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(54) **ROPES HAVING IMPROVED CYCLIC BEND OVER SHEAVE PERFORMANCE**

SEILE MIT VERBESSERTER ZYKLISCHER BIEGUNGSLEISTUNG UM SEILSCHEIBE

CORDES AYANT UNE RESISTANCE AMELIOREE A LA COURBURE CYCLIQUE SUR POULIE

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WO-A-2006/086338 **US-B2- 6 945 153**

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Description

Field of the Invention

[0001] This invention relates to improvements in ropes, and in particular to high tenacity synthetic ropes suitable for use in marine applications.

Description of the Related Art

[0002] Synthetic fiber ropes have been used in a variety of applications, including various marine applications. One type of rope that has excellent properties is rope made from high modulus polyolefin fibers and/or yarns. High tenacity polyolefin fibers are also known as extended chain or high molecular weight fibers. These fibers and yarns are available, for example, as SPECTRA® extended chain polyethylene fibers and yarns from Honeywell International Inc.

[0003] Ropes formed from extended chain polyethylene fibers have been suggested for use in marine applications. See, for example, U.S. Patents 5,901,632 and 5,931,076 both to Ryan. In some marine applications, extended chain polyethylene ropes are repeatedly bent over sheaves, pulleys or posts as they are being used. Some synthetic ropes experience premature wear when they are subjected to repeated bending over sheaves, and particularly synthetic ropes used in marine industrial applications have experienced this problem.

[0004] Synthetic ropes continue to replace steel wire in many marine applications. As synthetic ropes progress to replace steel wire in many cyclic bend-over sheave (CBOS) applications, the need exists to improve the fatigue life of high performance synthetic ropes. In particular, the need exists to improve the performance of ropes made from high performance polyolefin fibers and yarns.

[0005] One proposed solution to provide a rope with improved properties is disclosed in U.S. Patent 6,945,153 to Knudsen et al. This patent discloses a large diameter rope that is formed from a blend of extended chain polyethylene fibers and liquid crystal polymer fibers. It would be desirable to improve the properties of such rope.

[0006] It would be desirable to provide a high tenacity polyolefin fiber rope which had improved wear resistance to repeated bending over sheaves and the like, especially in wet applications, while maintaining its otherwise excellent properties. It would also be desirable to provide a rope that is suitable for use in heavy lifting applications, e.g., to and from the seabed.

SUMMARY OF THE INVENTION

[0007] In accordance with this invention, there is provided a rope having improved CBOS fatigue resistance, the rope comprising high tenacity fibers, the rope and/or the fibers being coated with a composition comprising an amino functional silicone resin and a neutralized low molecular weight polyethylene.

[0008] In further accordance with this invention, there is provided a rope having improved CBOS fatigue resistance, the rope comprising a blend of high tenacity polyolefin fibers with other high tenacity fibers that are not polyolefin fibers, the rope and/or the fibers being coated with a composition comprising an amino functional silicone resin and a neutralized low molecular weight polyethylene.

[0009] Also in accordance with this invention, there is provided a rope having improved CBOS fatigue resistance, the rope comprising a blend of high tenacity polyolefin fibers with other high tenacity fibers, the other high tenacity fibers comprising aramid fibers and/or liquid crystal copolyester fibers, the rope and/or the fibers being coated with a composition comprising an amino functional silicone resin and a neutralized low molecular weight polyethylene.

[0010] In still further accordance with this invention, there is provided a method of improving the CBOS fatigue life of a rope, the method comprising forming the rope from high tenacity fibers, and coating the rope and/or the fibers forming such rope with a composition comprising an amino functional silicone resin and a neutralized low molecular weight polyethylene.

[0011] Also in accordance with this invention, there is provided in a method of lifting and placing heavy objects from and onto a seabed using a synthetic fiber rope, the improvement comprising utilizing as such rope a rope comprising high tenacity fibers, the rope and/or the fibers being coated with a composition comprising an amino functional silicone resin and a neutralized low molecular weight polyethylene.

[0012] It has been discovered that when high tenacity fibers are coated with a composition comprising an amino functional silicone resin and a neutralized low molecular weight polyethylene and formed into a rope, or if a rope formed from such uncoated fibers is coated with the composition, the cyclic bend over sheave resistance of such rope is unexpectedly improved. It has also been discovered that when high tenacity fibers are blended with other high tenacity fibers and the blended fibers are coated with a composition comprising an amino functional silicone resin and a neutralized low molecular weight polyethylene and formed into a rope, or if a rope formed from such blended fibers is coated with the composition, the cyclic bend over sheave resistance of such rope is unexpectedly improved.

DETAILED DESCRIPTION OF THE INVENTION

[0013] For the purposes of the present invention, a fiber is an elongate body the length dimension of which is much greater that the transverse dimensions of width and thickness. Accordingly, the term "fiber" includes monofilament, multifilament, ribbon, strip, staple and other forms of chopped, cut or discontinuous fiber and the like having regular or irregular cross-sections. The term

"fiber" includes a plurality of any of the foregoing or a combination thereof. A yarn is a continuous strand comprised of many fibers or filaments. Fibers may also be in the form of ribbon, strip or split film or tape.

[0014] The cross-sections of fibers useful herein may vary widely. They may be circular, flat or oblong in cross-section. They may also be of irregular or regular multilobal cross-section having one or more regular or irregular lobes projecting from the linear or longitudinal axis of the fibers. It is preferred that the fibers be of substantially circular, flat or oblong cross-section, most preferably substantially circular.

[0015] As mentioned above, ropes comprising high modulus polyolefin fibers, such as extended chain polyethylene fibers, and yarns made therefrom have been suggested for use in marine applications. One such use of the ropes is for heavy lifting and mooring of objects onto the seabed. Other applications include offshore oil and gas exploration, oceanographic, seismic and other industrial applications. The most preferred applications for ropes of this invention include deep sea lifting and placement.

[0016] The fibers used in the rope construction of this invention are high tenacity fibers. As used herein, the term "high tenacity fibers" means fibers which have tenacities equal to or greater than about 7 g/d. Preferably, these fibers have initial tensile moduli of at least about 150 g/d and energies-to-break of at least about 8 J/g as measured by ASTM D2256. As used herein, the terms "initial tensile modulus", "tensile modulus" and "modulus" mean the modulus of elasticity as measured by ASTM 2256 for a yarn.

