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LUBRICATING ELASTOMERS WITH SILICATE ESTERS

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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 comprised of organic silicate esters.

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 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, makes a satisfactory 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 on filament guides and needles in knitting machines and other processing equipment for the elastic filaments. In addition, liquid finishes tend to be absorbed by the spandex filaments. Also, known liquid finishes for spandex filaments tend to foster discoloration of the filaments.

It is, therefore, an object of this invention to provide an elastic filament with a lubricating finish which may be processed without difficulty. A more particular object of this invention is to provide an elastic filament with a stable finish which need not contain any particulate solid material and yet provides adequate frictional properties on the filament. Another object is to provide an elastic filament with a lubricating finish that may be used in lesser amounts on the filament that have heretofore been required. Still another object is to provide an elastic filament with a lubricating finish which inhibits fume discoloration, especially in comparison with mineral oil base formulations. Other objects will be apparent from the following detailed description.

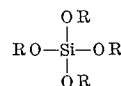
The objects of this invention are accomplished by providing a lubricated elastic structure comprising a filament of a synthetic segmented elastomeric copolymer and a higher organic silicate ester. Surprisingly, I have discovered that the higher organic silicates are good not only as lubricants for spandex filaments without the need for solid particles dispersed therein, but also that they afford

a substantial degree of protection against fume discoloration of spandex filaments.

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, bis-ureylene 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.

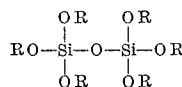
The segmented copolymers described in several patents are useful in the practice of this invention. Among these are U.S. Patents 2,929,801, 2,929,802, 2,929,803, 2,929,804, 2,957,852, 2,962,470, 3,009,901, 3,023,192, 3,037,960, 3,040,003, 3,044,987, 3,44,989, and 3,044,990. As disclosed in these references, 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 decays below about 20%. The terms "elastic recovery" and "stress decay" are defined in U.S. 2,957,852.

The organic silicate esters which provide the base of the lubricant of this invention include the orthosilicate esters having the formula:



wherein R represents monovalent organic radicals which may be the same or different. The higher orthosilicate esters are the compounds wherein each R group is an alkyl radical containing at least 6 carbon atoms. The maximum number of carbon atoms in the R groups is not critical, but as a practical matter, 18 carbon atoms may be considered an upper limit. The alkyl radicals may have substituents, such as chloro, nitro, fluoro, alkoxy, etc., groups.

Also included within the term "organic silicate esters" is a class of compounds sometimes called "dimer silicates." These compounds are the hexaalkoxydisiloxanes having the formula:



in which the R groups may be any of the organic radicals previously described having at least 6 carbon atoms. The radicals may be identical or dissimilar.

The organic silicate esters having 6 or more carbon atoms in the alkyl chain are generally quite resistant to hydrolysis and therefore comprise the silicates useful in this invention. The various R groups in the orthosilicates and in the hexaalkoxydisiloxanes may be primary, secondary or tertiary alkyl groups, i.e., the carbon atom attached to the oxygen atom may bear, respectively, two, one, or no hydrogen atoms. A preferred group of organic silicate esters in the practice of this invention comprises compounds in which all R groups are (1) tertiary, (2) secondary, or (3) primary with alkyl-substitution on the second carbon atom of the chain. Specific silicate compounds for use in this invention are: tetra-n-hexyl silicate, tetra-n-heptyl silicate, tetra-n-octyl silicate, tetra-n-decyl silicate, tetrakis(1-ethyl-pentyl) silicate, tetrakis(2-ethylbutyl) silicate, tetrakis(2-ethylhexyl) silicate, hexaalkoxydisiloxane, hexakis(2-ethylbutoxy)disiloxane, and hexakis(2-ethylhexoxy)disiloxane. Mixtures of organic silicates may be used if desired. Preferably, the organic silicate esters have viscosities at a temperature of about 25° C. in the range from about 10 to 100 centi-

poises. If the viscosity is too great at a particular application temperature, a diluent such as a silicone oil or a volatile diluent may be used to facilitate application. While solid organic silicate esters are not preferred, they could be finely ground and applied, using a diluent of the type just described.

