United States Patent Office 3,704,160
Patented Nov. 28, 1972

3,704,160

FINISH FOR NYLON OR POLYESTER ROPE

William George Steinmiller, Charlotte, N.C., assignor to Fiber Industries, Inc.

No Drawing. Filed Dec. 30, 1970, Ser. No. 102,888
Int. Cl. B32b 27/02; C10m 3/20
U.S. Cl. 117—138.8 F 12 Claims

ABSTRACT OF THE DISCLOSURE

Yarn, suited for making rope, comprising nylon or polyester carrying about 1 to 5% by weight of a finish comprising, by weight,

(a) about 5 to 25% of a described tri-fatty acid ester of a cross-linked, tetra-alkyl, hydroxy substituted furan or pyran,
(b) about 1 to 5% of a metallic fatty acid soap, and
(c) about 70 to 90% of an oil carrier.

The present invention relates to a finish for nylon or polyester yarn for use in rope and cord-like structures.

For cordage purposes conventional textile lubricants are not always adequate. Oftentimes it is found the yarn loses strength upon exposure to heat or water. If the yarn is plied to make large bundles, a considerable fraction of the strength of the component yarns is not carried through the conversion. In addition, the frictional properties required of ropes are different from those of yarns intended for normal textile applications, i.e. for ropes the structure should run smoothly rather than alternately slipping and sticking.

While various finishes have been proposed for yarns intended for cordage, they have suffered from being inapplicable to nylon or polyester, or from cost, or they have improved one property while leaving others unaffected or impaired.

It is accordingly an object of the invention to provide a novel finish for nylon and polyester yarns which render them especially suited for use in cordage.

These and other objects and advantages are realized in accordance with the present invention wherein there is provided a nylon or polyester yarn carrying about 1 to 5%, and preferably about 2 to 4% by weight of a finish comprising, by weight,

(a) about 5 to 25% of a cross-linked, tri-fatty acid ester, of a tetra-alkyl, hydroxy-substituted furan or pyran as hereinafter described,
(b) about 1 to 5% of a metallic fatty acid soap, and
(c) about 70 to 90% of an oil carrier.

While the foregoing values are based on the weight of fibrous material, since that is quite close to the weight of fiber plus finish, for ease values may be computed approximately based on either.

Yarns so finished can be used as rope or cord per se or can be plied, as by simple twisting, braiding, interlacing, or the like, into larger composite structures such as used for baling twine, venetian blind cords, tow lines, marine hawsers, and the like. Thus, the yarns embraced by the present invention may be free and independent of other yarns or they may be present as part of a larger plied structure.

The finishes referred to herein are applied hot and may be applied to the individual yarns or they may be applied to the plied structure. Such application may be by causing the yarns to run over a surface wetted with the finish, e.g., a rotating roll whose lower portion dips into a reservoir containing the hot finish heated to between 50–80° C. preferably 60–70° C. Alternatively, the running yarn by a system of guides may be caused to run through a trough containing the heated finish. In such event, since the liquid pick-up will be much greater, the finish may be diluted with a volatile solvent which will subsequently evaporate, e.g. low molecular weight alcohols, ketones, halogenated hydrocarbons, and the like. If inflammable solvents are used, special measures will of course have to be taken with respect to venting and solvent recovery. The finish can also be applied by spraying, as by passing the running yarn through a chamber wherein there is a mist of hot finish.

The finish is heated in order to liquidize the cross-linked triester which is a solid at room temperature, and the fatty acid soaps which may also be solids at room temperature. The finish is maintained at a temperature at least sufficient to retain a homogeneous liquid character. At times it is also desirable to preheat the fibrous substrate. Following hot finish application, the substrate is cooled, generally by exposure to ambient conditions although positive cooling means could be employed, and the finish forms a wax-like water impervious coating resistant to subsequent aqueous washing.

Ropes carrying such finish are characterized by high strength and elongation, i.e. a load is transmitted and distributed substantially uniformly amongst the components making up the yarn, and good fiber to fiber lubrication at high loads. This applies to the individual yarns as well as to plies thereof, whether by twisting or braiding, both dry and wet. The strength is retained even upon prolonged exposure to heat and/or water. The yarns are also characterized by good fiber to metal lubrication at high loads, i.e. as yarns will not alternately grab or bind and then suddenly jerk free but will move smoothly. This fiber to metal friction property is hereinafter denoted as slip-stick performance.

