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(54) **Title:**

**STABILIZED ULTRA HIGH MOLECULAR WEIGHT
POLYOLEFIN FIBER**

(57) **Abstract:**

The present invention provides an ultrahigh molecular weight polyolefin fiber coated with a coating composition, wherein the coating composition contains a UV stabilizer, characterized in that the amount of UV stabilizer is between 2 wt% and 80 wt.% compared to the total weight of the coating composition based on solids. The UV absorber can be selected from the group consisting of hydroxybenzophenones, hydroxyphenylbenzotriazoles, oxalanilides, phenyl esters, benzooxazinones, cyanoacrylates, formamidine, benzyldiene malonates and hydroxyphenyl triazines and combinations thereof. Such fibers are particularly useful in ropes and fishing nets.



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(54) Title: STABILIZED ULTRA HIGH MOLECULAR WEIGHT POLYOLEFIN FIBER

(57) Abstract: The present invention provides an ultrahigh molecular weight polyolefin fiber coated with a coating composition, wherein the coating composition contains a UV stabilizer, characterized in that the amount of UV stabilizer is between 2 wt% and 80 wt.% compared to the total weight of the coating composition based on solids. The UV absorber can be selected from the group consisting of hydroxybenzophenones, hydroxyphenylbenzotriazoles, oxalanilides, phenyl esters, benzoxazinones, cyanoacrylates, formamidine, benzyldene malonates and hydroxyphenyl triazines and combinations thereof. Such fibers are particularly useful in ropes and fishing nets.



STABILIZED ULTRA HIGH MOLECULAR WEIGHT POLYOLEFIN FIBER

The present invention relates to high strength fibers and in particular ultrahigh molecular weight polyolefin fibers having improved UV stability and the use thereof in, for instance, ropes and fishing nets.

Although high strength fibers and in particular ultrahigh molecular weight polyolefin fibers such as high performance polyethylene (HPPE) fibers are generally considered to be relatively stable when exposed to UV, under certain circumstances such fibers may show a loss in tenacity as a result of weathering, which in turn may lead to a reduced life time. These circumstances can in particular occur when such fibers are used in ropes or in fishing lines or fishing nets.

In US5246988 it is described how to make a heat and oxidation stable article where a nitrogen-containing antioxidant is included in a carrier which is a lubricant. Such heat and oxidation stable coatings are not always suitable to improve stability or resistance to UV radiation. Moreover, there is a need to improve the coating compositions used therein.

US 2010/007119 describes a fabric or a yarn comprised of oxidized polyacrylonitrile which is at least partially coated with a cured silicon polymer resin. The silicon polymer resin may be blended with UV stabilizers such as a benzophenone in an amount of from 0.3 to 10 parts by weight of the silicone polymer. The silicon polymer coating may be applied to the yarn or fabric in an amount of about 5 wt% to 200 wt% of the original yarn or fabric. JP 3 249 289 also provides a generic disclosure on ropes made from ultrahigh molecular weight polyolefin fibers and coated with a thermosetting or thermoplastic resin that may contain a UV-absorber. It was however observed that the stability to UV irradiation of the products of US 2010/007119 or JP 3 249 289 can still be optimized.

A further method to improve the UV stability of a polymeric yarn is to use fibers containing a filler having UV stabilisation properties instead of using fibers coated with a coating containing a UV stabilizer. Such a method is for example described in JP 5 287 680 A wherein it is disclosed a method of spinning a fiber from a composition containing a polymer blended with a UV stabilizer. However, it was noticed that the UV stabilisation of yarns obtained by such methods can also be further optimized.

In a first embodiment, the present invention provides an ultrahigh molecular weight polyolefin fiber coated with a coating composition, wherein the

coating composition contains a UV stabilizer, characterized in that the amount of UV stabilizer is between 2 wt% and 80 wt.% compared to the total weight of the coating composition based on solids. Preferably, said amount of UV stabilizer is at least 5 wt%, more preferably at least 10 wt %, even more preferably at least 20 wt%, most preferably at least 30 wt%. Preferably, said amount of UV stabilizer is at most 75 wt%, more preferably at most 70 wt %, even more preferably at most 65 wt%, most preferably at most 60 wt.%. The weight of the fibers before and after coating followed by drying if necessary is measured to calculate the amount or the weight of the preferably dried coating composition. Preferably, the amount of the coating composition compared to the total weight of the ultrahigh molecular weight polyolefin fiber and based on solids is at least 1 wt %, more preferably at least 4 wt%, most preferably at least 8 wt%. Preferably, said amount of the coating composition is at most 20 wt%, more preferably at most 17 wt%, most preferably at most 15 wt %. In a preferred embodiment, a rope is provided comprising ultrahigh molecular weight polyolefin fibers, wherein the amount of the coating composition compared to the total weight of the rope and based on solids is at between 1 wt % and 30 wt%, more preferably between 2 wt% and 15 wt%. In a further preferred embodiment, a rope is provided, said rope comprising the coated ultrahigh molecular weight polyolefin fibers of the invention, wherein the amount of the coating composition compared to the total weight of the rope and based on solids is at between 1 wt % and 30 wt%, more preferably between 2 wt% and 15 wt%.