While the organic silicate esters may be used as the sole component in the finish in the practice of this invention, other ingredients may advantageously be present in the finish. For example, the organic silicate esters may be mixed with the silicone oils, such as the dimethylpolysiloxanes having viscosities from about 10 to about 50 centipoises, to provide a particular useful finish. Plasticizers for spandex, such as an ethylene oxide/fatty acid adduct (e.g., polyethylene oxide ester of stearic acid) may be used in small amounts in the finish. Metal soaps as disclosed in the aforementioned Yuk patent, such as zinc stearate and magnesium stearate, may be used in small amounts (e.g., less than about 2%), and emulsifying aids such as morpholine oleate may be used in amounts up to about 5%.

The finishes of this invention may be applied to the spandex filaments 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 spandex 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 spandex filaments contact after leaving the spinneret.

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-diphenyldiisocyanate 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:

63.8% tetrakis(2-ethylhexyl) silicate
35.0% DC-200-20 silicon¹
1.0% "Myrj 45"²
0.2% magnesium stearate

¹ A dimethylpolysiloxane sold by Dow-Corning (viscosity 20 centipoises).

² A 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.

Similar results are obtained with related formulations. In some of these, the percentage of the above silicate is varied from about 45% to 100%. In others, silicone oils varying in viscosity from 10 to 50 centipoises are used. In others, the magnesium stearate is varied from 0% to 2%, and in still others "Myrj 45" is varied (or replaced with morpholine oleate) from 0% to 5%.

Example II

Finishes having the following compositions are applied in the amounts indicated to coalesced spandex multifilament yarn of 420 denier, prepared as in Example I.

Finish	Percent Finish on Yarn	"b" Values	
		As Prepared	After Fume Exposure
None	0	-0.9	11.2
2-ethylbutyl silicate	10.1	-0.5	8.6
2-ethylhexyl silicate	13.9	-0.4	8.2
95% mineral oil (No. 50), 3% "Myrj 45," 2% magnesium stearate (dispersed as in U.S. 3,039,895)	11.4	-0.4	12.0

The "b" values in the table above and in Example IV below refer to the degree of yellowness of a yarn sample. The difference in "b" values indicates the discoloration which develops in fume-fading tests, which are carried out according to AATCC standard test method 23-1957, as described at pages 104-106 of The Technical Manual of the American Association of Textile Chemists and Colorists (1960). The samples are exposed for 16 hours in the test oven. The "b" values are determined from colorimetric data obtained by analyzing continuous filament samples which are about three inches square. The reflectance ratios of the samples in the green and blue filter settings of a colorimeter are measured, using a Model IV Color Master Differential Colorimeter, manufactured by Manufacturing Engineering and Equipment Company, Hatboro, Pennsylvania, and calibrated against the manufacturer's standard reference plates and the National Bureau of Standard's certified reflectance plates. Three readings are taken on each of the samples, one of the measurements for the filament sample being made with the sample rotated 90° from the position of the first reading. The "b" values are then calculated from the average of three readings using the following formula:

$$b = 42.34 G\% B\%$$

where G represents the reflectance ratio with the green filter and B represents the reflectance ratio with the blue filter.

The data given above clearly show that the finishes based on the organic silicates contribute to a marked decrease in discoloration of the yarn on exposure to acid fumes.

Example III

Finishes having the following compositions are applied in the amounts indicated to coalesced multifilament yarn of 70 denier, prepared as in Example I of U.S. 3,039,895.

Finish	Percent Finish on Yarn	Frictional Force (grams)
50% 2-ethylhexyl silicate, 50% silicone (DC-200-10)-----	4.5	8
Do-----	8.4	6
95% mineral oil (No. 50), 3% "Myrj 45," 2% magnesium stearate-----	4.7	37
Do-----	8.4	16

The frictional force in the table above refers to the force required to overcome the friction between yarn and guide in a running end of lubricated yarn and is measured at 70° angle on a dual strain gauge recording yarn frictionometer at 100 yards per minute with a 10 gram input load using a dull Cr₂O₃ pin. From these data, it is evident that the organic silicates provide a much lower running tension at the same finish content than does a finish based on mineral oil. Accordingly, the organic silicates provide equal surface lubrication at much lower finish contents than is possible with finishes based on mineral oil. The sample of yarn having the mineral oil finish at a level of 4.7% breaks for want of satisfactory lubrication when pulled through a knitting needle, whereas samples of yarn containing 4.5% of the silicate-containing finish run well. In hosiery knitting tests, samples of these yarns containing from about 3% to about 8% of the silicate-containing finish run as well or better than yarns containing 15% of the mineral oil finish.