[0017] Preferably, the high tenacity fibers have tenacities equal to or greater than about 10 g/d, more preferably equal to or greater than about 16 g/d, even more preferably equal to or greater than about 22 g/d, and most preferably equal to or greater than about 28 g/d.

[0018] The high tenacity fibers may be used alone in the rope construction, or more preferably are used as blends of two or more high tenacity fibers of different chemical composition in the rope construction.

[0019] High tenacity fibers useful herein include highly oriented high molecular weight polyolefin fibers, particularly high modulus polyethylene fibers and polypropylene fibers, aramid fibers, polybenzazole fibers such as polybenzoxazole (PBO) and polybenzothiazole (PBT), polyvinyl alcohol fibers, polyacrylonitrile fibers, polyamide fibers, polyester fibers, liquid crystal copolyester fibers, glass fibers, carbon fibers or basalt or other mineral fibers, as well as rigid rod polymer fibers, and mixtures and blends thereof. Preferred high strength fibers useful in this invention include polyolefin fibers, aramid fibers and liquid copolyester fibers, and mixtures and blends thereof. Most preferred are high molecular weight polyethylene fibers, aramid fibers and liquid copolyester fibers, and blends and mixtures thereof. Although yarns that form the ropes can be made from a blend of two or more of such high tenacity fibers, preferably the yarns that make up the rope are formed from a single high tenacity fiber type, and two or more yarns of different fiber types are used to form the rope.

[0020] Preferred blends are blends of high tenacity polyethylene fibers and aramid fibers, and blends of high tenacity fibers and liquid crystal copolyester fibers, as well as blends of aramid fibers and liquid crystal copolyester fibers.

[0021] The fibers utilized in the rope construction preferably comprise extended chain (also known as high molecular weight, high tenacity or high modulus) polyolefin fibers, particularly high modulus polyethylene fibers and polypropylene fibers.

[0022] U.S. Pat. No. 4,457,985 generally discusses such high molecular weight polyethylene and polypropylene fibers, and the disclosure of this patent is hereby incorporated by reference to the extent that it is not inconsistent herewith. In the case of polyethylene, suitable fibers are those of weight average molecular weight of at least about 150,000, preferably at least about one million and more preferably between about two million and about five million. Such high molecular weight polyethylene fibers may be spun in solution (see U.S. Pat. No. 4,137,394 and U.S. Pat. No. 4,356,138), or a filament spun from a solution to form a gel structure (see U.S. Pat. No. 4,413,110, German Off. No. 3,004, 699 and GB Patent No. 2051667), or the polyethylene fibers may be produced by a rolling and drawing process (see U.S. Pat. No. 5,702,657). As used herein, the term polyethylene means a predominantly linear polyethylene material that may contain minor amounts of chain branching or comonomers not exceeding about 5 modifying units per 100 main chain carbon atoms, and that may also contain admixed therewith not more than about 50 wt % of one or more polymeric additives such as alkene-1-polymers, in particular low density polyethylene, polypropylene or polybutylene, copolymers containing mono-olefins as primary monomers, oxidized polyolefins, graft polyolefin copolymers and polyoxymethylenes, or low molecular weight additives such as antioxidants, lubricants, ultraviolet screening agents, colorants and the like which are commonly incorporated.

[0023] High tenacity polyethylene fibers are available, for example, under the trademark SPECTRA® fibers and yarns from Honeywell International Inc. of Morristown, New Jersey, U.S.A

[0024] Depending upon the formation technique, the draw ratio and temperatures, and other conditions, a variety of properties can be imparted to these fibers. The tenacity of the polyethylene fibers are at least about 7 g/d, preferably at least about 15 g/d, more preferably at least about 20 g/d, still more preferably at least about 25 g/d and most preferably at least about 30 g/d. Similarly, the initial tensile modulus of the fibers, as measured by an Instron tensile testing machine, is preferably at least about 300 g/d, more preferably at least about 500 g/d, still more preferably at least about 1,000 g/d and most preferably at least about 1,200 g/d. These highest values

for initial tensile modulus and tenacity are generally obtainable only by employing solution grown or gel spinning processes. Many of the filaments have melting points higher than the melting point of the polymer from which they were formed. Thus, for example, high molecular weight polyethylene of about 150,000, about one million and about two million molecular weight generally have melting points in the bulk of 138°C. The highly oriented polyethylene filaments made of these materials have melting points of from about 7°C to about 13°C higher. Thus, a slight increase in melting point reflects the crystalline perfection and higher crystalline orientation of the filaments as compared to the bulk polymer.

[0025] Preferably the polyethylene employed is a polyethylene having fewer than about one methyl group per thousand carbon atoms, more preferably fewer than about 0.5 methyl groups per thousand carbon atoms, and less than about 1 wt. % of other constituents.

[0026] Similarly, highly oriented high molecular weight polypropylene fibers of weight average molecular weight at least about 200,000, preferably at least about one million and more preferably at least about two million may be used. Such extended chain polypropylene may be formed into reasonably well oriented filaments by the techniques prescribed in the various references referred to above, and especially by the technique of U.S. Pat. No. 4,413,110. Since polypropylene is a much less crystalline material than polyethylene and contains pendant methyl groups, tenacity values achievable with polypropylene are generally substantially lower than the corresponding values for polyethylene. Accordingly, a suitable tenacity is preferably at least about 8 g/d, more preferably at least about 11 g/d. The initial tensile modulus for polypropylene is preferably at least about 160 g/d, more preferably at least about 200 g/d. The melting point of the polypropylene is generally raised several degrees by the orientation process, such that the polypropylene filament preferably has a main melting point of at least 168°C, more preferably at least 170°C. The particularly preferred ranges for the above described parameters can advantageously provide improved performance in the final article. Employing fibers having a weight average molecular weight of at least about 200,000 coupled with the preferred ranges for the above-described parameters (modulus and tenacity) can provide advantageously improved performance in the final article.