In a second embodiment, the present invention provides a high strength fiber coated with a coating composition, wherein the coating composition contains a UV absorber, characterized in that the amount of the UV absorber is at least 10 wt % compared to the total weight of the coating composition based on solids. Preferably, said amount of UV absorber is at least 20 wt%, most preferably at least 30 wt%. Preferably, said amount of UV absorber is at most 80 wt%, more preferably at most 70 wt %, most preferably at most 60 wt.%. Preferably, the amount of the coating composition compared to the total weight of the high strength fiber and based on solids is at least 1 wt %, more preferably at least 4 wt%, most preferably at least 8 wt%. Preferably, said amount of the coating composition is at most 20 wt%, more preferably at most 17 wt%, most preferably at most 15 wt %. In a preferred embodiment, a rope is provided comprising high strength fibers, wherein the amount of the coating composition compared to the total weight of the rope and based on solids is at between 1 wt % and 30 wt%, more preferably between 2 wt% and 15 wt%. In a further preferred

embodiment, a rope is provided, said rope comprising the high strength fibers of the invention, wherein the amount of the coating composition compared to the total weight of the rope and based on solids is at between 1 wt % and 30 wt%, more preferably between 2 wt% and 15 wt%.

5 The advantage of applying the UV absorber in the coating of the fiber is that the stabiliser protects the fiber against the influence of UV light without having an effect on the mechanical properties of the fiber. Most importantly it was observed that the fibers of the invention may show an improved retention of their mechanical properties and in particular of their tenacity. Moreover, the use of such an absorber
10 does not affect the manufacturing process of the fiber in any way. For the present invention the terms "UV stabilizer" and "UV absorber" are interchangeably used.

 In the embodiments of the invention, the UV stabiliser is preferably present in an amount of from 2 wt% to 80 wt.% compared to the total weight of the coating composition, based on solids, i.e. the dry coating composition. Preferably the
15 amount is from 5 wt% to 60 wt.% of stabiliser.

 Preferred UV absorbers used in accordance with the invention are compounds that absorb UV radiation such that the UV radiation interacts less with the polymer used to manufacture the fibers. Preferred stabilisers absorb UV in the range of 290 to 400 nm. The stabilisers according to the invention can be organic or inorganic
20 absorbers.

 Examples of inorganic stabilisers are carbon black, titanium dioxide (TiO₂), ZnO and CeO₂.

 Examples of organic stabilisers are those falling in the classes of hydroxybenzophenones, hydroxyphenylbenzotriazoles, oxalanilides, phenyl esters,
25 benzooxazinones, cyanoacrylates, formamidine, benzylidene malonates and hydroxyphenyl triazines.

 Examples of UV stabilisers suitable for the invention are for instance described in EP 0 697 481 A2, WO2006/082145, WO2009/060043 and WO2007/08814.

30 Further examples of hydroxybenzophenones are 2-Hydroxy-4-n-octoxybenzophenone; 2-Hydroxy-4-methoxybenzophenone; 2-Hydroxy-4-n-dodecyloxy-benzophenone; 2,4-Dihydroxybenzophenone; 2-Propenoic acid, 2-(4-benzoyl-3-hydroxyphenoxy)ethyl ester; Methanone, [2-hydroxy-4-(phenylmethoxy)phenyl]phenyl-; 2,2'-Dihydroxy-4-methoxybenzophenone; 2,2',4,4'-
35 Tetrahydroxy benzophenone; 2,2'-Dihydroxy-4,4'-dimethoxybenzophenone; Poly-4-(2-