The yarn which carries the finish comprises nylon or polyester. Blends of these with each other or with other fibers can also be employed, such other fibers including cotton, polypropylene, rayon, polyvinyl chloride, glass, metal, and the like, i.e. any other fibers whether natural or synthetic. Such other fibrous material may be included to reduce the overall specific gravity of the rope, to impart predetermined dyeability characteristics, for fire protection, etc.

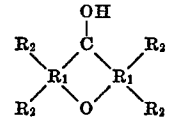
Nylon has reference to linear polyamides whose monomer units comprise radicals of dicarboxylic acids, diamines, amino carboxylic acids, or mixtures thereof, e.g. aliphatic dicarboxylic acids such as adipic acid, dodecanedioic acid or sebacic acid, aromatc dicarboxylic acids such as terephthalic acid or isophthalic acid, diamines such as hexamethylene diamine and bis (para amino cyclohexyl) methane, aminoalkane carboxylic acids such as -aminocaproic acid, -aminoundecanoic acid, and the like, including amino amides such as p-aminobenzamide. Polyester has reference to linear polymers wherein monomer units are linked to one another by ester bonds and includes structures whose monomer units comprise radicals of dicarboxylic acids, glycols, hydroxycarboxylic acids, or mixtures thereof, e.g. aromatic dicarboxylic acids such as terephthalic acid and isophthalic acid, glycols such as ethylene glycol, propylene glycol, butylene glycol or diethylene glycol, hydroxy aromatic carboxylic acids such as p-hydroxy-benzoic acid, and the like. If desired, the fibers may comprise both ester and amide linkages and thus may be an ester-amide blend down at the molecular level. In addition, minor amounts of other monomer units may also be present to function as dye sites, chain stoppers, internal antioxidants or plasticizers, or for other purposes. The preferred polymers, however, are nylon 66 (polyhexamethylene adipamide), nylon 6 (polycaprolactam) and polyethylene terephthalate.

The fibrous material may be in the form of staple fibers twisted into a yarn, in the form of a split film, or the like, but preferably it is in the form of continuous filaments. The denier of the individual filaments may range from as little as 1 or less up to 50 or more although generally it will range from about 3 to 10 and preferably from about 5 to 8. The denier of the yarn and/or plied structures can likewise vary widely. Thus a yarn made up of about 140 nylon filaments each of 6 denier is quite suitable for tire cord, ropes, fabric reinforcement and the like. Three such yarns plied together with twist into a 2520 denier cord is useful for heavier duty, e.g. rope use. For marine and construction applications, hawsers of nylon or polyester as large as (8) eight inches in diameter can be used to tie up ships, lift cargo, and the like. The number of turns per inch of twist in the singles and/or plies, as well as the number of plaits per inch, depend upon the denier and end use and may be varied widely.

The filaments making up the yarn may also comprise fillers, delustrants, stabilizers, or the like, conventional in the art, e.g. titanium dioxide, copper acetate, potassium iodide, etc.

The yarn finish, as noted, comprises three essential ingredients, viz an oil carrier, a metallic fatty acid soap and a tri-fatty acid ester of a compound of the formula

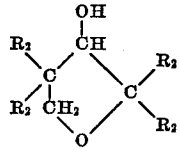
(I)



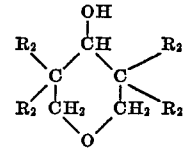
wherein R_1 is a 1 or 2 carbon atom chain alkylene, R_2 is independently selected from 1 to 4 carbon atom chain lower alkyl hydroxy, with each of the R_2 groups being on a single side of the ring attached to the same ring carbon atom, cross linked with a dicarboxylic acid or functional equivalent thereof having a 2 to 6 carbon atom chain between terminal carboxy groups.

Considering the tri-fatty acid ester in greater detail, the ring nucleus thereof can be considered an ester of a furan (5 membered ring) or pyran (6 membered ring). Preferably no unsaturation is present in the ring nucleus, that is, the furan is dihydro and the pyran is tetrahydro; R_2 can be methyl, ethyl, propyl or butyl hydroxy, preferably is methyl or ethyl hydroxy and most preferably is methyl hydroxy. Of course, combinations thereof can be employed but both of the R_2 groups attached to the same ring carbon atom are desirably identical. Also, at least one pair of R_2 groups should desirably be attached to a ring carbon atom adjacent the ring carbon atom to which the hydroxyl group is directly attached and preferably both pairs of R_2 groups so positioned. Therefore, in certain preferred embodiments of the invention the ring compound (I) has a structure selected from the following:

(II)



(III)



wherein R_2 is methyl hydroxy or ethyl hydroxy. More preferably the compound (I) is 3,3,5,5-tetrakis(hydroxymethyl - 4 - hydroxy tetrahydropyran, 3,3,5,5 - tetrakis (hydroxyethyl) - 4 - hydroxy - tetrahydropyran, 2,2,4,4-tetrakis (hydroxymethyl) - 3 - hydroxy- dihydrofuran and 2,2,4,4-tetrakis (hydroxyethyl)-3-hydroxy dihydrofuran. Most preferred compound (I) is 3,3,5,5 - tetrakis (hydroxymethyl)-4-hydroxy-tetrahydropyran.

