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TIRE CORD FIBER LUBRICANT

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The present invention relates to textiles which carry a softening and lubricating composition and particularly to finishing compositions which are resistant to oxidation under processing and service conditions to which the textile in which they are incorporated may be subjected.

Materials which are currently available for the softening and lubrication of textiles, particularly strands of rayon fibers, are long-chain fatty materials, i.e., fatty acids, alcohols, amines, amides, and esters which have been reacted with relatively large amounts of ethylene oxide, for example, castor oil reacted with 300 moles of ethylene oxide. These materials make excellent lubricants for rayon yarn and are ordinarily applied thereto in the form of emulsions. Long-chain waxy polymers of ethylene oxide itself are also useful as softening agents. When subjected to substantial heating and oxidative atmosphere, these compounds are not stable and the ethylene oxide chains thereof tend to oxidize into volatile oils thus causing substantial loss of the finish material and greatly reducing the effectiveness thereof. The strength of, for example, rayon tire cord, is dependent upon "softness" as derived from a lubricant and thus the loss of an appreciable amount of the lubricant or softener may affect test data or render finished products made from such strands inferior. Such losses of the softener may occur during the manufacturing or in service periods of the manufactured products made from the "softened" strands if the strands have been subjected to hot oxidizing conditions.

The problem of finding an antioxidant material is complicated by the fact that a great number of well-known antioxidant materials do not perform effectively as antioxidants in textile softening materials contemplated in this invention. Furthermore, as the oily or waxy materials named above are most desirably applied in the form of aqueous emulsions, it is necessary that a material functioning as an antioxidant remain in association with the emulsified matter without settling out. It is furthermore essential that such material has no adverse effect on the base textile material.

Thus it is a primary object, under the present invention, to prevent breakdown of polyoxyethylene adducts of fatty materials used as textile lubricating and softening agents whereby the effectiveness of these materials may be maintained through severe conditions of processing and service.

A further object ancillary to the foregoing object is to provide stable aqueous suspensions of polyoxyethylene adducts of oily organic materials that contain an antioxidant.

In fulfilling the foregoing objects, it is an additional object to produce stronger and more durable tire cord.

Briefly stated, the invention resides in the treatment of textiles, particularly hydrophilic fibers, with lubricant-type compositions comprising organic compounds characterized by molecules which contain long chain polyoxyethylene groups, and as an antioxidant, polymerized 1,2-dihydro-2,2,4-trimethyl quinoline. In a preferred em-

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bodiment these compositions are applied to the fibers in the form of stable aqueous suspensions.

Some of the desirable characteristics of fiber finishes are that (1) they are sufficiently waxy as to be lubricating under various processing conditions and to provide good fiber-to-fiber lubrication which adds to the strength of the strand or fabric, and (2) that the finish is highly emulsifiable or water-soluble. In respect to this latter characteristic, it is urgently desired in tire yarn or fabric that the yarn or fabric containing the textile finish be capable of being quickly "wetted out," i.e., that the finish be surface active to the extent that the yarns and fabrics may be wetted by an aqueous liquid. This is necessary in order to effectively apply aqueous latex dip solutions to the tire fabric.

Many ordinarily hydrophobic lubricants, i.e., oils or waxy materials, may be modified in either one or both of the two characteristics named above to make them satisfactory as fiber finishing materials. By modification with sufficient ethylene oxide they may be brought to a hard waxy condition at room temperature and rendered readily water-dispersible. The term "dispersible" as used herein refers to any aqueous system comprising compounds having high ethylene oxide content disclosed herein regardless of whether the compound be dispersed as a true solute or in colloidal form. Some of the lubricating materials to which ethylene oxide is added are normally oils and as such, they are unsuitable as finishes for fibrous materials, particularly tire yarn, because they do not provide adequate lubrication and softness. Such materials, for example, castor oil, may be modified to produce a wax of adequate viscosity or hardness by sufficient addition of ethylene oxide by associating polyoxyethylene chains of sufficient length with the castor oil molecule.

The amount of ethylene oxide addition to the original lubricating material will vary in accordance with the characteristics of each compound. In general, the molecule of the hydrophobic material must be modified with 20 ethylene oxide units to become sufficiently water-soluble as required in the present invention. To convert the material into a wax of sufficient hardness may require considerably more ethylene oxide modification; e.g., the castor oil-polyoxyethylene ether, preferred in the practice of this invention, has a polyoxyethylene chain of 300 units of ethylene oxide, i.e., a degree of polymerization (DP number) of 300. As will be seen in the examples, polyoxyethylene glycol itself is, when formed to a wax of sufficient hardness (e.g., Carbowax, DP number of about 135), may be used as the lubricating ingredient of the textile finish.