[0027] In the case of extended chain polyethylene fibers, preparation and drawing of gel-spun polyethylene fibers are described in various publications, including U.S. Patents 4,413,110; 4,430,383; 4,436,689; 4,536,536; 4,545,950; 4,551,296; 4,612,148; 4,617,233; 4,663,101; 5,032,338; 5,246,657; 5,286,435; 5,342,567; 5,578,374; 5,736,244; 5,741,451; 5,958,582; 5,972,498; 6,448,359; 6,969,553 and U.S. patent application publication 2005/0093200. In the case of aramid fibers, suitable fibers formed from aromatic polyamides are described in U.S. Pat. No. 3,671,542, which is incorporated herein by reference to the extent not inconsistent herewith. Preferred aramid fibers will have a tenacity of at least about 20 g/d, an initial tensile modulus of at least about 400 g/d and an energy-to-break at least about 8 J/g, and particularly preferred aramid fibers will have a tenacity of at least about 20 g/d and an energy-to-break of at least about 20 J/g. Most preferred aramid fibers will have a tenacity of at least about 23 g/d, a modulus of at least about 500 g/d and an energy-to-break of at least about 30 J/g. For example, poly(p-phenylene terephthalamide) filaments which have moderately high moduli and tenacity values are particularly useful in forming ballistic resistant composites. Examples are Twaron® T2000 from Teijin which has a denier of 1000. Other examples are Kevlar® 29 which has 500 g/d and 22 g/d as values of initial tensile modulus and tenacity, respectively, as well as Kevlar® 129 and KM2 which are available in 400, 640 and 840 deniers from du Pont. Aramid fibers from other manufacturers can also be used in this invention. Copolymers of poly(p-phenylene terephthalamide) may also be used, such as co-poly(p-phenylene terephthalamide 3,4' oxydiphenylene terephthalamide). Also useful in the practice of this invention are poly(m-phenylene isophthalamide) fibers sold by du Pont under the trade name Nomex®.

[0028] High molecular weight polyvinyl alcohol (PV-OH) fibers having high tensile modulus are described in U.S. Pat. No. 4,440,711 to Kwon et al. High molecular weight PV-OH fibers should have a weight average molecular weight of at least about 200,000. Particularly useful PV-OH fibers should have a modulus of at least about 300 g/d, a tenacity preferably at least about 10 g/d, more preferably at least about 14 g/d and most preferably at least about 17 g/d, and an energy to break of at least about 8 J/g. PV-OH fiber having such properties can be produced, for example, by the process disclosed in U.S. Pat. No. 4,599,267.

[0029] In the case of polyacrylonitrile (PAN), the PAN fiber should have a weight average molecular weight of at least about 400,000. Particularly useful PAN fiber should have a tenacity of preferably at least about 10 g/d and an energy to break of at least about 8 J/g. PAN fiber having a molecular weight of at least about 400,000, a tenacity of at least about 15 to 20 g/d and an energy to break of at least about 8 J/g is most useful; and such fibers are disclosed, for example, in U.S. Pat. No. 4,535,027.

[0030] Suitable liquid crystal copolyester fibers for the practice of this invention are disclosed, for example, in U.S. Pat. Nos. 3,975,487; 4,118,372 and 4,161,470. Liquid crystal copolyester fibers are available under the designation Vectran® fibers from Kuraray America Inc.

[0031] Suitable polybenzazole fibers for the practice of this invention are disclosed, for example, in U.S. Pat. Nos. 5,286,833, 5,296,185, 5,356,584, 5,534,205 and 6,040,050. Polybenzazole fibers are available under the designation Zylon® fibers from Toyobo Co.

[0032] Rigid rod fibers are disclosed, for example, in U.S. Pat. Nos. 5,674,969, 5,939,553, 5,945,537 and

6,040,478. Such fibers are available under the designation M5® fibers from Magellan Systems International.

[0033] When two or more types of high tenacity fibers are employed in the ropes of this invention, preferably one type of high tenacity fibers is a polyolefin fiber, more preferably a polyethylene fiber. The percent of high tenacity polyethylene fibers in the ropes may vary widely, depending upon the other type of high tenacity fibers employed and the desired properties of the fibers. The high tenacity polyethylene fibers may comprise from about 20 to about 80 weight percent, more preferably from about 30 to about 70 weight percent, and most preferably from about 40 to about 60 weight percent, based on the total weight of the high tenacity fibers in the rope. For example, ropes may be formed from about 80 to about 20 weight percent high tenacity polyethylene fibers and correspondingly from about 20 to about 80 weight percent of aramid fibers; more preferably from about 70 to about 30 weight percent of the high tenacity polyethylene fibers and correspondingly from about 30 to about 70 weight percent of aramid fibers; most preferably from about 40 to about 60 weight percent high tenacity polyethylene fibers and correspondingly from about 60 to about 40 weight percent of aramid fibers. In one particularly preferred embodiment, the rope comprises from about 70 to 55 weight percent aramid fibers and correspondingly from about 30 to about 45 weight percent high tenacity polyethylene fibers, based on the total weight of the high tenacity fibers in the rope. In another embodiment of the invention all or substantially all of the fibers in the rope are formed from aramid fibers.

[0034] When liquid crystal copolyester fibers are used in conjunction with high tenacity polyethylene fibers, ropes may be formed from about 80 to about 20 weight percent high tenacity polyethylene fibers and correspondingly from about 20 to about 80 weight percent of liquid crystal copolyester fibers; more preferably from about 70 to about 30 weight percent of the high tenacity polyethylene fibers and correspondingly from about 30 to about 70 weight percent of liquid crystal copolyester fibers; most preferably from about 40 to about 60 weight percent high tenacity polyethylene fibers and correspondingly from about 60 to about 40 weight percent of liquid crystal copolyester fibers. In one particularly preferred embodiment, the rope comprises from about 70 to 55 weight percent liquid crystal copolyester fibers and correspondingly from about 30 to about 45 weight percent high tenacity polyethylene fibers, based on the total weight of the high tenacity fibers in the rope. In another embodiment of the invention all or substantially all of the fibers in the rope are formed from liquid crystal copolyester fibers.

[0035] If desired, other types of fibers may be employed in addition to the high tenacity fibers mentioned above. Another type of fiber that may be present in the rope construction of this invention together with the high tenacity fibers is fibers formed from fluoropolymers. Such fluoropolymer fibers include fibers formed, for example, from polytetrafluoroethylene (preferably expanded polytetrafluoroethylene), polychorotrifluoroethylene (both homopolymers and copolymers (including terpolymers)), polyvinyl fluoride, polyvinylidene fluoride, ethylene-tetrafluoroethylene copolymers, ethylene-chlorotrifluorethylene copolymers, fluorinated ethylene-propylene copolymers, perfluoroalkoxy polymer, and the like, as well as blends of two or more of the foregoing. Especially preferred fluoropolymer fibers are those formed from polytetrafluoroethylene, and in particular expanded polytetrafluoroethylene fibers. Such fibers are available, for example, from Lenzing Plastics GmbH & Co. KG and WL Gore & Associates.