acryloyloxyethoxy)-2-hydroxybenzophenone; Bis-(2-methoxy-4-hydroxy-5-benzoyl-phenyl)-methane; Methanone, [3-(2,4-dihydroxybenzoyl)phenyl][2-hydroxy-4-(2-propenyloxy)phenyl]-; 2,2-Dihydroxy-4,4'-dimethoxy-benzophenone-5,5'-bis-(sodiumsulphonate); 2-Hydroxy-4-methoxy-benzophenone-5-sulfonic acid; Methanone, [2-hydroxy-4-(2-hydroxyethoxy)phenyl]phenyl-; Mixture of 2,2',4,4'-tetrahydroxybenzophenone and 2,2'-dihydroxy-4,4'-dimethoxybenzophenone ; 1,4-bis(4-benzoyl-3-hydroxyphenoxy)-butane; 2-Butenoic acid, 2-(4-benzoyl-3-hydroxyphenoxy)-1-[(4-benzoyl-3-hydroxyphenoxy)methyl]ethyl ester.

Further examples of hydroxyphenylbenzotriazoles are 2-(2'-Hydroxy-3',5'-di-t-butyl-phenyl)-benzotriazole; 2-(2'-Hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole; Phenol, 2-(5-chloro-2H-benzotriazol-2-yl)-4,6-bis-(1,1-dimethylethyl)-; 2-(2'-Hydroxy-3,5'-di-t-amylphenyl) benzotriazole; Phenol, 2-(2H-benzotriazol-2-yl)-4-methyl- ; Phenol, 2-(2H-benzotriazol-2-yl)-4-(1,1-dimethylethyl)-; Phenol, 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)-; Benzene propanoic acid, 3-(2H-benzotriazole-2-yl)-5-(1,1-dimethylethyl)-4-hydroxy-1,6-hexanediylester; Bis[2-hydroxy-5-t-octyl-3-(benzotriazol-2-yl)phenyl]methane; 2-[2-Hydroxy-3,5-di(1,1-dimethylbenzyl)phenyl]2H-benzotriazole; 2-[2-Hydroxy-3-(3,4,5,6-tetrahydrophthalimidomethyl)-5-methylphenyl]benzotriazole; Bis[2-hydroxy-5-methyl-3-(benzotriazol-2-yl)phenyl]methane; 2(2'-Hydroxy-5-metacryloyloxyethylphenyl)2H-benzotriazole; Phenol, 2-(2H-benzotriazol-2-yl)-4-(1,1-dimethylethyl)-6-(2-methylpropyl)-; Isomer mixture from the alkylation of 2-(2H-benzotriazole-2-yl)-p-cresol with dodecane; α -[3-[3-(2H-Benzotriazole-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropyl]- ω -hydrxypoly(oxo-1,2-ethanediyl); α -[3-[3-(2H-Benzotriazole-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropyl]- ω -[3-[3-(2H-Benzotriazole-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]]poly(oxy-1,2-ethanediyl); Benzenepropanoic acid, 3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxy- C7-9-branched and linear alkyl esters; 2-(2H-Benzotriazol-2-yl)-6-(1-methyl-1-phenylethyl)-4-(1,1,3,3-tetramethylbutyl)phenol; 2-(2'-Hydroxy-5'-(2-hydroxyethyl))-benzotriazole; 2-(2-hydroxy-4-octyloxyphenyl)- 2H-benzotriazole; Sodium Benzotriazolyl Butylphenol Sulfonate; Octyl-3-[3-tert-butyl-4-hydroxy-5-(5-chloro-2H-benzotriazole-2-yl)phenyl]propionaat ; 2-Ethylhexyl-3-[3-tertbutyl-4-hydroxy-5-(5-chloro-2H-benzotriazole-2-yl) phenyl]propionaat; Phenol, 2-(2H-benzotriazol-2-yl)-6-[[3-(1,1-dimethylethyl)-2-hydroxy-5-methylphenyl]methyl]-4-(1,1,3,3-tetramethylbutyl)-.

Further examples of oxalanilides are 2-Ethoxy-5-t-butyl-2'-ethyl-oxalanilide; 2-Ethyl, 2'-ethoxy-oxalanilide; N-(2-ethoxy-phenyl)-N'-(4-iso-dodecyl-

phenyl)-ethanediamin.

Further examples of phenyl esters are 4-t-Butyl-phenyl-salicylate; 2,4-Di-t-butylphenyl 3,5-di-t-butyl-4-hydroxybenzoate; Benzoic acid, 2-hydroxy-, phenyl ester.

