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(54) **Fatty acid esters of phenol derivative alkoxylates and their use as fiber finish components.**

(57) A fatty acid ester of alkoxylated phenol derivatives provides an effective fiber lubricant when applied pure or in a water emulsion.

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FATTY ACID ESTERS OF PHENOL DERIVATIVE ALKOXYLATES AND THEIR USE AS FIBER FINISH COMPONENTS

The invention relates to a fiber lubricant, a fatty acid ester of an alkoxylated phenol derivative, which has effective thermal and oxidative stability, non-volatility, product stability and, in a preferred embodiment, emulsification properties and which when applied to a fiber, as a fiber lubricant formulation, exhibits effective viscosity and lubricity.

Traditionally, a fiber lubricant formulation consists of a base material, or lubricant, such as mineral oil, alkyl esters of fatty acids or vegetable oils; emulsifiers that allow the lubricant to be applied from a water solution; antistatic agents; antioxidants; bacteriocides; friction modifiers; and buffering agents.

A fiber lubricant is critical to the conversion of nylon or polyester fiber into useful yarn for textile manufacturing. The fiber lubricant has several functions. One function is to control friction. The fiber lubricant may protect the newly spun fiber from fusion or breakage by controlling the yarn-to-metal friction at frictional contact points between the yarn and machine guides, rollers, draw

plates, heater plate and texturing false twist spindles or friction discs. The lubricant also functions to provide yarn cohesion giving strength to the yarn by holding the yarn bundled together and by allowing the yarn to build up an acceptable package at the end of processing. Static electricity that is formed as the yarn rapidly moves through the processing equipment would also be controlled. The lubricant must also protect machine surfaces from wear.

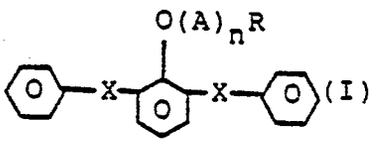
U.S. 4,165,405 discloses fiber lubricants based upon fatty esters of heteric polyoxyalkylated alcohols wherein mononuclear, monofunctional initiators are alkoxylated and then esterified. U.S 4,127,490 relates to lubricating fibers with a major amount of lubricant and a minor amount of a stabilizer, said stabilizer being the reaction product of one mole of dicyclopentadiene and at least one mole of p-cresol, further reacted with at least one-half mole of isobutylene. U.S. 4,134,841 relates to a fiber lubricant which is a composition comprising a non-hindered polyphenyl stabilizer and a polyether lubricant. U.S. 4,252,528 relates to a spin finish for synthetic fibers of a thermally stable lubricant and a surfactant derived from an ethylene oxide-propylene oxide block copolymer adduct of an alkylated phenol. U.S. 3,578,594 relates to a fiber treating composition ccnsisting essentially of about 90 percent to about 25 percent by weight of at least one

ester of an ethoxylated aliphatic alcohol and about 10 percent to about 75 percent by weight of at least one ester of an ethoxylated arylphenol. The examples relate to α-methyl benzyl phenol or bis α-methyl benzyl phenol as the aryl phenol. A problem of the prior art fiber lubricants mentioned above is that they are not disclosed as being capable of being used alone or in a water emulsion as a fiber lubricant formulation. None of the above references discloses the use as a fiber lubricant of the products of applicants' invention, nor do they suggest the use of applicants' product alone or as a water emulsion.

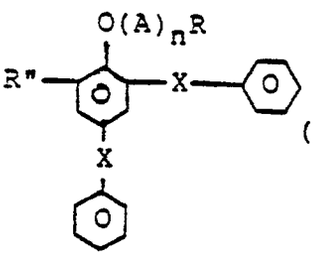
A purpose of the invention was to provide a fiber lubricant which may be used by itself in pure form as a fiber lubricant formulation. Another purpose of the invention was to provide a self-emulsifiable fiber lubricant for use as a fiber lubricant formulation.