[0036] The portion of the fluoropolymer fibers that are blended with the high tenacity fibers may vary widely depending on the type of fluoropolymer and the end use application. For example, the amount of fluoropolymer fibers in the blend may range from about 1 to about 40 percent by weight, more preferably from about 5 to about 25 percent by weight, and most preferably from about 10 to about 20 percent by weight, based on the total weight of the blended fibers. Correspondingly, the amount of the high tenacity fibers may range from about 60 to about 99 percent by weight, more preferably from about 75 to about 95 percent by weight, and most preferably from about 80 to about 90 percent by weight, based on the total weight of the blended fibers.

[0037] The different types of fibers useful in the ropes of this invention may be blended in any suitable manner. For example, strands of one type of fibers may be twisted with strands of another type of fibers to form a combined strand that is then braided into a rope. Alternatively, the fibers can be combined as a bicomponent fiber, having a sheath and a core. Other constructions may also be employed. The different types of fibers may be present at any desired location in the rope.

[0038] The ropes of this invention preferably comprise blends of two or more high tenacity fibers, or consist essentially of blends of two or more high tenacity fibers, optionally together with the fluoropolymer fibers. These ropes may be of any suitable construction, such as braided ropes, twisted ropes, wire-lay ropes, parallel core ropes, and the like. Most preferably, the rope is a braided rope. The ropes may be of any suitable diameter and may be formed in any suitable manner from the desired fibers and/or yarns. For example, in forming a braided rope a conventional braiding machine may be employed which has a plurality of yarn bobbins. As is known in the art, as the bobbins move about, the yarns are woven over and under each other and are eventually collected on a take-up reel. Details of braiding machines and the formation of ropes therefrom are known in the art and are therefore not disclosed in detail herein.

[0039] Yarns from one type of high tenacity fibers may be formed into a subrope which is then formed into a rope (such as by braiding) with a subrope formed of yarns from the other type of high tenacity fibers. Alternatively, a subrope may be formed from blends of the high tenacity fib-

ers and such subrope may be formed into a rope using other such subropes or different types of subropes, by braiding or any other desired technique.

[0040] The high tenacity yarns that form the rope may be of any suitable denier, and the yarns of the fluoropolymer fiber may be of the same or different denier than the yarns of the high tenacity fibers. For example, the high tenacity yarns may have a denier of from about 50 to about 5000, more preferably from about 75 to about 2000 denier, still more preferably from about 200 to about 2000, and most preferably from about 650 to about 1500 denier. The fluoropolymer yarns may have a denier of from about 50 to about 2500, and more preferably from about 400 to about 1600.

[0041] In accordance with this invention, a certain coating composition is applied to the rope construction. Either the individual fibers or yarns, or blends of the fibers or yarns, are coated with the coating composition and then a rope is formed from the coated fibers or yarns, or the rope is first formed and then is coated with the coating composition. The coating composition comprises an amino functional silicone resin and a neutralized low molecular weight polyethylene. The two components may be admixed in any desired ratio, such as from about 1 to about 99 percent by weight of the neutralized low molecular weight polyethylene and a corresponding amount of the amino functional silicone resin. All percents are by weight of the total weight of the composition, unless otherwise indicated. Preferably, the neutralized low molecular weight polyethylene is present in an amount of from about 30 to about 90 percent by weight, with the amino functional silicone resin correspondingly being present in an amount of from about 10 to about 70 percent by weight. More preferably, the neutralized low molecular weight polyethylene is the major component of the coating, such as from about 55 to about 85 percent by weight of coating composition, with the amino functional silicone resin being present in an amount of from about 15 to about 45 percent by weight. The composition may contain a variety of other additives, depending on the desired end properties.

[0042] Since some high tenacity fibers such as high modulus polyolefin fibers usually have a spin finish applied when formed, in the present invention the coating composition used herein is sometimes referred to as an overfinish composition.

[0043] The amino functional silicone is preferably in the form of an emulsion. Preferably, the emulsion comprises from about 20 to about 40 percent by weight of the silicone resin, and has a pH in the range of about 4.5 to about 6.5. The emulsion preferably includes a nonionic emulsifier.

[0044] Likewise, the neutralized low molecular weight polyethylene is in the form of an emulsion. Preferably, the polyethylene is fully neutralized. The low molecular weight polyethylenes are also known as polyethylene waxes and are sometimes called wax dispersions. As is known in the art, these polyethylene waxes, also called resins, generally have a molecular weight of less than about 6000 Dalton, more preferably less than about 5000 Dalton, even more preferably below about 3500 Dalton, and most preferably between about 300 and about 3000 Dalton.

[0045] The coating components may be mixed in any suitable manner. For example, the amino functional silicone emulsion may be added to the neutralized low molecular weight polyethylene in a stainless steel or other inert vessel The vessel is preferably equipped with an agitator for appropriate mixing under low shear conditions (laminar flow). By adding the amino functional silicone emulsion to the neutralized low molecular weight polyethylene permits the pH of the system to remain on the basic side. Alternatively, the low molecular weight polyethylene may be added to the amino functional silicone emulsion. The mixing may be conducted at any suitable temperature, preferably between about 15 and about 45 °C, more preferably between about 20 to about 30 °C. It is preferred that the coating composition has a relatively high solids content, such as on the order of at least about 25% by weight and more preferably at least about 30% by weight. Most preferably, the solids content of the coating composition is from about 33 to about 35% by weight. It has been found that the use of high solids content coating emulsions permits higher pick up of the coating composition on the fiber/yarn or rope.

[0046] If the composition is coated directly on the fiber or yarn, any suitable coating device may be employed. Examples of such coating apparatus include lube rolls, kiss rolls, dip baths and finish applicators. A constant temperature is desired to provide uniform application and superior performance as the viscosity of the system is impacted by temperature differences. If the composition is applied to the rope, the rope may be dipped into a bath containing the coating composition, with excess composition squeezed out followed by air drying, or the rope may be coated and then passed through a heating device to accelerate drying followed by air drying.