The tri-fatty acid ester of compound (I) is formed by conventional esterification techniques using a 9–20 carbon atom chain fatty acid. Obviously about three moles of acid would be employed per mol of compound (I). It is

believed that the hydroxyl directly linked to the ring is selectively least susceptible to esterification and consequently participates in the subsequent cross-linking reaction with one of the pendant R_2 hydroxyl groups. The fatty acid may contain some unsaturation, generally only one —CH=CH— group, and have pendant chains such as lower alkyl and hydroxyl. For example the acid or functional equivalent thereof (i.e. acid chloride) may be selected from the group consisting of lauric acid, myristic acid, palmetic acid, ricinoleic acid, oleic acid, pelargonic acid, isostearic acid, stearic acid, and mixtures thereof. Preferably a single acid is used, which acid is most preferably stearic acid to form the tristearate of compound (I).

Cross-linking proceeds easily using about 0.5 to 1.0 or more mol of cross-linking agent per mol of triester so that at least one half of the triester is cross-linked. As examples of diacid cross-linking agents, which can be saturated or unsaturated, there may be mentioned maleic anhydride, pentanedioic acid, heptanedioic acid, the diacid chloride of octane-dioic acid and the like.

While it is not possible to isolate the effect of each component, the tri-fatty acid ester component appears to contribute primarily to the improved fiber/fiber lubrication at high load performance as evidenced by the fact that if it is used in less than about 5% the strength before and after heat ageing is inadequate. Poor fiber/fiber lubrication does not allow an even distribution of load between the cord fiber components.

If more than about 15% is present it is difficult to apply because of its pasty consistency, although such concentrations are usable where properly dispersed. The cross-linked tri-fatty acid ester may be replaced in part with an alkane of about 30 to 60 carbon atoms, provided at least about 5% of the tri-fatty acid ester is still present. When used, advantageously the alkane is present to the extent of at least about 5% to be of significant effect. Thus the preferred range of alkane content is from about 5 to 20%, more preferably 10 to 15%. Such alkane may be the residue of a distillation of aliphatic hydrocarbons of petroleum source.

The metallic fatty acid soap is preferably the salt of a polyvalent metal and an aliphatic carboxylic acid containing about 16 to 22 carbon atoms. Representative polyvalent metals include zinc, aluminum, antimony, calcium, magnesium, barium, sodium, lithium or potassium and the like. Representative fatty acids include stearic, palmitic, oleic, myristic and the like, as well as commercial mixtures thereof. The preferred soaps include zinc stearate, aluminum palmitate and antimony oleate. The soaps can be mono-, bi-, or tris- salts, for example antimony tris-oleate and aluminum mono-palmitate. If present in less than about 1% the soap does not adequately exert its principal influence which appears to be to boundry lubrication, hence in this regard it exerts an effect similar to the tri-fatty acid ester but does not have sufficient activity to provide the needed lubrication under high loads by itself without the presence of the tri-fatty acid ester.

The balance of the finish, i.e. about 70 to 90% comprises mineral oil to impart lubricity to the finish and to yarns and rope made therefrom and to dissolve or disperse the other ingredients. Suitable mineral oils comprise natural or synthetic hydrocarbons having a boiling point within the range of about 105 to 135° C. and a viscosity within the range of about 40 SUS to 355 SUS @ 100° F. (SUS is saybolt universal viscosity).

Optionally, the finish may include a minor amount of an anti-oxidant, e.g. about 0.1 to 1% of a substance such as 3,5-di-tertiary-butyl-4-hydroxy anisole (Topanol 345 available from ICI, America) to inhibit oxidation of the other ingredients.

The finish may be prepared by blending the ingredients, with stirring, in any sequence, although advantageously all ingredients are added to the mineral oil.

The invention will be further described in the following illustrative examples wherein all parts are by weight unless otherwise specified.