A fiber lubricant has been discovered having effective thermal and oxidative stability, non-volatility, product stability, and, in a preferred embodiment, emulsification properties, and which when applied to a fiber, as a fiber lubricant formulation, exhibits effective viscosity and lubricity. The fiber lubricant is useful as a fiber lubricant formulation in pure application to polyester or nylon fiber during a drawing and texturing operation. The

fiber lubricant formulation is used in a process of lubricating synthetic fibers which comprises applying the fiber lubricant to the fiber in an amount between 0.05 percent by weight and 5 percent by weight, based on the weight of the lubricated fiber. The fiber lubricant comprises a compound selected from the group consisting of



(I)



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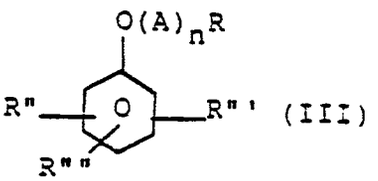

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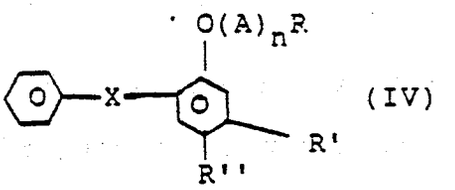
and

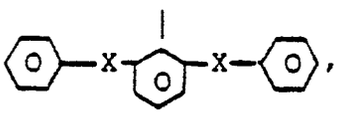


(IV)

wherein A is an oxyalkylene radical having 2 carbon atoms to 4 carbon atoms or mixtures thereof, R is hydrogen or acyl containing from 8 carbon atoms to 22 carbon atoms, R' is alkyl containing from 1 carbon atom to 10 carbon atoms, R'' is alkyl containing from 1 carbon atom to 22 carbon atoms, R''' is alkyl containing from 4 carbon atoms to 8 carbon atoms and R'''' is R'' or R''', X is an alkylidene radical containing from 1 carbon atom to 3 carbon atoms and n is an integer such that the molecular weight of the compound is between 500 and 2500 and with the proviso that either R'' or R''' is ortho to the oxygen in formula III. In preferred embodiments the oxyalkylene radical is oxyethylene or a mixture of oxyethylene and up to 50 percent by weight of an oxyalkylene radical having 3 carbon atoms to 4 carbon atoms and provides effective hydrophilicity to the compound to enable it to self emulsify in water.

The lubricants of the present invention are prepared from three essential ingredients, i.e., certain phenol derivatives, alkylene oxides and fatty acids.

Useful as the phenol derivatives are compounds selected from the group consisting of the following formulas:



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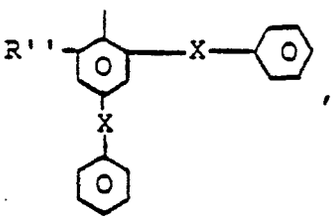

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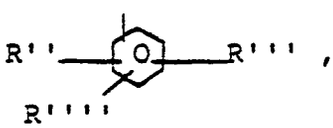

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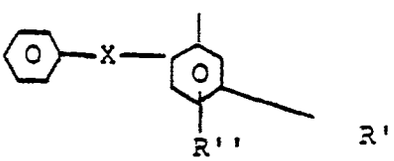
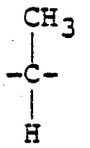


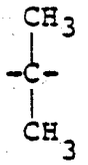
(VIII)

wherein X, R', R'', R''' and R'''' are as described above. Examples of X are alkylidene radicals such as methylene, ethylene and propylidene. Examples of R' and R'' are methyl

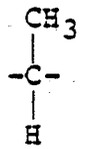
and isobutyl. Examples of R''' and R'''' are butyl and octyl. Preferably used as the phenol derivative of formula V is a compound wherein X is



as the phenol derivative of formula VI is a compound wherein x is



as the phenol derivative of formula VII is a compound wherein R'' is C_4H_9-, R''' is C_8H_{17}- and R'''' is C_8H_{17} - or C_4H_9- or a compound wherein R'' is C_4H_9-, R''' is C_4H_9- and R'''' is CH_3- and as the phenol derivative of formula VIII is a compound wherein X is



R' is CH_3- and R'' is C_4H_9-.