[0047] It is desired to have a relatively high final pick up of the coating solids on the fiber/yarn or rope. Preferably, the final pick up is at least about 0.5 percent by weight, more preferably at least about 5 percent by weight, and most preferably from about 10 to about 30% by weight.

[0048] The following non-limiting examples are presented to provide a more complete understanding of the invention. The specific techniques, conditions, materials, proportions and reported data set forth to illustrate the principles of the invention are exemplary and should not be construed as limiting the scope of the invention. All parts are by weight, unless otherwise stated.

EXAMPLES

Example 1

[0049] A braided rope was formed from high tenacity

polyethylene yarns and from liquid crystal copolyester yarns. The polyethylene yarn employed was SPECTRA® 1000 yarn from Honeywell International Inc., having a denier of 1300, a tenacity of 35 g/d and a modulus of 1150 g/d. The liquid crystal copolyester yarn was Vectran® HT Type 97 yarn from Kuraray America Inc., having a denier of 1500, a tenacity of about 25 g/d and a modulus of about 600 g/d. The yarns were coated with an overfinish composition.

[0050] The overfinish composition was prepared from an amino functional silicone resin and a neutralized low molecular weight polyethylene. The amino functional silicone resin was an emulsion having a silicone content of 35 weight percent, a pH of 4.5-6.5 and included a non-ionic emulsifier, available from Dow Corning (2-8818 emulsion). The neutralized low molecular weight polyethylene was a neutralized non-ionic polyethylene wax emulsion (Fluftone® 1566 from Apollo Chemical), having a solids content between 29% and 31%, and pH in the range of between 9.0 and 11.

[0051] The coating composition was prepared by blending the neutralized low molecular weight polyethylene into the amino functional silicone resin emulsion, with the resulting composition comprising 70% by weight of the neutralized low molecular weight polyethylene. The yarn was coated by dipping the fiber in the overfinish composition at room temperature. The amount of pick up of the coating on the yarn was approximately 15 percent.

[0052] The coated yarn was braided into a 12-strand rope with an approximate diameter of 5 mm diameter. The yarn was braided into a rope by first twisting three coated yarns together into a cord at 0.5 turns per inch. Cords were twisted in the "S" direction and the "Z" direction. Twelve cords were then loaded onto a 12-strand braider in an alternating fashion (S, Z, S, Z, etc.). Three cords were then braided together resulting in a 12-strand braided rope. The rope was comprised of about 63% by weight of the polyethylene fibers and about 37% by weight of the liquid crystal copolyester fibers.

[0053] The rope was tested for its cyclic bend over sheave (CBOS) resistance. In this test the ropes are bent approximately 180 degrees over a free rolling sheave or pulley. The ropes are placed under load and cycled over the sheave until the rope reaches failure. The test was run with a D:d ratio of 10 over a 1.3 inch (3.3 cm) pulley at 75 cycles per minute, with a 100 kg load on the sheave (50 kg of tension on each side of the rope). The number of cycles was determined based on an average of 5 positions before there was failure of the rope. The results are shown in Table 1, below.

Example 2 (comparative)

[0054] As a control for Example 1, a braided rope was formed in the same manner but no overfinish composition was used. This rope was also tested for its CBOS resistance, and the results are shown in Table 1, below.

TABLE 1

Example	Coating	Cycles to Failure
1	Yes	97,295
2*	No	57,457
*comparative		

[0055] The data in Table 1 demonstrates that the ropes formed from blends of high tenacity polyethylene fibers and liquid crystal copolyester fibers that are coated with the coating composition of the invention have significantly higher CBOS fatigue resistance.

Example 3

[0056] Example 1 is repeated, except that the rope is formed from 40% by weight of high tenacity polyethylene fibers and 60% by weight of liquid crystal copolyester fibers, and has a diameter of about 40 mm. Similar results are noted.

Example 4

[0057] Example 1 is repeated, except that the rope is formed from 40% by weight of high tenacity polyethylene fibers and 60% by weight of aramid fibers, and has a diameter of about 40 mm. Similar results are noted.

Example 5

[0058] Example 1 is repeated except that the ropes are formed from uncoated yarns and after fabrication the ropes are coated with the overfinish composition by dipping the rope in the overfinish composition at room temperature. Similar results are noted.

[0059] It can be seen that the present invention provides ropes which have significantly improved CBOS fatigue resistance. As a result, these ropes can be employed in many demanding applications, including such marine applications as lifting and lowering heavy objects from the seabed.

[0060] Having thus described the invention in rather full detail, it will be understood that such detail need not be strictly adhered to but that further changes and modifications may suggest themselves to one skilled in the art, all falling within the scope of the invention as defined by the subjoined claims.

Claims

1. A rope having improved cyclic bend over sheave (CBOS) fatigue resistance, said rope comprising high tenacity fibers, said rope and/or said fibers being coated with a composition, **characterised by** the

composition comprising an amino functional silicone resin and a neutralized low molecular weight polyethylene.

2. The rope of claim 1 wherein said high tenacity fibers are selected from the group consisting of high molecular weight polyolefins, aramid, polyvinyl alcohol, polyacrylonitrile, polybenzazole, polyamide, polyester, liquid crystal polyesters, glass, carbon, basalt, mineral fibers and rigid rod fibers, and blends thereof.

3. The rope of claim 1 wherein said high tenacity fibers are selected from the group consisting of high molecular weight polyethylene fibers, aramid fibers, liquid crystal copolyester fibers, and blends thereof.

4. The rope of claim 1 wherein said high tenacity fibers comprise a blend of high tenacity polyethylene fibers and other high tenacity fibers that are not polyolefin fibers, said other fibers being aramid fibers and/or liquid crystal copolyester fibers.

5. The rope of claim 4 wherein said high tenacity polyethylene fibers are present in an amount ranging from about 40 to about 60 weight percent, and said other fibers are present in an amount ranging from about 60 to about 40 weight percent, based on the total weight of said high tenacity fibers in said rope.

6. The rope of claim 4 wherein said high tenacity fibers comprise a blend of high tenacity polyethylene fibers and aramid fibers.

7. The rope of claim 4 wherein said high tenacity fibers comprise a blend of high tenacity polyethylene fibers and liquid crystal copolyester fibers.

8. The rope of claim 4 wherein said composition is present on said rope in an amount of at least about 5 weight percent based on the weight of said rope.

