifilament yarns of 420 denier (46 Tex), prepared as described in Example I.

Finish	Percent Finish on Yarn	Take-off Tension (grams)	Frictional Force (grams)
None.....	0	( <sup>1</sup> )	( <sup>1</sup> )
10% Polyamylsiloxane.....	1.3	1.2	10.5
90% Polydimethylsiloxane.....			
10% Polyamylsiloxane.....	3.9	0.8	9.5
90% Polydimethylsiloxane.....			
100% Polydimethylsiloxane.....	3.2	1.9	14
95% Mineral oil (No. 50).....	15.3	1.0	15.5
5% Magnesium stearate (Dispersed as described in U.S. 3,039,895)			

<sup>1</sup> Too high to measure.

The take-off tension in the table above refers to the tension required for over-end delivery at 90 yards (82.3 meters) per minute from the package of yarn. The frictional force in the table refers to the force required to overcome the friction between yarn and guide in a running end of yarn and is measured at 70° angle on a dual strain-gauge frictometer at 100 yards (91.4 meters) per minute with a 10-gram input load using a Cr<sub>2</sub>O<sub>3</sub> pin having a matte finish. From these data, it is evident that a finish containing polyamylsiloxane provides equivalent or better running and take-off tensions at lower finish levels than do the finishes of the prior art.

## EXAMPLE III

Finishes consisting of varying amounts of polyamylsiloxane in polydimethylsiloxane are applied with a roller applicator to coalesced multifilament yarn of 420 denier (46 Tex), prepared as described in Example I. Static generation of the yarn samples is determined with the following results.

Percent Polyamylsiloxane In Finish	Percent Finish on Yarn	Percent Polyamylsiloxane on Yarn	Static (volts)
0.....	3.3	0	-1,800
1.0.....	2.2	0.02	-1,700
7.5.....	2.7	0.20	-750
10.0.....	3.2	0.32	-400
0.....	8.8	0	-800
0.75.....	6.2	0.05	-700
10.0.....	7.1	0.71	+200

The static generation in the table above is determined at a yarn speed of 100 yards (91.4 meters) per minute. This yarn speed represents a more severe antistatic test than does a yarn speed of 20 yards (18.3 meters) per minute. From the data above, it is evident that as little as 0.2% of polyamylsiloxane on the yarn is effective in significantly reducing the static-generating properties of the yarn having the polydimethylsiloxane finish and that about 0.7% is sufficient to reverse the charge from negative to positive.

## EXAMPLE IV

Finishes consisting of varying amounts of polyamylsiloxane having a viscosity of 16,130 centistokes at 25° C. in polydimethylsiloxane having a viscosity of 10 centistokes at 25° C. are applied with a roller applicator to coalesced multifilament yarn of 420 denier (46 Tex), prepared as described in Example I. Static generation

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of the yarn samples is determined with the following results.

Percent Polyamylsiloxane in Finish	Percent Finish on Yarn	Percent Polyamylsiloxane on Yarn	Static (volts)
0.....	0	0	>10,000
0.....	1.1	0	-2,000
2.5.....	1.1	0.028	-1,000
7.5.....	1.2	0.09	-400
10.0.....	1.3	0.13	-200

From the data above, it is evident that as little as about 0.025% of polyamylsiloxane on the yarn is effective in reducing the static-generating properties of the yarn to an acceptable level.

## EXAMPLE V

Finishes consisting of varying amounts of the polyamylsiloxane and polydimethylsiloxane of Example IV are applied with a roller applicator to coalesced multifilament yarn of 420 denier (46 Tex), prepared as described in Example I except that in place of the p,p'-methylenediphenyl diisocyanate of that example there is used an equivalent amount of 4,4'-methylenedicyclohexyl diisocyanate of which 50 mol percent is the trans-trans isomer, and in place of the metaxylylenediamine there is used an equivalent amount of 4,4'-methylenedi(cyclohexylamine) of which 15 mol percent is the trans-trans isomer. This yarn contains none of the three additives specified in Example I as based on the elastomeric solids. Static generation of the yarn samples is determined with the following results.

Percent Polyamylsiloxane in Finish	Percent Finish on Yarn	Percent Polyamylsiloxane on Yarn	Static (volts)
0.....	7.0	0	-1,100
2.5.....	7.0	0.175	-80

## EXAMPLE VI

Finishes having the following compositions are applied in the amounts indicated to coalesced multifilament yarn of 420 denier (46 Tex), prepared as described in Example I. Skeins of the yarn are exposed for 77 days to the ambient atmosphere and are measured for "b" values as indicated below.