EXAMPLE 1 (XF 461)

(a) A nylon 66 yarn of about 840 total denier and comprising 140 filaments held together by ¼–½ turns per inch of S-twist was passed over a rotating roll which dipped into a trough containing a finish comprising, by weight

15% of the tri-stearate ester of 3,3,5,5-tetrakis (hydroxymethyl) - 4 - hydroxy - tetrahydropyran cross-linked with about 0.75 mol maleic anhydride per mol ester, available from the Proctor Chemical Co. of Salisbury, N.C.
2.5% antimony tris-oleate,
0.5% 3,5-di-tertiary-butyl-4-hydroxy anisole, and
82% mineral oil, boiling point 105 to 135° C., viscosity 50 SUS @ 100° F.

The running and rotation speeds were set so that the yarn picked up 3.6% of its weight of finish and the physical properties of the yarn were tested.

(b) The finished yarn of (a) was plied with two other identical yarns by twisting to the extent of about 1 Z turn per inch and the physical properties again tested.

(c) Another sample of the finished yarn of (a) was braided with two other like yarns to the extent of 12 plaits per inch, using a conventional braider and the physical properties again measured.

TABLE

Example	1	2	3	4	5	6
Greige yarn:						
Finish, wt. percent	3.6	1.8	3.2	3.3	3.2	3.1
Denier	867	856	877	882	892	856
Tenacity g./d.	8.32	8.45	8.57	8.64	8.57	8.49
Greige cord:						
Conversion efficiency of tenacity, percent	99	100	99	99	99	102
Braided cord:						
Conversion efficiency, percent	77	77	70	77	66	72
Slip-stick rating	Good	Excellent	Good	Fair	Poor	Good
Conversion efficiency after 5 days in 175° F. air	93	95	97	94	86	99
Slip-stick rating	Excellent	Excellent	Excellent	Good	Poor	Excellent
Conversion efficiency after 8 hrs. in room temp. water, wet	89	90	84	91	----------	89

The physical properties are given in the table hereinbelow.

EXAMPLE 2 (XF 577)

The process of Example 1 was exactly repeated except that the antimony tris-oleate was replaced by the same amount of zinc stearate, and the yarn picked up only 1.8% its weight of finish. The results are given in the table.

EXAMPLE 3

Example 1 was again repeated except that the yarn picked up 3.2% its weight of a finish identical except for replacement of the antimony salt by aluminum palmitate and replacement of half the cross-linked tri-stearate by a straight chain alkane having 33 carbon atoms. Its physical properties are also reported in the table.

Comparative runs were made with the same yarn but using the following finish compositions at the indicated pick ups.

EXAMPLE 4

79% mineral oil
20% C_{33} alkane
1% aluminum palmitate
0.1% 3,5-di-tertiary-butyl-4-hydroxy anisole
3.3% finish on yarn

EXAMPLE 5

74.9% mineral oil
20% C_{22} paraffin
5% sorbitan mono-laurate
1% aluminum palmitate
0.1% 3,5-di-tertiary-butyl-4-hydroxy anisole
3.2% finish on yarn

EXAMPLE 6

A commercial rope finish comprising:

mineral oil,
microcrystalline wax, and
metallic soap used as a control
3.1% finish on yarn

EXAMPLE 7

The finish of Example 1 is used on a polyethylene terephthalate yarn of about 100 denier comprising 192 filaments in a manner essentially identical with the process of Example 1 with equally good results.

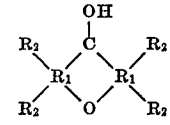
From the following table it can be seen that the novel finishes give yarn physical properties as good as the control but with superior slip-stick performance, which was observed visually in the course of running yarn about a metal capstan during the breaking strength test.

While nylon yarns have been primarly exemplified, substantially similar advantageous properties are achieved by substituting polyester yarns for the nylon.

It will be appreciated that the instant specification and examples are set forth by way of illustration and not limitation, and that various modifications and changes may be made without departing from the spirit and scope of the present invention.

What is claimed is:

1. A polyester or nylon yarn carrying about 1 to 5 percent by weight of a finish comprising, by weight
(a) about 70 to 90% of an oil carrier,
(b) about 1 to 5% of a metallic fatty acid soap, and
(c) about 5 to 25% of a tri-fatty acid ester of a compound of the Formula I

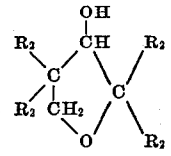


wherein R_1 is a 1 or 2 carbon atom chain alkylene with the proviso that the total of the carbon atoms in both R_1 alkylene radicals be at least 3, R_2 is independently selected from 1 to 4 carbon atom chain lower alkyl hydroxy, with each of the R_2 groups on a single side of the ring being attached to the same ring carbon atom, cross linked with a dicarboxylic acid or functional equivalent thereof having a 2 to 6 carbon atom chain between terminal carboxyl groups.