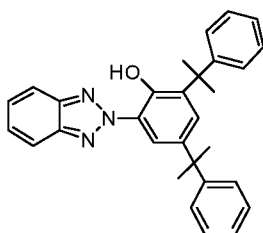
5 Further examples of Benzooxazinones are 2,2'-(1,4-Phenylene)bis[4H-3,1-benzoxazin-4-one.

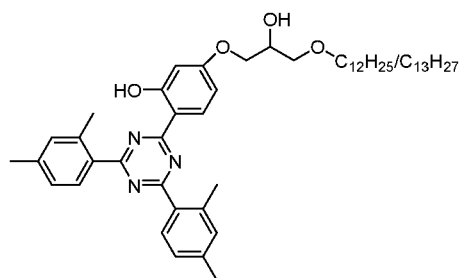
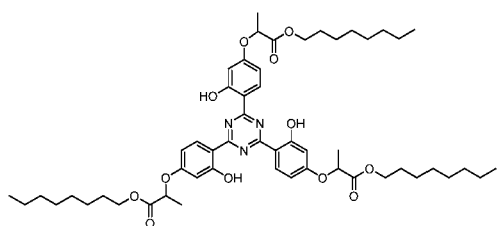
Examples of cyanoacrylates are Ethyl 2-cyano-3,3-diphenylacrylate; 2-Ethylhexyl 2-cyano-3,3-diphenylacrylate; 1,3-bis-[2'-cyano-3',3-diphenylacryloyl)oxy]-2,2-bis-[[2-cyano- 3',3'-diphenylacryloyl)oxy]methyl}propane.

10 Further examples include N-(p-Ethoxy-carbonylphenyl)-N'-methyl-N'-phenylformamidine; N-(p-Ethoxy-carbonylphenyl)-N'-ethyl-N'-phenylformamidine, and 2-Propenoic acid, 3-(4-methoxyphenyl)-, 2-ethylhexyl ester; Propanedioic acid, [(4-methoxyphenyl)-methylene]-dimethyl ester; Tetra-ethyl-2,2'-(1,4-phenylene-dimethylidene)-bismalonate.

15 Examples of hydroxyphenyl triazines are 2-[4,6-Diphenyl-1,3,5-triazin-2-yl]-5-(hexyl)oxy-phenol; Propanoic acid, 2-[4-[4,6-bis([1,1'-biphenyl]-4-yl)-1,3,5-triazin-2-yl]-3-hydroxyphenoxy]-, isooctyl ester; Phenol, 2-[4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl]-5-(octyloxy)- ; 2-[4-[(2-Hydroxy-3-(2'-ethyl)hexyl)oxy]-2-hydroxyphenyl]-4,6- bis(2,4-dimethylphenyl)-1,3,5-triazine;; 2-[4-[(2-Hydroxy-3-dodecyloxypropyl)oxy]-2-hydroxyphenyl]-4,6-bis(2,4- dimethylphenyl)-1,3,5-triazine; 2-[4-[(2-Hydroxy-3-tridecyloxypropyl)oxy]-2-hydroxyphenyl]-4,6-bis(2,4- dimethylphenyl)-1,3,5-triazine; 2,4-Bis[2-hydroxy-4-butoxyphenyl]-6-(2,4-dibutoxyphenyl)-1,3,5-triazine; 5,5'-Bis(2-ethylhexyloxy)-2,2'-[6-(4-methoxyphenyl)-1,3,5-triazine-2,4-diyl]diphenol; Propanoic acid, 2,2',2''-[1,3,5-triazine-2,4,6-triyl]tris[(3-hydroxy-4,1-phenylene)oxy]]tris-,
25 1,1',1''-trioctyl ester;

Most preferred compounds are those with the structures as shown below:





5 According to a preferred aspect of the invention the coating composition containing the UV absorber further comprises a carrier.

The carrier can be any known coating for ultrahigh molecular weight polyolefin fibers or high strength fibers such as a wax, a polyacrylate coating, a polyurethane coating or silicone coating.

10 Preferably, the coating composition used in accordance with the invention comprises a silicon polymer, more preferably a cross-linked silicone polymer as a carrier for the UV stabilizer.

In particular, the invention provides an ultrahigh molecular weight polyolefin fiber or a high strength fiber as described above wherein the coating
15 comprises a cross-linked silicone polymer as a carrier for the UV stabiliser.

Such a coating is for instance described in unpublished patent application PCT/EP2010/060813 which is incorporated herein by reference.