9. The rope of claim 4 wherein said low molecular weight polyethylene is the major component of said composition.

10. The rope of claim 4 wherein said low molecular weight polyethylene is present in an amount of from about 55 percent to about 85 percent by weight based on the total weight of said composition.

11. The rope of claim 10 wherein said low molecular weight polyethylene is fully neutralized.

12. The rope of claim 4 further comprising fluoropolymer fibers.

13. The rope of claim 4 wherein said rope is a braided rope.

14. The rope of claim 1 wherein said high tenacity fibers have a tenacity of at least about 16 g/d.

15. The rope of claim 1 wherein said high tenacity fibers consist essentially of aramid fibers.

16. The rope of claim 1 comprising a blend of high tenacity polyolefin fibers with other high tenacity fibers that are not polyolefin fibers.

17. The rope of claim 16 wherein said other high tenacity fibers that are not polyolefin fibers comprise aramid fibers and/or liquid crystal copolyester fibers.

18. The rope of claim 17 wherein said high tenacity polyolefin fibers are high tenacity polyethylene fibers which are present in an amount ranging from about 40 to about 60 weight percent, and said other high tenacity fibers that are not polyolefin fibers comprise aramid fibers which are present in an amount ranging from about 60 to about 40 weight percent, based on the total weight of high tenacity fibers in said rope.

19. The rope of claim 18 wherein said low molecular weight polyethylene is present in an amount of from about 55 percent to about 85 percent by weight based on the total weight of said composition, and wherein said low molecular weight polyethylene is fully neutralized.

20. The rope of claim 1 comprising a blend of high tenacity polyolefin fibers with other high tenacity fibers, said other high tenacity fibers comprising aramid fibers and/or liquid crystal copolyester fibers.

21. The rope of claim 20 wherein said low molecular weight polyethylene is present in an amount of from about 55 percent to about 85 percent by weight based on the total weight of said composition and wherein said low molecular weight polyethylene is fully neutralized.

22. A method of improving the cyclic bend over sheave (CBOS) fatigue life of a rope, said method comprising forming said rope from high tenacity fibers, and coating said rope and/or said fibers forming said rope with a composition, **characterised by** coating with a composition comprising an amino functional silicone resin and a neutralized low molecular weight polyethylene.

23. The method of claim 22 wherein said high tenacity fibers comprise a blend of high tenacity polyethylene fibers with other high tenacity fibers, said other high tenacity fibers comprising aramid fibers and/or liquid crystal copolyester fibers.

24. The method of claim 23 including coating said rope with said composition, wherein said low molecular weight polyethylene is present in an amount of from about 55 percent to about 85 percent by weight based on the total weight of said composition and wherein said low molecular weight polyethylene is fully neutralized.

25. The method of claim 24 wherein said composition has a solids content of at least about 25 % by weight.

26. The method of claim 25 wherein said amino functional silicone resin is in the form of an emulsion having a pH of from about 9 to about 11.

27. The method of claim 23 including coating said fibers with said composition, wherein said low molecular weight polyethylene is present in an amount of from about 55 percent to about 85 percent by weight based on the total weight of said composition and wherein said low molecular weight polyethylene is fully neutralized.

28. Use of a synthetic fiber rope in a method of lifting and placing heavy objects from and onto a seabed comprising utilizing as said rope a rope comprising high tenacity fibers, said rope and/or said fibers being coated with a composition, **characterised by** the composition comprising an amino functional silicone resin and a neutralized low molecular weight polyethylene.

29. The method of claim 28 wherein said rope comprises a blend of high tenacity polyethylene fibers and aramid fibers.

30. The method of claim 28 wherein said rope comprises a blend of high tenacity polyethylene fibers and liquid crystal copolyester fibers.

Patentansprüche

1. Seil aus hochfesten Fasern mit verbesserter Biegewechselfestigkeit beim Lauf über die Seilscheibe (CBOS), bei dem Seil und/oder Fasern mit einer Zubereitung beschichtet sind, **dadurch gekennzeichnet, dass** die Zubereitung aminofunktionelles Siliconharz und neutralisiertes niedermolekulares Polyethylen enthält.

2. Seil nach Anspruch 1, bei dem die hochfesten Fasern ausgewählt sind aus der Gruppe bestehend aus hochmolekularen Polyolefinen, Aramid, Polyvinylalkohol, Polyacrylnitril, Polybenzazol, Polyamid, Polyester, Flüssigkristallpolyester, Glas-, Carbon-, Basalt-, Mineral- und Stabfasern sowie deren Mischungen.

3. Seil nach Anspruch 1, bei dem die hochfesten Fasern ausgewählt sind aus der Gruppe bestehend aus Fasern aus hochmolekularem Polyethylen, Aramidfasern, Fasern aus Flüssigkristallcopolyester und deren Mischungen.

4. Seil nach Anspruch 1, bei dem die hochfesten Fasern wenigstens teilweise aus der Mischung hochfester Polyethylenfasern mit anderen, von Polyolefinfasern verschiedenen hochfesten Fasern bestehen, wobei es sich bei den anderen Fasern um Aramidfasern und/oder Fasern aus Flüssigkristallcopolyester handelt.

5. Seil nach Anspruch 4, bei dem bezogen auf das Gesamtgewicht der hochfesten Fasern im Seil die hochfesten Polethylenfasern in einer Menge von etwa 40 bis etwa 60 Gewichtsprozent und die anderen Fasern in einer Menge von etwa 60 bis etwa 40 Gewichtsprozent enthalten sind.

6. Seil nach Anspruch 4, bei dem die hochfesten Fasern wenigstens teilweise aus der Mischung hochfester Polyethylenfasern mit Aramidfasern bestehen.

7. Seil nach Anspruch 4, bei dem die hochfesten Fasern wenigstens teilweise aus der Mischung hochfester Polyethylenfasern mit Fasern aus Flüssigkristallcopolyester bestehen.

8. Seil nach Anspruch 4, bei dem die Zubereitung auf dem Seil in einer auf das Gewicht des Seils bezogenen Menge von mindestens etwa 5 Gewichtsprozent vorliegt.

9. Seil nach Anspruch 4, bei dem das niedermolekulare Polyethylen den größeren Anteil der Zubereitung ausmacht.

10. Seil nach Anspruch 4, bei dem das niedermolekulare Polyethylen in einem auf das Gesamtgewicht der Zubereitung bezogenen Gewichtsanteil von etwa 55 bis etwa 85 Prozent enthalten ist.