Finish	Percent Finish on Yarn	"b" Values	
		As Prepared	After Exposure
None.....	0	0.7	3.8
95% Mineral oil (No. 50).....	15.3	0.6	6.7
5% Magnesium Stearate (Dispersed as described in U.S. 3,039,895)			
10% Polyamylsiloxane.....	3.9	0.9	4.0
90% Polydimethylsiloxane.....			

The "b" values in the table refer to the degree of yellowness of a yarn sample. The difference in "b" values indicates the discoloration which develops on exposure of the samples. The "b" values are determined from colorimetric data obtained by analyzing continuous filament samples in which the filaments are arranged in a three-inch square. The reflectance ratios of the samples are determined by measurement with a Hunter Reflectometer, and the "b" values calculated as more particularly described in U.S. 3,095,322.

The data given above show that the finish containing the polyamylsiloxane is superior to the finish containing mineral oil and does not contribute significantly to the yellowing of the spandex yarn.

In the above examples, the physical properties of the elastomeric yarn are not adversely affected by the presence

of the polyamylsiloxane in the finish. Tenacity, elongation, modulus, stress decay, and elastic or tensile recovery are measured and found to be essentially equal to the same properties of the identical elastic filament having no finish. Substantially similar results are obtained when a polyester or N-alkylated polyurethane is substituted for the polyether in the spandex yarn of the examples. Substantially similar results are also obtained when a urethane segment or amide segment is substituted for the bis-ureylene or urea segments of the spandex yarn of the examples.

As illustrated in some of the examples, finishes containing polyamylsiloxane and polydimethylsiloxane perform well on yarn when used at extremely low levels. While no absolute minimum can be specified for all uses of spandex yarn, generally at least about 1% of finish by weight is necessary for lubrication of the yarn. The preferred amount of finish on an elastic yarn of this invention is in the range from about 2% to about 4%, based on the weight of the yarn.

Although the essential ingredients of the finish of this invention are the polyamylsiloxane and the polydimethylsiloxane, other ingredients may be added without detrimental effect to the lubricating and antistatic properties provided by the essential ingredients. For example, minor amounts of other silicone oils, mineral oil, butyl stearate, methyl ricinoleate, butyl acetylrucinoleate, oil-soluble polyether glycols, and alkyl phenol ethers may be added. Isopropyl alcohol and trichloroethylene are also compatible with the polyamylsiloxane and may be used with it. Special plasticizers for spandex filaments may be used although they are not generally required when using the finish of this invention because of the beneficial plasticizing effect of the polyamylsiloxane. Such plasticizers include ethylene oxide/fatty acid adducts, e.g., a polyethylene oxide ester of stearic acid. In some instances, metal soaps such as those disclosed in U.S. 3,039,895, e.g., zinc stearate and magnesium stearate may be used in small amounts i.e., less than about 2% by weight. It is to be noted, however, that mineral oil and dispersed solids such as those just mentioned can be completely eliminated when using the finish of this invention. The elimination of this material results in obvious advantages in cleanliness and in safety.

The elimination of mineral oil from the present finishes for spandex and the elimination of the need for using dispersed solids, such as magnesium stearate as taught in U.S. 3,039,895, result in obvious advantages in cleanliness and in safety, when the finishes of this invention are used.

In the above examples, a multifilament yarn of large denier is formed by coalescence of many smaller filaments before applying the polyamylsiloxane/polydimethylsiloxane finish. Alternatively, a single monofil may be extruded and treated; or, individual fine denier filaments, for example, 6 denier or less, may first be treated with the

finish, then collected into a continuous filament tow, which may be cut into staple. The 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, as taught in U.S. 3,077,006.

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. Use of the present invention provides reduced streakiness in hosiery and power nets.

I claim:

1. A filament prepared from a synthetic segmented elastomeric copolymer having a lubricating finish thereon, said finish having a viscosity of less than about 100 centistokes measured at 25° C. and having as essential ingredients a minor proportion of a polyamylsiloxane component having a viscosity of from about 8000 to about 20000 centistokes measured at 25° C. and a major proportion of a polydimethylsiloxane component having a viscosity within the range of from about 5 to about 100 centistokes measured at 25° C., said polyamylsiloxane being present in an amount equal to at least about 0.025% by weight of said filament.

2. A filament according to claim 1, the finish containing about 2.5 to 10% of the polyamylsiloxane and the remainder the polydimethylsiloxane.

3. The filament of claim 1 wherein said finish is present on said filament in an amount from about 2% to about 4% by weight of said filament.

4. The filament of claim 1 wherein said filament is a spandex filament.

5. The filament of claim 3 wherein said finish contains about 10% of said polyamylsiloxane and about 90% of said polydimethylsiloxane.

#### References Cited by the Examiner

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