In the present invention, the coating on the ultrahigh molecular weight polyolefin fiber or on the high strength fibers is preferably obtained by applying a
20 coating composition comprising a cross-linkable silicone polymer. After the application of the coating composition to the fibers, the coating composition may be cured, e.g. by heating to cause cross-linking of the cross-linkable silicone polymer. The cross-linking may also be induced by any other suitable methods known to the skilled person. The temperature for curing the coating composition is from 20 to 200 °C, preferably from 50
25 to 170 °C, more preferably 120 to 150 °C. The curing temperature should not be too low, for the curing to be effective. Should the curing temperature become too high,

there is a risk that the ultrahigh molecular weight polyolefin fiber or the high strength fiber deteriorates and loses its strength.

The weight of the fibers before and after coating followed by curing is measured to calculate the weight of the cross-linked coating. For a fiber, the weight of the cross-linked coating is 1 to 20 wt.%, based on the total weight of the fiber, preferably 1 to 10 wt.%. For a rope, preferably, the weight of the cross-linked coating is 1 to 30 wt.% based on the total weight of rope and coating, preferably 2 to 15 wt.%.

The degree of the cross-linking may be controlled. The degree of the cross-linking may be controlled by e.g. the temperature or the time period of the heating. The degree of the cross-linking, if performed in other ways, may be controlled in methods known to the skilled person. The measurement of the degree of the cross-linking may be performed as follows:

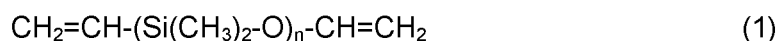
The fibers provided with the (at least partially) cross-linked coating is dipped in a solvent. The solvent is chosen with which the extractables (mainly monomers) groups in the polymer would dissolve which are not cross-linked and the cross-linked network would not dissolve. A preferred solvent is hexane. By weighing the rope or the fibers after the dipping in such a solvent, the weight of the non-cross-linked portion can be determined and the ratio of the cross-linked silicone to the extractables can be calculated.

The preferred degree of cross-linking is at least 30%, i.e. at least 30 wt%, based on the total weight of the coating, of the coating remains on the fibers or rope after extraction with the solvent. More preferably the degree of cross-linking is at least 50%. The maximum degree of cross-linking is about 100%.

Preferably, the cross-linkable silicone polymer comprises a silicone polymer having a reactive end-group. It was found that a cross-linking in the end-groups of the silicone polymer results in a good bending resistance. A silicone polymer which is cross-linked at the end groups rather than at the branches in the repeating unit results in a less rigid coating. Without being limited thereto, the inventors attribute the improved properties of the rope to the less rigid structure of the coating.

Preferably, the cross-linkable end-group is an alkylene end group, more preferably a C₂-C₆ alkylene end group. In particular the end group is a vinyl group or a hexenyl group. In general, a vinyl group is preferred.

Preferably, the cross-linkable silicone polymer has the formula:

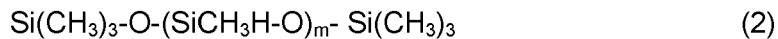


wherein n is a number from 2 to 200, preferably from 10 to 100, more preferably from

20 to 50.

Preferably, the coating composition further contains a cross-linker.

The cross-linker preferably has the formula:



5 wherein m is a number n is a number from 2 to 200, preferably from 10 to 100, more preferably from 20 to 50.

Preferably, the coating composition further comprises a metal catalyst for cross-linking the cross-linkable silicone polymer, the metal catalyst preferably being a platinum, palladium or rhodium, more preferably platinum metal complex catalyst. Such catalysts are known to the skilled person.

Preferably, the coating composition is a multi-component silicone system comprising a first emulsion comprising the cross-linkable silicone polymer and the cross-linker and a second emulsion comprising the cross-linkable silicone polymer and the metal catalyst.

15 Preferably, the weight ratio between the first emulsion and the second emulsion is from about 100:1 to about 100:30, preferably 100:5 to 100:20, more preferably 100:7 to 100:15.

The coating compositions as described above are known in the art. They are often referred to as addition-curing silicone coatings or coating emulsions. The cross-linking or curing takes place when the vinyl end groups react with the SiH group of the cross-linker.

20 Examples of such coatings are Dehesive® 430 (cross-linker) and Dehesive® 440 (catalyst) from Wacker Silicones; Silcolease® Emulsion 912 and Silcolease® catalyst 913 from Bluestar Silicones; and Syl-off® 7950 Emulsion Coating and Syl-off® 7922 Catalyst Emulsion from Dow Corning.

The UV stabiliser of the invention can be included in the carrier composition prior to cross-linking.