However, such polyethylene oxide-type compounds have the disadvantage of breaking down in an oxidative atmosphere, particularly if heated at above 100° C. The increase in breakdown accelerates with increases in temperature above 100° C. Furthermore, the prevention of such breakdown of textile finishes which are adducts of polyethylene oxide is particularly important in tire fabric preparation since the tire fabric is dried by heat just after dipping and in some processes is heat-stretched before dipping. The latter is particularly true with respect to fabrics comprising nylon.

Although the present invention is described with respect to the application of finishes to cellulosic fibers, the mixtures which are suspended in liquid media may be readily applied to textile fibers of any type including those of various cellulose esters (cellulose acetate) and ethers, regenerated cellulose, vegetable matter (cotton), nylon, polyesters (Dacron), and polyacrylonitrile. Any of the lubricating ingredients and the anti-oxidants used therewith may be combined in aqueous suspensions, solutions

comprising organic solvents, or melts and applied by dip, spray, casting, or by such other techniques known to those skilled in the art.

The anti-oxidants contemplated in this invention may be maintained by polymerizing 1,2-dihydro-2,2,4-trimethyl quinoline. Lower order polymers having softening points as low as 75° C., were found to be effective as anti-oxidants although the effectiveness of such polymers increases in accordance with increases in their softening or melting points and corresponding increases in molecular weight. For substantially full protection of the lubricating ingredient in an oxidizing atmosphere at temperatures up to 200° C., a satisfactory antioxidant-polymer was found to have a melting point of approximately 120° C., and an average molecular weight of 700. The dihydro-trimethyl quinoline polymers having molecular weights above 700 are highly satisfactory for the practice of this invention. In mixing these antioxidant polymers in various proportions with the polyoxyethylene modified lubricants, optimum proportions were determined which were not of highly critical nature in the sense that although these proportions are preferred, fairly satisfactory results are achieved by small deviations from the optimum amounts of ingredients. For example, it was found that the antioxidant polymer having a molecular weight of 700 was noticeably effective when used in an amount of ½ percent by weight of that of the lubricating ingredient. The effectiveness increased until almost practically complete protection against oxidation was obtained at 3 to 4 percent. The amount of antioxidant can be increased to as much as 35 percent without seriously or adversely changing the characteristics desired in the finish with respect to the fibers to which it is applied.

For purposes of description of the invention, the finish solutions herein described comprise aqueous suspensions for application to regenerated cellulose fibers. In applying such a solution or suspension to cellulosic fibers there has been found, by long experience, that the amount of finish carried by a yarn lies within a rather narrow optimum range. Below this range, insufficient lubrication is obtained, while above this range such properties as tensile strength and processability are effected. While the amount of finish carried by the fibers may range from approximately 0.3 to 3 percent of the weight of the fibers, an optimum value for twisted strand regenerated cellulose fibers falls approximately within the range 0.6 to 1 percent. The finishes herein described were applied from solutions which had pH values within a range of from 7 to 10 although the invention is not limited to this range. No variation in the nature of the finish or the properties of the finish yarn were observed which might be attributed to the various pH values in the finish solutions.

The following examples are included herein to describe and illustrate various features and advantages of the invention.

EXAMPLE I

This example illustrates the effect of the presence of the polymer-type antioxidant included in the finish composition on tire yarn which has been subjected to different periods of heating in an oxidative atmosphere.

Samples 1 and 2 comprise green tire yarn, i.e., yarn which has never been completely dried after spinning before the application of a finish solution. The yarn comprises 980 filaments of 1650 total denier. Finish ingredient A in Table A is an ether of castor oil and approximately 300 moles of ethylene oxide. Ingredient B (antioxidant) is a polymer of 1,2-dihydro-2,2,4-trimethyl quinoline (Flectol H) having an average molecular weight of about 700 and a minimum melting point of about 120° C. After treatment with aqueous emulsions containing finish ingredients as indicated in Table A, the yarns were twisted and corded into Samples 1 and 2 heated for the periods indicated at 110° C., and tested for tensile strength.

Table A

Sample	Ingredients	Tensile Strength In gms./denier		Loss in Strength in Percent
		After 3 Hrs.	After 24 Hrs.	
1.....	1% A.....	3.57	2.87	19.6
2.....	1% A to 0.03% B.....	3.39	3.48	+2.7(gain)

From Table A it may be seen that, although Samples 1 and 2 both had a finish which contained the same lubricating ingredient, the finish of Sample 2 contained ingredient B and sustained markedly less loss of strength during the 21 hour heating period which followed the initial 3 hour heating period. This loss of strength, as will be shown in the following examples, corresponds to a loss of the finish ingredient A in Sample 1 by volatilization of the polyoxyethylene component of ingredient A. The loss of fiber lubrication in Sample 1 at the end of 24 hours of heating was also accompanied by a loss of "softness" which may be readily apparent to human touch.