Useful as alkylene oxides, from which the oxyalkylene radical derives, are alkylene oxides containing 2 carbon atoms to 4 carbon atoms such as ethylene oxide,

propylene oxide and butylene oxide. Useful in a preferred embodiment is ethylene oxide or a mixture of ethylene oxide and other alkylene oxides which when used in a mixture with ethylene oxide impart a hydrophilicity effective to self emulsify the compound. In lieu of the other alkylene oxides, other 3 or 4-carbon cyclic ethers such as tetrahydrofuran, oxetane, and methyl oxetane may be used. Preferaby used are mixtures of ethylene oxide and propylene oxide.

The oxyalkylene is present in the fiber lubricant in an amount, as represented by n, such that the molecular weight of the compound is between 500 and 2500. Preferably used is a block of between 5 and 20 moles, such as 5, 10 or 15 moles of ethylene oxide per mole of phenol derivative. Also preferably used is a heteric mixture of about 70 percent by weight oxyethylene and about 30 percent by weight oxypropylene.

Useful as fatty acids are those containing between 8 carbon atoms and 22 carbon atoms, preferably between 16 and 20 carbon atoms and more preferably 18 carbon atoms, such as isostearic acid.

The phenol derivative is ethoxylated by adding the phenol derivative and a basic catalyst to an autoclave evacuated to a vacuum and pressurized with nitrogen and equipped with temperature, pressure and vacuum controls, and thereafter heated. The alkylene oxide is added at a constant rate until all the oxide is added. The reaction then proceeds at a temperature between 90°C and 130°C until a constant pressure is observed. Esterification is then

accomplished by adding approximately equal molar amounts of fatty acid and alkoxylated phenol derivative. Acid catalysts, such as methane sulfonic acid and hypophosphorus acid are added and the esterification reaction is allowed to proceed at a constant temperature, such as 165°C under a nitrogen blanket.

The lubricants of this invention are applied to the fiber in an amount between 0.05 percent by weight and 5 percent by weight, based on the weight of the lubricated fiber.

The lubricity of the products of this invention on synthetic yarns may be determined using any reasonable method. One useful test method measures the lubricity, in units of the coefficient of friction, of nylon filaments having fiber lubricants applied to them at a concentration of about 1 percent lubricant by weight of filament by the procedure of the following two paragraphs.

A stable aqueous emulsion of the lubricant is prepared. This emulsion is applied to the yarn, such as nylon or polyester, using an apparatus in which the yarn is passed at a controlled speed through a continually replenished drop of finished solution or dispersion of specified concentration. A suitable apparatus is the ATLAS yarn finish applicator sold by the Precision Machine and Development Company of Wilmington, Delaware. The lubricant

dispersion is metered to the continually replenished drop of solution using a syringe pump. Tne yarn is fed over an adjustable canter roller which functions to space the yarn over a drying drum used to remove water. The yarn is finally passed over a winding tube and subsequently conditioned for 16 to 24 hours at 65 percent relative humidity and 70°F before being tested.

The coefficient of friction (f) may be determined on any suitable machine, such as a Rothschild F Meter utilizing 0.313 inch diameter ceramic (Al Si Mg) and satin chrome friction pins that has friction surface at a yarn contact angle of 180°. The yarn speed is varied, such as at 50, 100, 150, 200, and 250 meters per minute. The yarn tension may be varied such as at 4 or 6 grams on the input side as determined by tensiometers by the Rothschild F meter. The (f) values are determined directly by reading the chart produced by the Rothschild F meter.

Viscosity may be determined by any standard procedure, such as using a Brookfield viscometer or Ubelohde tube following ASTM D444 71/79 or D2161-79. The viscosity of the fiber lubricants of this invention have a controlled viscosity range, from 500 to 1500 Saybolt universal seconds. A viscosity below this range is detrimental to processing the fibers and a viscosity above this range causes excessive add-on to the fibers.