Within the context of the present invention, fibers are understood to mean elongated bodies of indefinite length and with length dimension much greater than width and thickness. In one embodiment, the term fiber includes a body chosen from the group consisting of a monofilament, a multifilament yarn, a ribbon, a strip or tape. The fiber can have a regular or an irregular cross-section. The term fibers also includes a plurality of any one or combination of the above.

Thus, the coating according to the invention can be applied to a single fiber or filament, but also to a bundle of more than one fiber, also referred to as a yarn.

Fibers having the form of monofilaments or tape-like fibers can be of varying titer, but typically have a titer in the range of 10 to several thousand dtex, preferably in the range of 100 to 2500 dtex, more preferably 200-2000 dtex. Multifilament yarns contain a plurality of filaments having a titer typically in the 0.2 – 25 dtex range, preferably about 0.5-20 dtex. The titer of a multifilament yarn may also vary widely, for example from 50 to several thousand dtex, but is preferably in the range of about 200-4000 dtex, more preferably 300-3000 dtex.

With high strength fibers for use in the invention are meant having a tenacity of at least 1.5 N/tex, more preferably at least 2.0 N/tex, even more preferably at least 2.5 N/tex, most preferably at least 3.0 N/tex. In case of ultrahigh molecular weight polyolefin fibers, said fibers preferably have a tenacity of at least 2.0 N/tex, more preferably at least 2.5 N/tex, most preferably at least 3.0 N/tex. Tensile strength, also simply referred to as strength, or tenacity of filaments are determined by known methods, as based on ASTM D2256-97. Generally such high-strength polymeric filaments or ultrahigh molecular weight polyolefin fibers also have a high tensile modulus, e.g. at least 50 N/tex, preferably at least 75, 100 or even at least 125 N/tex.

Examples of high strength fibers are fibers manufactured from polyaramides, e.g. poly(p-phenylene terephthalamide) (known as Kevlar®); poly(tetrafluoroethylene) (PTFE); aromatic copolyamid (co-poly-(paraphenylene/3,4'-oxydiphenylene terephthalamide)) (known as Technora®); poly{2,6-diimidazo-[4,5b-4',5'e]pyridinylene-1,4(2,5-dihydroxy)phenylene} (known as M5); poly(p-phenylene-2,6-benzobisoxazole) (PBO) (known as Zylon®); thermotropic liquid crystal polymers (LCP) as known from e.g. US 4,384,016. but also polyolefins such as polyethylene or polypropylene, e.g. homopolymers and copolymers of polyethylene or polypropylene. Also combinations of fibers manufactured from the above referred polymers can be used in the rope of the invention. Preferred high-strength fibers are fibers of polyethylene, polyaramides or LCP.

A preferred example of ultrahigh molecular weight polyolefin fibers is ultrahigh molecular weight polyethylene fibers.

Most preferred fibers are high performance polyethylene (HPPE) fibers. HPPE fibers are herein understood to be fibers made from ultra-high molar mass polyethylene (also called ultra-high molecular weight polyethylene; UHMWPE),

and having a tenacity of at least 1.5 N/tex, preferably at least 2.0 N/tex, more preferably at least 2.5 N/tex or even at least 3.0 N/tex. There is no reason for an upper limit of tenacity of HPPE fibers as HPPE fibers having a tenacity of about 5 or 6 N/tex are also available. The HPPE fibers also have a high tensile modulus, e.g. of at least 75 N/tex, preferably at least 100 N/tex or at least 125 N/tex. HPPE fibers are also referred to as high-modulus polyethylene fibers.

In a preferred embodiment, the HPPE fibers in the invention are one or more multi-filament yarns.

HPPE fibers, filaments and multi-filament yarn, can be prepared by spinning of a solution of UHMWPE in a suitable solvent into gel fibers and drawing the fibers before, during and/or after partial or complete removal of the solvent; that is via a so-called gel-spinning process. Gel spinning of a solution of UHMWPE is well known to the skilled person; and is described in numerous publications, including EP 0205960 A, EP 0213208 A1, US 4413110, GB 2042414 A, EP 0200547 B1, EP 0472114 B1, WO 01/73173 A1, and in Advanced Fiber Spinning Technology, Ed. T. Nakajima, Woodhead Publ. Ltd (1994), ISBN 1-855-73182-7, and in references cited therein, all incorporated herein by reference.