EXAMPLE II

To ascertain the effectiveness of a polymer 1,2-dihydro-2,2,4-trimethyl quinoline as an antioxidant for preventing the break-down of polyoxyethylene glycol or polyoxyethylene components or adducts thereof used as textile lubricants, Flectol H (made by the Monsanto Chemical Co.) was mixed with the following list of ingredients (Table B) to form finish solutions as found in Table C. To obtain the values indicated in the "Percent finish on yarn" section of Table C, extractions of the finish of the yarn were made before and after the 25 hour heating period. It will be noted that, in general, the presence of ingredient B (polymer of 1,2-dihydro-2,2,4-trimethyl quinoline) made the loss of finish sustained by the yarn insignificant in all cases. The finish percentages noted with respect to Samples 16 and 20 may be particularly noted since ingredients I and K are similar except for difference in the length of the polyoxyethylene component thereof. The finish containing the ingredient K which has the longer polyoxyethylene chain (see Sample 20) sustains much greater finish degradation than Sample 16 containing the primary alkylamine of polyethylene glycol (50 units of ethylene oxide). That no degradation was indicated for this latter finish (see Sample 16) is apparently attributable to the antioxidative effect provided by the nitrogen in the alkylamine component. However, this effect is overshadowed in Sample 20 by the substantially longer polyoxyethylene component. However, the instability of the longer polyoxyethylene component is corrected in Sample 19 by use of the antioxidant B. Table C demonstrates that ingredient B may be used as an antioxidant generally in compounds in which a lubricant-type material is modified by extremely long polyoxyethylene components.

Table B

Ingredient	Chemical Name	Commercial Name
B.....	1,2-dihydro-2,2,4-trimethyl quinoline.....	Flectol H.
C.....	Mono ether of mixed stearyl and cetyl alcohols and 150 moles of ethylene oxide.	150d Stenol.
D.....	Mono ester of stearic acid and 100 moles of ethylene oxide.	100d Stearic Acid.
E.....	Mono ether-ester of sorbitan castor oil and 200 moles of ethylene oxide.	200d Sorbitan Castor Oil.
F.....	Mono ether of castor oil and 300 moles of ethylene oxide.	300 DCO.
G.....	Polyoxyethylene glycol comprising approx. 131 moles of ethylene oxide.	Carbowax 6000.
H.....	A diester of stearic acid and 75 moles of ethylene oxide.	75 Polyglycol Distearate.
I.....	Mixture of octadecylamine and hexadecylamine each modified with a polyoxyethylene chain of DP of 50.	50d Armeen 18D.
J.....	Hydrogenated tallow amide modified with polyoxyethylene (DP of 50).	50d Armid HT.
K.....	Mixture of octadecylamine and hexadecylamine each modified with a polyoxyethylene chain of DP of 150.	150d Armeen 18D.

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Table C

Sample	Composition of Finish Ingredient/See Table B	Percent Finish on Yarn	
		As Made	After 25 Hrs. at 150° C.
3.....	1%+0.03% B.....	.58	.50
4.....	1% C.....	.52	.01
5.....	1% D+0.03% B.....	.44	.46
6.....	1% D.....	.53	.02
7.....	1% E+0.03% B.....	.49	.44
8.....	1% E.....	.53	.02
9.....	1% F+0.03% B.....	.46	.51
10.....	1% F.....	.54	.02
11.....	1% G+0.03% B.....	.54	.49
12.....	1% G.....	.54	.02
13.....	1% H+0.03% B.....	.53	.49
14.....	1% H.....	.57	.03
15.....	1% I+0.03% B.....	.41	.36
16.....	1% I.....	.34	.34
17.....	1% J+0.03% B.....	.52	.46
18.....	1% J.....	.47	.06
19.....	1% K+0.03% B.....	.69	.66
20.....	1% K.....	.56	.39

EXAMPLE III

To determine the amount of antioxidant to be used in textile finishes made in accordance with this invention, ingredient B (antioxidant) was mixed in varying amounts with standard amounts of ingredient F (polyoxyethylene castor oil) suspended in an emulsion in water. Carboxymethyl cellulose (ingredient L) was included as a binding agent for promoting cohesiveness of fibers. The fibers, after application of the finish, were formed into 12 x 12 cord.