Thermal and oxidative stability as well as non-volatility of the fiber lubricant may be tested by a number of suitable procedures such as the hot plate test, the circulating air oven test, dynamic thermogravimetric analysis and isothermal thermogravimetric analysis. The hot plate test proceeds by placing metal cups, 3 for each example, on a heater and maintaining the temperature at 240°C for 24 hours. At intervals of time, the weight loss for each of the 3 samples is determined and averaged and the quality of residue determined. The hot plate test is representative of thermal stability as measured by the results at 240°C for 24 hours and of oxidative stability by the quality of the residue. The circulating air oven test proceeds as in the hot plate test except the hot plate and samples are placed in a circulating air oven. The thermogravimetric analyses proceed as follows: the dynamic thermogravimetric analysis measures the temperature in degrees centigrade at which a specific percentage by weight, such as 1 percent by weight and 10 percent by weight, of the sample is lost in a test atmosphere, such as air or nitrogen, while heating the sample at a constant heating rate, such as 20 degrees per minute; and the isothermal thermogravimetric analysis measures the percent by weight loss of the sample at a constant temperature, such as 210°C, for a specific time interval, such as 40 minutes, while the.

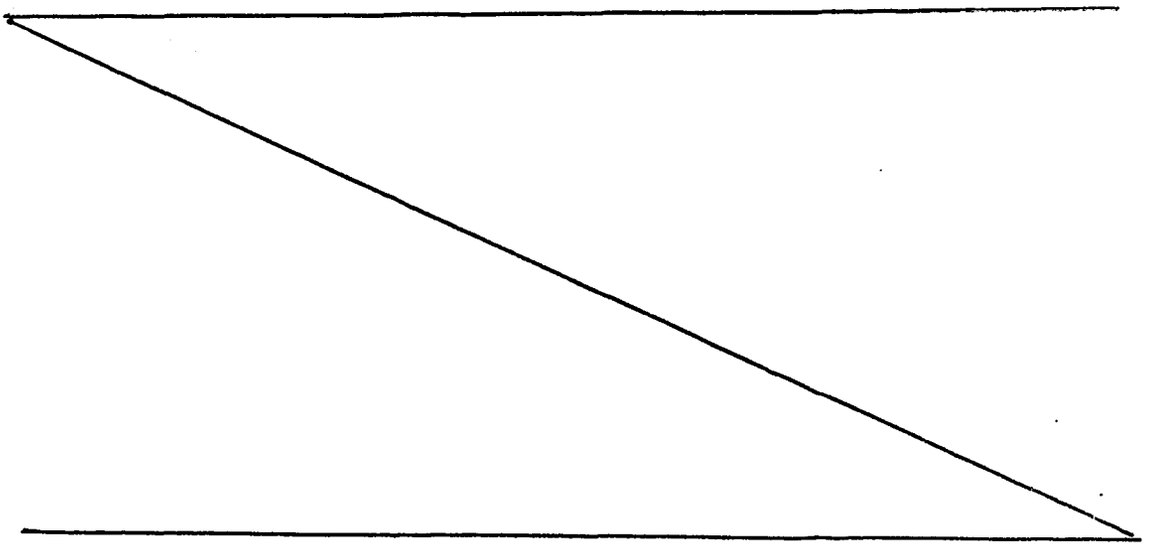
sample is continuously weighed.

The product stability of the fiber lubricant may be tested by any suitable method. The ability of the product of the invention to be storage stable is excellent.

The emulsification properties of the fiber lubricant may be tested by preparing a mixture containing 10 parts of fiber lubricant, 20 parts of mineral oil and 70 parts of water. The mixture is shaken vigorously and allowed to stand for 24 hours. If separation of the emulsion does not occur, the emulsion is considered stable.

The products of a preferred embodiment of the invention are self emulsifiable with water and do not require additives to make an emulsion.