HPPE fibers, filaments and multi-filament yarn can also be prepared by melt-spinning of UHMWPE, although the mechanical properties such as tenacity are more limited compared to HPPE fibers made by the gel-spinning process. The upper limit of the molecular weight of the UHMWPE which can be melt-spun is lower than the limit with the gel-spinning process. The melt-spinning process is widely known in the art, and involves heating a PE composition to form a PE melt, extruding the PE melt, cooling the extruded melt to obtain a solidified PE, and drawing the solidified PE at least once. The process is mentioned e.g. in EP1445356A1 and EP1743659A1, which are incorporated herein by reference.

UHMWPE is understood to be polyethylene having an intrinsic viscosity (IV, as measured on solution in decalin at 135°C) of at least 5 dl/g, preferably of between about 8 and 40 dl/g. Intrinsic viscosity is a measure for molar mass (also called molecular weight) that can more easily be determined than actual molar mass parameters like M_n and M_w . There are several empirical relations between IV and M_w , but such relation is dependent on molar mass distribution. Based on the equation $M_w = 5.37 \cdot 10^4 [IV]^{1.37}$ (see EP 0504954 A1) an IV of 8 dl/g would be equivalent to M_w of about 930 kg/mol. Preferably, the UHMWPE is a linear polyethylene with less than one branch per 100 carbon atoms, and preferably less than one branch per 300 carbon

atoms; a branch or side chain or chain branch usually containing at least 10 carbon atoms. The linear polyethylene may further contain up to 5 mol% of one or more comonomers, such as alkenes like propylene, butene, pentene, 4-methylpentene or octene.

5 In one embodiment, the UHMWPE contains a small amount, preferably at least 0.2, or at least 0.3 per 1000 carbon atoms, of relatively small groups as pending side groups, preferably a C1-C4 alkyl group. Such a fiber shows an advantageous combination of high strength and creep resistance. Too large a side group, or too high an amount of side groups, however, negatively affects the process of
10 making fibers. For this reason, the UHMWPE preferably contains methyl or ethyl side groups, more preferably methyl side groups. The amount of side groups is preferably at most 20, more preferably at most 10, 5 or at most 3 per 1000 carbon atoms.

 The HPPE according to the invention may further contain small amounts, generally less than 5 mass%, preferably less than 3 mass% of customary
15 additives, such as anti-oxidants, thermal stabilisers, colorants, flow promoters, etc. The UHMWPE can be a single polymer grade, but also a mixture of two or more different polyethylene grades, e.g. differing in IV or molar mass distribution, and/or type and number of comonomers or side groups.

 The ultrahigh molecular weight polyolefin fibers or the high strength
20 fibers of the invention can be used in any application where such fibers are normally applied. In particular the fibers of the invention can be used in ropes, fishing lines and nets.

 Although the invention is here described as a fiber with a coating, according to another embodiment, the coating can also be applied to an article
25 containing the fibers, such as a rope or fishing net. Thus, the invention also relates to an article, preferably a rope or fishing net, coated with a coating composition, wherein the coating composition contains a UV absorber. Preferred embodiments of UV absorber and of the coating composition are as described above.

 Methods of making a rope or fishing net are known to the skilled
30 person.

 The invention is further illustrated by the Examples below.

Analytical methods

Weathering

35 The samples were UV-tested according to ISO 4982-2 against their

untreated reference yarns over a maximum of 120 days. The time until tenacity decreased with 50% was determined.

Mechanical properties

- 5 Tensile properties were determined on a Zwick 1435, according to ASTM D 2256.

Examples

- 10 A coating composition was prepared from a first emulsion comprising a reactive silicone polymer preformulated with a cross-linker and a second emulsion comprising a silicone polymer and a metal catalyst. The first emulsion was an emulsion available from Dow Corning containing 30.0-60.0 wt% of dimethylvinyl-terminated dimethyl siloxane and 1.0-5.0 wt% of dimethyl, methylhydrogen siloxane (Syl-off® 7950 Emulsion Coating). The second emulsion was an emulsion available from Dow
15 Corning containing 30.0-60.0 wt% of dimethylvinyl-terminated dimethyl siloxane and a platinum catalyst (Syl-off® 7922 Catalyst Emulsion). The first emulsion and the second emulsion were mixed at a weight ratio of 8.3:1.

- A third solution is prepared of water and the UV stabiliser, or if the UV stabiliser is in itself a water based solution, this is used as is. The mixture of first
20 emulsion and second emulsion is diluted with this third solution to a predetermined solid content (see Table 1). The amount of UV stabiliser can be determined by adjusting the amount of third solution added.