Table D

Sample	Finish Composition Ingredients in Percent			Strength in lbs. per cord		Loss in Strength in Percent
	F	B	L	Oven dried at 110° C.	Heat at 144 Hrs. at 120° C.	
21.....	1	0.03	0.3	28.7	22.2	23
22.....	1	0.10	0.3	28.3	26.8	5
23.....	1	0.25	0.3	27.9	26.7	4
24.....	1	0.33	0.3	27.1	26.2	4

Another series of samples were compared in the following manner. Finish formulations were applied to 1650/980 tire yarn which included ingredients F and B and polyvinyl alcohol (ingredient M) as a binding agent.

Table E

Sample	Finish Composition Ingredients in Percent			Strength in lbs. per cord		Loss in Strength in Percent
	F	B	M	Oven dried at 110° C.	Heat at 90 Hrs. at 123° C.	
25.....	1.0	0.01	0.3	26.7	21.2	20.6
26.....	1.0	0.01	0.3	28.0	22.9	18.3
27.....	1.0	0.02	0.3	28.3	28.2	0
28.....	1.0	0.03	0.3	28.6	29.3	.24 (gain)
29.....	1.0	0.04	0.3	29.6	28.3	4.4

Example III is indicative of optimum amounts of the hydrotrimethyl quinoline polymer which are operative to inhibit breakdown in finishes comprising polyoxyethylene glycol or adducts thereof. The formulations of Table D are closely but not strictly analogous to those of Table E since one of the three ingredients found in each table, the binder L or M, is not common to both tables. However, the information provided by both tables and that of other investigations not described herein, indicate that optimum practical strength of the antioxidant may be, for

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most of the lubricant-type compounds contemplated by the present invention in the range of 3 to 4 percent by weight of the antioxidant based on the weight of the polyoxyethylene modified textile lubricant. It will be noted that the loss of finish is indicated by data which indicates loss of tensile strength in the investigations which related to the present invention; losses of tensile strength and losses of finish material by oxidation were closely parallel.

The use of the antioxidants in combination with polyoxyethylene modified textile lubricants are not known to have any pronounced adverse effects upon the properties of yarns, cords, fabrics, etc. When such textile materials are exposed to prolonged heating under oxidative conditions, the lubricant, unless it is protected from decomposition, volatilizes from the textile material with consequent loss of strength thereof. However, such antioxidants operate to prevent degradation of the finish and thus maintain the original properties, particularly the tensile strength of textile materials. The presence of the antioxidant is thus beneficial in maintaining the high potential strength of textile fibers in spite of severe processing or service conditions.

Various changes and modifications may be made in practicing the invention without departing from the spirit and scope thereof and, therefore, the invention is not to be limited except as defined in the appended claims.

I claim:

1. Hydrophilic tire cord fibers of which the surfaces are coated with a composition comprising a water-dispersible polymeric wax lubricant from the class consisting of polyoxyethylene glycol and its mono-fatty ethers, mono-fatty esters, mono-fatty ether-esters and di-fatty esters and polyoxyethylene glycol primary fatty alkylamines and primary fatty alkylamides, said polymeric textile lubricant containing at least 20 ethylene oxide units; and a polymer of 1,2-dihydro-2,2,4-trimethyl quinoline having a softening point of not less than about 75° C. in amounts of 0.5 to 35 percent by weight of said lubricant and said coating being present in amounts of from 0.3 to 3 percent by weight of the fibers.

2. Cellulosic tire cord fibers, containing on their surface a coating comprising a water-dispersible polymer wax lubricant from the class consisting of polyoxyethylene glycol and its mono-fatty ethers, mono-fatty esters, mono-fatty ether-esters and di-fatty esters and polyoxyethylene glycol primary fatty alkylamines and primary alkylamides, said polymeric textile lubricant containing at least 20 ethylene oxide units; and a polymer of 1,2-dihydro-2,2,4-trimethyl quinoline having a molecular weight of not less than about 700 in amounts of about 3 to 35 percent by weight of said lubricant and said coating being not less than about 0.6 percent of the weight of the yarn.

3. Twisted strands of regenerated cellulosic tire cord fibers of which the surfaces of the fibers are coated with a composition comprising a water-dispersible polyethylene oxide ether adduct of castor oil containing about 300 ethylene oxide units per molecule and having the consistency and lubricating properties of wax, and a polymer of 1,2-dihydro-2,2,4-trimethyl quinoline having an average molecular weight of not less than approximately 700; said polymer being present in amounts of about 3 to 35 percent by weight based on the polyethylene oxide ether adduct of castor oil, the amount of the coating composition on the fibers being approximately within the range of from 0.6 to 1 percent of the weight of the fibers.

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