Additional additives may, however, be added to the fiber lubricants in preparing fiber lubricant formulations. These additives are described in U.S. 4,134,841.



The following examples will further illustrate the various aspects of the invention. Where not otherwise specified throughout the specification and claims, temperatures are in degrees Centigrade, and parts, percentages and proportions are by weight.

Example 1

To an autoclave equipped with temperature, pressure, and vacuum controls was added 780 parts of butylated, styrenated cresol (WINGSTAY® V - Goodyear Company) and 8 parts of 45 percent potassium hydroxide solution. The autoclave was heated to 125°C after evacuating to a vacuum of less than 10 millimeters mercury and then pressurizing to 34 lbs./square inch with nitrogen. Ethylene oxide was added at a rate of 250 parts/hour until 1921 parts were added. When constant pressure was observed, the catalyst was removed by deionization and the mixture was further stripped to remove volatiles. This ethoxylate, Example 1A, had a hydroxyl number of 66.2 and a viscosity of 883 Saybolt universal seconds at 100°F.

To a 2 liter flask having temperature control, stirrer and distillation apparatus were added 891 parts of the above ethoxylate. Next, 279.1 parts of isostearic acid, 4.12 parts of methanesulfonic acid, (70 percent), and 4.0 parts of hypophosphorous acid were added. The temperature was held at a constant 165°C in a nitrogen atmosphere until

the esterification reaction was complete. After catalyst removal, the product of Example 1 of this invention, the isostearate ester of ethoxylated butylated styrenated cresol, a specific product containing compounds of formula IV above, was obtained having a hydroxyl number of 4.4, an acid number of 1.56 and a viscosity of 781 Saybolt universal seconds at 100°F.

Comparison Examples A, B, C and D

A is a polyoxypropylene block adduct of a polyoxyethylene adduct of ethylene glycol of approximate average molecular weight of the hydrophobe of 1000 and an oxyethylene content of about 50 percent by weight.

B is a polyoxyethylene block adduct of a polyoxypropylene adduct of propylene glycol of approximate average molecular weight of the hydrophobe of 950 and an oxyethylene content of about 50 percent by weight.

C is a heteric ethylene oxide propylene oxide adduct of a C_{12}-C_{15} fatty alcohol, having an overall approximate average molecular weight of 1280 and containing about 50 percent ethylene oxide.

D is a polyoxyethylene block adduct of a polyoxypropylene adduct of bisphenol A of approximate average overall molecular weight of 8350 and an oxyethylene content of about 80 percent by weight.

Lubricity, heat stability and emulsion properties were obtained as follows: An aqueous emulsion of the lubricant of Example 1 was prepared. This emulsion was applied to yarn using an Atlas yarn finish applicator. The coefficient of friction (f) was determined on a Rothschild F meter utilizing 0.313 inch diameter ceramic (Al Si Mag) and satin chrome friction pins as the friction surface at a yarn contact angle of 180°. The ASTM procedure Standard Test Method for Coefficient Friction, Yarn to Metal Designation 03108-76 was generally followed. The lubricity results, using 40/12 denier nylon 6 yarn, are shown in Table I for the products of Example 1 and comparison Example A.

TABLE I

Input Tension (Grams)	Speed Meters/ Minute	Coefficient of Friction Example 1 f	Comparison Example A f
4	50	.70	.73
4	100	.71	.76
4	150	.71	.77
4	200	.71	.77
6	50	.64	.67
6	100	.66	.69
6	150	.67	.70
6	200	.67	.71

Thermal and oxidative stability of the products of Example 1 and comparisons B and C, using a hot plate set at 240°C and 3 gram samples, are shown in Table II.

TABLE II

Heat Stability
Hot Plate Test

Example	Percent Residue After 24 Hours	Nature of Residue
1	76.7	Light brown liquid
B	2.9	Varnish
C	38.8	Dark Brown Liquid

Heat stability results for the products of Example 1 and Comparison Example C, using a circulating air oven set at 210°C and 3 gram samples, are shown in Table III.