11. Seil nach Anspruch 10, bei dem das niedermolekulare Polyethylen vollständig neutralisiert ist.

12. Seil nach Anspruch 4, ferner Fluorpolymerfasern umfassend.

13. Seil nach Anspruch 4, bei dem es sich um ein geflochtenes Seil handelt.

14. Seil nach Anspruch 1, bei dem die hochfesten Fasern über eine Feinheitsfestigkeit von mindestens etwa 16 g/den verfügen.

15. Seil nach Anspruch 1, bei dem die hochfesten Fasern im Wesentlichen aus Aramidfasern bestehen.

16. Seil nach Anspruch 1, umfassend die Mischung hochfester Polyolefinfasern mit anderen, von Polyolefinfasern verschiedenen hochfesten Fasern.

17. Seil nach Anspruch 16, bei dem die anderen hochfesten Fasern wenigstens teilweise aus Aramidfasern und/oder Fasern aus Flüssigkristallcopolyester bestehen.

18. Seil nach Anspruch 17, bei dem bezogen auf das Gesamtgewicht der hochfesten Fasern im Seil die hochfesten Polethylenfasern in einer Menge von etwa 40 bis etwa 60 Gewichtsprozent enthalten sind und die anderen hochfesten Fasern Aramidfasern umfassen, welche in einer Menge von etwa 60 bis etwa 80 Gewichtsprozent enthalten sind.

19. Seil nach Anspruch 18, bei dem das niedermolekulare Polyethylen vollständig neutralisiert vorliegt und in einem auf das Gesamtgewicht der Zubereitung bezogenen Gewichtsanteil von etwa 55 bis etwa 85 Prozent enthalten ist.

20. Seil nach Anspruch 1, umfassend die Mischung hochfester Polyolefinfasern mit anderen hochfesten Fasern, wobei die anderen hochfesten Fasern wenigstens teilweise aus Aramidfasern und/oder Fasern aus Flüssigkristallcopolyester bestehen.

21. Seil nach Anspruch 20, bei dem das niedermolekulare Polyethylen vollständig neutralisiert vorliegt und in einem auf das Gesamtgewicht der Zubereitung bezogenen Gewichtsanteil von etwa 55 bis etwa 85 Prozent enthalten ist.

22. Verfahren zur Verbesserung der Biegewechselfestigkeit eines Seils beim Lauf über die Seilscheibe (CBOS), bei dem man das Seil aus hochfesten Fasern herstellt und das Seil und/oder die das Seil bildenden Fasern mit einer Zubereitung beschichtet, **gekennzeichnet durch** Beschichten mit einer Zubereitung, enthaltend aminofunktionelles Siliconharz und neutralisiertes niedermolekulares Polyethylen.

23. Verfahren nach Anspruch 22, bei dem die hochfesten Fasern wenigstens teilweise aus der Mischung hochfester Polyethylenfasern mit anderen hochfesten Fasern bestehen, wobei die anderen hochfesten Fasern wenigstens teilweise aus Aramidfasern und/oder Fasern aus Flüssigkristallcopolyester bestehen.

24. Verfahren nach Anspruch 23, bei dem man das Seil mit der Zubereitung beschichtet, wobei das niedermolekulare Polyethylen vollständig neutralisiert vorliegt und in einem auf das Gesamtgewicht der Zubereitung bezogenen Gewichtsanteil von etwa 55 bis etwa 85 Prozent enthalten ist.

25. Verfahren nach Anspruch 24, bei dem die Zubereitung über einen Festgehalt von mindestens etwa 25 Gew.-% verfügt.

26. Verfahren nach Anspruch 25, bei dem das aminofunktionelle Siliconharz als Emulsion mit einem pH-Wert von etwa 9 bis etwa 11 vorliegt.

27. Verfahren nach Anspruch 23, bei dem man die Fasern mit der Zubereitung beschichtet, wobei das niedermolekulare Polyethylen vollständig neutralisiert vorliegt und in einem auf das Gesamtgewicht der Zubereitung bezogenen Gewichtsanteil von etwa 55 bis etwa 85 Prozent enthalten ist.

28. Verwendung eines Synthesefaserseils in einem Verfahren zum Aufnehmen und Absetzen schwerer Lasten vom bzw. am Meeresgrund, bei dem man als Seil ein Seil aus hochfesten Fasern einsetzt, wobei Seil und/oder Fasern mit einer Zubereitung beschichtet sind, **dadurch gekennzeichnet, dass** die Zubereitung aminofunktionelles Siliconharz und neutralisiertes niedermolekulares Polyethylen enthält.

29. Verfahren gemäß Anspruch 28, bei dem das Seil wenigstens teilweise aus der Mischung hochfester Polyethylenfasern mit Aramidfasern besteht.

30. Verfahren gemäß Anspruch 28, bei dem das Seil wenigstens teilweise aus der Mischung hochfester Polyethylenfasern mit Fasern aus Flüssigkristallcopolyester besteht.

Revendications

1. Corde présentant une résistance améliorée à la fatigue par courbure cyclique sur poulie (CCSP), ladite corde comprenant des fibres à haute ténacité, ladite corde et/ou lesdites fibres étant revêtues d'une composition **caractérisée en ce que** la composition comprend une résine de silicone à fonctionnalité amino et un polyéthylène neutralisé de faible masse moléculaire.

2. Corde selon la revendication 1, dans laquelle lesdites fibres à haute ténacité sont sélectionnées dans le groupe constitué de polyoléfines à haute masse moléculaire, d'aramides, de l'alcool polyvinylique, du polyacrylonitrile, du polybenzazole, de polyamides, de polyesters, de polyesters à cristaux liquides, du verre, du carbone, du basalte, de fibres minérales

et de fibres sous forme de tiges rigides, et de mélanges de ceux-ci.

3. Corde selon la revendication 1, dans laquelle lesdites fibres à haute ténacité sont sélectionnées dans le groupe constitué de fibres de polyéthylène à haute masse moléculaire, de fibres aramides, de fibres de copolyester à cristaux liquides, et de mélanges de celles-ci.