Example IV

Finishes having the following compositions are applied 420-denier, as-spun, untreated coalesced spandex multifilaments, prepared as in Example I. Skeins of yarn are measured for "b" value and then exposed for six weeks to the ambient atmosphere of the laboratory and again measured. Results are as follows:

Finish	Percent Finish on Yarn	"b" Values	
		As Prepared	6 Weeks' Atmospheric Exposure
50.0% (2-ethylhexyl) silicate, 48.5% DC-200-20 silicone, 0.5% morpholine, 0.8% oleic acid, 0.2% magnesium stearate-----	5.6	0	8.9
None-----	0	0	7.3
95% mineral oil (No. 50), 3% "Myrj 45," 2% magnesium stearate-----	12.7	-0.1	12.5

In the above examples, the physical properties of the elastomeric yarn are not adversely affected by the presence of the silicate-based 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 urea segment, urethane segment, or amide segment is substituted for the bis-ureylene segment of the spandex yarn of the examples.

As noted in the example, an outstanding advantage of the organic silicates is that they provide equivalent surface lubrication at much lower finish contents than do the mineral oil-based finishes of the prior art. As illustrated in some of the examples, finishes containing the organic silicates 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 2.5% of finish by weight is adequate for lubrication of the spandex yarn. However, a spandex yarn having 0.5% of tetrakis (2-ethylhexyl) silicate as the sole finish component ran on a Tompkins knitting machine satisfactorily and with no yarn breaks. The preferred amount of finish on an elastic

yarn of this invention is in the range from 3% to about 5%, based on the weight of the yarn. Good results are obtained when from about 1½% to about 10% by weight of the silicate ester is present on the yarn.

Another outstanding advantage of the finishes of this invention is their contribution to reduction in fume discoloration of spandex, a somewhat pressing problem at the present state of the art. The reason for this protection from fume discoloration is not known, but it may possibly be attributed to low sorption of the silicate by the spandex yarn. However, I do not wish to be bound by any particular theory or mechanism in explanation of the advantages of this invention.

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 housekeeping and safety, when the finishes of this invention are used. Additional advantages which the organic silicate esters possess are their low surface tension, high boiling point, minimum change in viscosity with temperature, ease of scour, good hydrolytic stability, and low toxicity.

In the above examples, a multifilament yarn of large denier is formed by coalescence of many smaller filaments before applying the organic silicates to produce the filaments of this invention. Alternatively, individual fine denier filaments, for example, 6 denier or less may first be treated with the finish based on organic silicates, 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 blends 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 lubricated elastic structure having improved color stability comprising a filament of a synthetic segmented elastomeric copolymer having thereon at least about 0.5% by weight of an organic silicate ester selected from the group consisting of orthosilicate esters and dimer silicates in which each organic radical which is attached through an oxygen to the silicon atoms is an alkyl radical and contains at least six carbon atoms.

2. The elastic structure of claim 1 wherein said organic radical has from six to eighteen carbon atoms and said organic silicate ester is present in an amount of at least about 2.5% by weight.

3. The elastic structure of claim 2 wherein said organic silicate ester has a viscosity at a temperature of about 25° C. in the range from about 10 to 100 centipoises.

4. The elastic structure of claim 2 wherein said organic silicate ester is tetrakis(2-ethylbutyl)silicate.

5. The elastic structure of claim 2 wherein said organic silicate ester is tetrakis(2-ethylhexyl)silicate.

6. The elastic structure of claim 2 wherein said organic silicate ester is hexakis(2-ethylbutoxy) disiloxane.

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7. The elastic structure of claim 2 wherein said filament is a spandex filament.

8. The elastic structure of claim 7 wherein said organic silicate ester is present in an amount from about 3% to about 5% by weight.

9. A lubricated elastic structure having improved color stability comprising a spandex filament having thereon at least about 2.5% by weight of an organic silicate ester having a viscosity at a temperature of about 25° C. in the range from about 10 to 100 centipoises, said silicate ester being selected from the group consisting of alkyl silicate esters and hexaalkoxydisiloxanes, each of the alkyl groups which are attached through an oxygen atom containing six to eighteen carbon atoms to the silicon atoms.

10. The elastic structure of claim 9 wherein said organic silicate ester is present in an amount from about 3% to about 5% by weight.

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