TABLE III

Heat Stability
Circulating Air Oven Test

Example	Percent Residue After 24 Hours	Nature of Residue
1	87.6	Light Brown Liquid
C	22.9	Dark Brown Liquid

Heat stability results for the product of Example 1 of the invention using thermogravimetric analysis and isothermal percent weight loss are shown in Table IV.

TABLE IV

Thermogravimetric Analysis

Example	Dynamic °C Weight Loss of 1% Air/ N_2	10% Air/ N_2	50% Air/N_2
1	150/315	287/370	318/395

Example	Isothermal % Weight Loss at 210°C -40 Minutes	Smoke Point °C
1	18.0/4.0	187

Stable emulsions, made with the product of Example 1, and water and with the product of Example 1, water and other materials are shown in Table V.

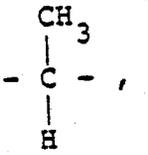
TABLE V

Emulsions

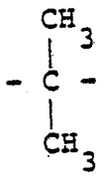
Component	Stable Emulsion 1 parts	2 parts	3 parts	4 parts
Product of Example 1	12	5	2	20
Tridecyl Stearate	36	-	-	-
Butyl Stearate	-	15.0	-	-
Mineral Oil (Crystosol TW)	-	-	8	-
KLEARFAC® A270 (neutralized)	-	3	-	-
Water	52	77	90	80

Examples 2-20

Examples 3-10 and 14-19 were prepared using the procedure to prepare Example 1A. Examples 2, 11-13 and 20 were prepared using the procedure for preparing the product of Example 1. EO is ethylene oxide, PO is propylene oxide, product Y_1 is a commercial product of formula V wherein X is



(WINGSTAY® S - Goodyear Company), product Y_2 is a commercial product of formula VII wherein R" is C_4H_9-, R"' is C_8H_{17}- and R"" is either C_4H_9- or C_8H_{17}- (WINGSTAY® T - Goodyear Company) and product Y_3 is a commercial product of formula VI wherein X is



and R" is C_4H_9- (WINGSTAY® C - Goodyear Company).

The products are as follows:

Example	Composition
2	Laurate ester of Example 1A
3	5 mole ethoxylate of the butylated styrenated cresol of Example 1
4	10 mole ethoxylate of the butylated styrenated cresol of Example 1
5	5 EO adduct of product Y_1
6	10 EO "
7	15 EO "
8	70/30 EO/PO "
9	11 PO + 9 EO + 11 PO "
10	25 EO "
11	isostearate ester of Example 7
12	isostearate ester of Example 10
13	isostearate ester of Example 9
14	5 EO adduct of product Y_2
15	10 EO "
16	15 EO "
17	5 EO adduct of product Y_3
18	10 EO "
19	15 EO "
20	the isostearate ester of Example 1A

The physical properties of the fiber lubricants of Examples 2-20 are shown below in Table VI.

Table VI

Example	Molecular Weight	Hydroxyl No.	Viscosity SUS at 100°F
2	1047	7.6	905
3	467	120.2	1406
4	680	82.5	936
5	504	111.2	1570
6	742	75.6	1111
7	946	59.3	1088
8	1465	38.3	1320
9	1556	36.1	1243
10	1320	42.5	1657
11	1200	6.0	974
12	1580	6.5	1320
13	1800	10.0	1162
14	576	97.4	1470
15	695	80.7	1159
16	1578	71.1	981
17	610	91.9	2599
18	851	65.9	1139
19	1024	54.8	1094
20	1134	12.8	1096

Thermal properties of heat resistant lubricants of the invention and comparison Example B, determined in an aluminum pan test on a hot plate set at 240°C are shown in Table VII.