- HPPE fibers, delivered by DSM in the Netherlands as Dyneema® SK 75, 1760dtex, were dipped in the coating composition at room temperature. The
25 fibers were heated in an oven at a temperature of 120°C so that cross linking takes place.

Table 1

Example	Silicone coating wt. %	Stabiliser type	Stabiliser in final dried coating wt. %	Time until tenacity is reduced with 50% hours
Comparative A	0	None	--	1618
Comparative B	4	None	--	1618
Comparative C	8	None	--	1618
1	4	Tinuvin 477-DW®*	10	2747
2	4	Tinuvin 477-DW®	20	2049
3	4	Tinuvin 477-DW®	30	2747
4	8	Tinuvin 477-DW®	10	2500
5	8	Tinuvin 477-DW®	20	2750
6	8	Tinuvin 477-DW®	30	3250

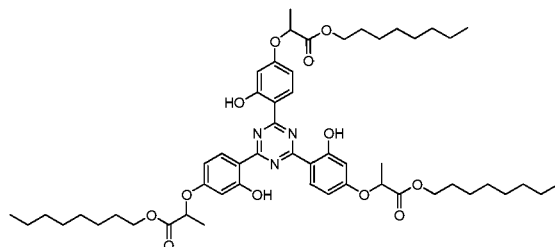
*Obtainable from Ciba Inc.

5

It can be seen from the examples above that the addition of stabiliser significantly improves the time until tenacity is reduced when the fiber is exposed to UV radiation.

CLAIMS

1. An ultrahigh molecular weight polyolefin fiber coated with a coating composition, wherein the coating composition contains a UV stabilizer,
5 characterized in that the amount of UV stabilizer is between 2 wt% and 80 wt.% compared to the total weight of the coating composition based on solids.
2. The high strength fiber according to claim 1, wherein the UV absorber is capable of absorbing UV radiation in the range of 290 to 400 nm.
3. The high strength fiber according to claim 1 or 2, wherein the UV absorber is
10 selected from the group consisting of hydroxybenzophenones, hydroxyphenylbenzotriazoles, oxalanilides, phenyl esters, benzooxazinones, cyanoacrylates, formamidine, benzylidene malonates and hydroxyphenyl triazines or combinations thereof.
4. The high strength fiber according to claim 3, wherein the UV stabiliser
15 is selected from hydroxybenzotriazoles and hydroxyphenyl triazines.
5. The high strength fiber according to claim 4, wherein the UV stabiliser is a compound having the formula:



6. The high strength fiber according to any of the preceding claims, which is a
20 high performance polyethylene (HPPE) fiber, made of ultrahigh molecular weight polyethylene (UHMWPE) having an intrinsic viscosity of at least 5 dl/g determined in decalin at 135 °C.
7. The high strength fiber according to any of the preceding claims, wherein the coating comprises a cross-linked silicone polymer as a carrier for the UV
25 absorber.
8. The high strength fiber according to claim 7, wherein the degree of cross-linking of the cross-linked silicone polymer is at least 20%.
9. The high strength fiber according to claim 7 or 8, wherein the coating comprising the cross-linked silicone polymer is obtained by
30 applying to the fiber, a coating composition comprising a cross-linkable

silicone polymer; and

cross-linking the cross-linkable silicone polymer.

10. The high strength fiber according to claim 9, wherein the cross-linkable
silicone polymer comprises a silicone polymer having a cross-linkable end-
5 group, preferably an C₂-C₆ alkylene end group.
11. The high strength fiber according to claim 9 or 10, wherein the cross-linkable
silicone polymer has the formula:
- $$\text{CH}_2=\text{CH}-(\text{Si}(\text{CH}_3)_2\text{O})_n-\text{CH}=\text{CH}_2 \quad (1)$$
- wherein n is a number from 2 to 200.
- 10 12. The high strength fiber according to any one of claims 9 to 11, wherein the
coating composition further comprises a cross-linker having the formula:
- $$\text{Si}(\text{CH}_3)_3\text{O}-(\text{SiCH}_3\text{HO})_m-\text{Si}(\text{CH}_3)_3 \quad (2)$$
- wherein m is a number of 2 to 200.
13. The high strength fiber according to any one of claims 9 to 11, wherein the
15 coating composition further comprises a platinum catalyst.
14. Use of a high strength fiber according to any of claims 1 to 13 for making a
rope or a fishing net.
15. An article, preferably a rope or fishing net, containing high strength fibers,
wherein the article is coated with a coating composition containing a UV
20 absorber.