2. The yarn of claim **1** wherein ingredient (c) of the carried finish is further characterized by not containing unsaturation, R_2 is independently hydroxymethyl, hydroxyethyl, hydroxyprpoyl or hydroxybutyl, at least one pair of R_2 groups are attached to a ring carbon atom

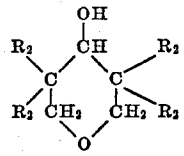
adjacent the ring carbon atom to which the direct ring linked hydroxyl is attached, and about 0.5 to 1.0 mol of cross linking agent is present per mol of triester.

3. The yarn of claim 2 wherein ingredient (c) of the carried finish is 9–10 carbon atoms fatty acid ester of a compound of the formula



wherein R_2 is hydroxymethyl or hydroxyethyl, cross linked with said cross linking agent.

4. The yarn of claim 2 wherein ingredient (c) of the carried finish is 9–20 carbon atoms fatty acid ester of a compound of the formula



wherein R_2 is hydroxymethyl or hydroxyethyl, cross linked with said cross linking agent.

5. The yarn of claim 2 wherein ingredient (c) of the carried finish is a tri-9–20 carbon atom fatty acid ester of 3,3,5,5-tetrakis (hydroxy methyl)-4-hydroxy-tetrahydro pyran; 3,3,5,5-tetrakis (hydroxy ethyl)-4-hydroxy-tetrahydro pyran; 2,2,4,4-tetrakis (hydroxy methyl)-3-hydroxy-dihydrofuran; or 2,2,4,4-tetrakis (hydroxyethyl)-3-hydroxy-dihydrofuran, each of which being cross linked with maleic anhydride or functional equivalent thereof.

6. A yarn according to claim 1, said carried finish including about 10 to 20% by weight of an alkane wax containing about 30 to 60 carbon atoms, the weight of alkane not exceeding the weight of (c) and the total of alkane and (c) not exceeding about 25%.

7. A yarn according to claim 1, wherein said metallic fatty acid soap of the carried finish is a polyvalent metal salt of an aliphatic carboxylic acid containing about 16 to 22 carbon atoms.

8. A yarn according to claim 7, wherein said polyvalent metal comprises at least one of antimony, zinc or aluminum and said carboxylic acid comprises at least one of oleic acid, stearic acid or palmitic acid.

9. A yarn according to claim 5, wherein said yarn carries about 2 to 4% of finish comprising:

(a) about 15% of the tristearate ester of 3,3,5,5-tetrakis (hydroxymethyl)-4-hydroxy-tetrahydropyran,

(b) about 2.5% of antimony tris-oleate,

(c) the balance consisting essentially of mineral oil.

10. A yarn according to claim 5, wherein said yarn carries about 2 to 4% of finish comprising:

(a) about 15% of the tristearate ester of 3,3,5,5-tetrakis (hydroxymethyl)-4-hydroxy-tetrahydropyran,

(b) about 2.5% of zinc stearate,

(c) the balance consisting essentially of mineral oil.

11. A yarn according to claim 5, wehrein said yarn carries about 2 to 4% of finish comprising

(a) (I) about 7.5% of the tristearate ester of 3,3,5,5-tetrakis (hydroxymethyl) - 4 - hydroxy-tetrahydropyran, (II) about 7.5% of a C_{33} alkane, and

(b) about 2.5% of aluminum palmitate,

(c) the balance consisting essentially of mineral oil.

12. A rope comprising a plurality of plied yarns each according to claim 1.

References Cited

UNITED STATES PATENTS

3,503,880	3/1970	McMicken	117—138.8 X
2,436,979	3/1948	Standley	117—139.5 X
2,590,911	4/1952	Wittcoff	260—345.8
2,513,133	6/1950	Hatch et al.	260—345.8 X
3,039,895	6/1962	Yuk	252—8.6 X
2,944,920	7/1960	Shields et al.	117—139.5
3,277,000	10/1966	Chandler	117—139.5 X
3,575,856	4/1971	Anton	117—138.8

FOREIGN PATENTS

729,583	3/1966	Canada	117—138.8

WILLIAM D. MARTIN, Primary Examiner

S. L. CHILDS, Assistant Examiner

U.S. Cl. X.R.

117—138.8 N, 139.5 F; 260—345.8, 347.4