4. Corde selon la revendication 1, dans laquelle lesdites fibres à haute ténacité comprennent un mélange de fibres de polyéthylène à haute ténacité et d'autres fibres à haute ténacité qui ne sont pas des fibres de polyoléfine, lesdites autres fibres étant des fibres d'aramide et/ou des fibres de copolyester à cristaux liquides.

5. Corde selon la revendication 4, dans laquelle lesdites fibres de polyéthylène à haute ténacité sont présentes dans une quantité d'environ 40 à environ 60 % en poids, et lesdites autres fibres sont présentes dans une quantité d'environ 60 à environ 40 % en poids, relativement au poids total desdites fibres à haute ténacité dans ladite corde.

6. Corde selon la revendication 4, dans laquelle lesdites fibres à haute ténacité comprennent un mélange de fibres de polyéthylène à haute ténacité et de fibres aramides.

7. Corde selon la revendication 4, dans laquelle lesdites fibres à haute ténacité comprennent un mélange de fibres de polyéthylène à haute ténacité et de fibres de copolyester à cristaux liquides.

8. Corde selon la revendication 4, ladite composition étant présente sur ladite corde dans une quantité d'au moins environ 5 % en poids relativement au poids de ladite corde.

9. Corde selon la revendication 4, dans laquelle ledit polyéthylène de faible masse moléculaire est le principal constituant de ladite composition.

10. Corde selon la revendication 4, dans laquelle ledit polyéthylène de faible masse moléculaire est présent dans une quantité d'environ 55 % à environ 85 % en poids relativement au poids total de ladite composition.

11. Corde selon la revendication 10, dans laquelle ledit polyéthylène de faible masse moléculaire est entièrement neutralisé.

12. Corde selon la revendication 4, comprenant en outre des fibres de fluoropolymère.

13. Corde selon la revendication 4, dans laquelle ladite corde est une corde tressée.

14. Corde selon la revendication 1, dans laquelle lesdites fibres à haute ténacité ont une ténacité d'au moins environ 16 g/d.

15. Corde selon la revendication 1, dans laquelle lesdites fibres à haute ténacité consistent essentiellement en fibres aramides.

16. Corde selon la revendication 1, comprenant un mélange de fibres de polyoléfine à haute ténacité avec d'autres fibres à haute ténacité qui ne sont pas des fibres de polyoléfine.

17. Corde selon la revendication 16, dans laquelle lesdites autres fibres à haute ténacité comprennent des fibres aramides et/ou des fibres de copolyester à cristaux liquides.

18. Corde selon la revendication 17, dans laquelle lesdites fibres de polyoléfine à haute ténacité sont des fibres de polyéthylène à haute ténacité qui sont présentes dans une quantité d'environ 40 à environ 60 % en poids, et lesdites autres fibres à haute ténacité qui ne sont pas des fibres de polyoléfine comprennent des fibres aramides, qui sont présentes dans une quantité d'environ 60 à environ 40 % en poids, relativement au poids total desdites fibres à haute ténacité dans ladite corde.

19. Corde selon la revendication 18, dans laquelle ledit polyéthylène de faible masse moléculaire est présent dans une quantité d'environ 55 % à environ 85 % en poids relativement au poids total de ladite composition, et dans laquelle ledit polyéthylène de faible masse moléculaire est entièrement neutralisé.

20. Corde selon la revendication 1, comprenant un mélange de fibres de polyoléfine à haute ténacité avec d'autres fibres à haute ténacité, lesdites autres fibres à haute ténacité comprenant des fibres aramides et/ou des fibres de copolyester à cristaux liquides.

21. Corde selon la revendication 20, dans laquelle ledit polyéthylène de faible masse moléculaire est présent dans une quantité d'environ 55 % à environ 85 % en poids relativement au poids total de ladite composition et dans laquelle ledit polyéthylène de faible masse moléculaire est entièrement neutralisé.

22. Procédé d'amélioration de la durée de vie en fatigue d'une corde soumise à une courbure cyclique sur poulie (CCSP), ledit procédé comprenant la formation de ladite corde à partir de fibres à haute ténacité, et le revêtement de ladite corde et/ou desdites fibres formant ladite corde avec une composition, **carac-**

térisé par un revêtement avec une composition comprenant une résine de silicone à fonctionnalité amino et un polyéthylène neutralisé de faible masse moléculaire.

23. Procédé selon la revendication 22, dans lequel lesdites fibres à haute ténacité comprennent un mélange de fibres de polyéthylène à haute ténacité avec d'autres fibres à haute ténacité, lesdites autres fibres à haute ténacité comprenant des fibres aramides et/ou des fibres de copolyester à cristaux liquides.

24. Procédé selon la revendication 23, comprenant le revêtement de ladite corde avec ladite composition, dans lequel ledit polyéthylène de faible masse moléculaire est présent dans une quantité d'environ 55 % à environ 85 % en poids relativement au poids total de ladite composition et dans lequel ledit polyéthylène de faible masse moléculaire est entièrement neutralisé.

25. Procédé selon la revendication 24, dans lequel ladite composition a une teneur en solides d'au moins environ 25 % en poids.

26. Procédé selon la revendication 25, dans lequel ladite résine de silicone à fonctionnalité amino est sous la forme d'une émulsion ayant un pH d'environ 9 à environ 11.

27. Procédé selon la revendication 23, comprenant un revêtement desdites fibres avec ladite composition, dans lequel ledit polyéthylène de faible masse moléculaire est présent dans une quantité d'environ 55 % à environ 85 % en poids relativement au poids total de ladite composition et dans lequel ledit polyéthylène de faible masse moléculaire est entièrement neutralisé.

28. Utilisation d'une corde en fibres synthétiques dans un procédé de levage et de positionnement d'objets lourds à partir de et sur un fond marin, comprenant l'utilisation, comme ladite corde, d'une corde comprenant des fibres à haute ténacité, ladite corde et/ou lesdites fibres étant revêtues d'une composition **caractérisée en ce que** la composition comprend une résine de silicone à fonctionnalité amino et un polyéthylène neutralisé de faible masse moléculaire.

29. Procédé selon la revendication 28, dans lequel ladite corde comprend un mélange de fibres de polyéthylène à haute ténacité et de fibres aramides.

30. Procédé selon la revendication 28, dans lequel ladite corde comprend un mélange de fibres de polyéthylène à haute ténacité et de fibres de copolyester à cristaux liquides.

REFERENCES CITED IN THE DESCRIPTION

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