Table VII

Example	Percent Residue, Hours					Appearance*
	0.5	2	4	8	24	
2	99.4	98.6	97.0	93.3	78.2	b
3	97.8	93.6	89.1	82.7	76.1	b
4	99.6	97.6	95.0	89.4	71.9	b
5	99.3	97.3	95.2	91.6	86.1	a
6	99.8	99.3	98.8	97.6	93.0	b
7	99.7	99.2	97.9	94.8	84.5	b
8	99.5	98.3	95.9	90.7	80.4	b
9	98.7	95.0	89.6	79.2	62.9	b
14	92.9	85.2	79.6	72.1	61.0	b
15	98.9	96.7	94.3	89.0	64.8	b
16	97.6	95.7	93.3	88.4	65.5	b
17	94.1	88.8	85.5	78.9	71.0	b
18	95.9	93.0	90.0	83.7	57.0	b
19	96.6	94.9	92.3	86.2	65.0	b
B	97.3	80.8	41.4	6.6	2.4	c

* a-brown
b-light brown
c-varnish

Thermal properties of heat resistant lubricants of the invention and comparison examples B and D as determined in an aluminum pan in an air circulating oven at 210°C are shown below in Table VIII.

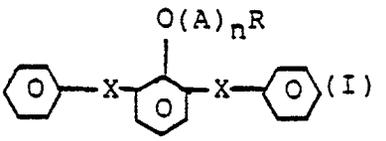
Table VIII

Example	Percent Residue, Hours					Appearance*
	0.5	2	4	8	24	
2	98.1	90.3	78.8	60.7	40.2	d
7	98.4	92.4	85.4	75.7	52.3	a
9	94.0	73.6	56.4	37.5	16.9	d
10	98.1	87.5	76.1	62.7	37.0	d
11	96.6	91.9	86.4	78.4	56.4	d
12	96.9	91.2	83.4	70.3	42.3	d
13	98.4	81.3	65.1	48.0	26.8	d
B	67.0	1.7	1.1	-	-	c
D	98.0	87.1	77.4	68.3	51.2	d

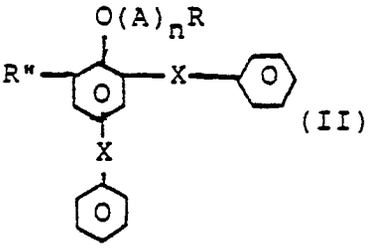
* a - brown
  c - varnish
  d - dark brown

The embodiments of the invention in which an exclusive priviledge or property is claimed are defined as follows:

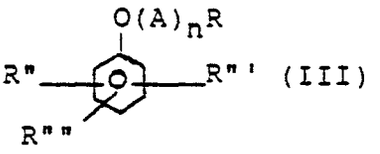
1. A fiber lubricant comprising a compound selected from the group consisting of:



(I)

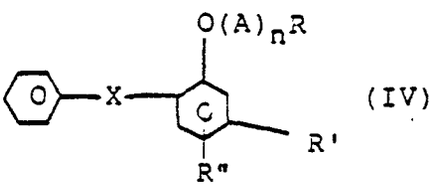


(II)



(III)

and



(IV)

wherein A is an oxyalkylene radical having 2 carbon atoms to 4 carbon atoms or mixtures thereof, R is hydrogen or acyl containing from 8 carbon atoms to 22 carbon atoms, R' is alkyl containing from 1 carbon atom to 10 carbon atoms, R'' is alkyl containing from 1 carbon atom to 22 carbon atoms, R''' is alkyl containing from 4 carbon atoms to 8 carbon atoms, and R'''' is R'' or R''', X is an alkylidene radical containing from 1 carbon atom to 3 carbon atoms, and n is an integer such that the molecular weight of the compound is between 500 and 2500 and with the proviso that either R'' or R''' is ortho to the oxygen in formula III.

2. A process of lubricating synthetic fibers which comprises applying to the fiber in an amount between 0.05 percent by weight and 5 percent by weight, based on the weight of lubricated fiber, the compound of claim 1.

3. The process of claim 2 consisting essentially of applying to the fiber, in an amount between 0.05 percent by weight and 5 percent by weight, based on the weight of lubricated fiber, a compound of claim 1.