The invention relates to a rope containing high modulus polyethylene (HMPE) yarns wherein the rope is coated with a plastomer, the plastomer being a semi-crystalline copolymer of ethylene or propylene and one or more C2 to C12 a-olefin co-monomers and the plastomer having a density as measured according to ISO 1183 of between 870 and 930 kg/m3.
PROTECTED HMPE ROPE

The invention relates to rope containing high modulus polyethylene (HMPE) yarns.

The use of ropes of HMPE yarns is generally known. Advantages of such ropes is the high strength of the rope whereas the rope is relatively light compared to traditional materials such as steel wire.

In order to protect the ropes made of HMPE yarns from external influences such as dust and other small particles, but also to protect the ropes against abrasion, it is known to put a protective cover on the rope.

However, the currently known covers are not always optimal. For instance the cover may protect sufficiently against external influences but may be less resistant to abrasion. There is therefore a need for an improved means of protecting ropes of HMPE yarns.

The current invention now provides a rope containing high modulus polyethylene (HMPE) yarns wherein the rope is coated with a plastomer, the plastomer being a semi-crystalline copolymer of ethylene or propylene and one or more C2 to C12 α-olefin co-monomers and the plastomer having a density as measured according to IS01 183 of between 870 and 930 kg/m³.

According to a second aspect the invention provides a rope containing high modulus polyethylene (HMPE) yarns containing HMPE fibers, the HPPE fibers being impregnated with a plastomer deposited between and around the fibers, the plastomer being a semi-crystalline copolymer of ethylene or propylene and one or more C2 to C12 α-olefin co-monomers and the plastomer having a density as measured according to IS01 183 of between 870 and 930 kg/m³.

The advantage of using the above-mentioned plastomer in the manufacture of this rope is that the plastomer has a processing temperature such that the mechanical properties of the HMPE core are not adversely affected by the processing conditions. Furthermore, since the plastomer is also based on polyolefin a good adhesion between the plastomer and HMPE core results.

The plastomer used in the invention is a plastic material that belongs to the class of thermoplastic materials. According to the invention, said plastomer is a semi-
crystalline copolymer of ethylene or propylene and one or more C2 to C12 a-olefin co-
monomers, said plastomer having a density of between 870 and 930 kg/m³. Preferably, the
plastomer is manufactured by a single site catalyst polymerization process, wherein in
particular said plastomer is a metallocene plastomer, i.e. a plastomer manufactured by a
metallocene single site catalyst. Ethylene is in particular the preferred co-monomer in
copolymers of propylene while butene, hexene and octene are being among the preferred
a-olefin co-monomers for both ethylene and propylene copolymers.

In a preferred embodiment, the plastomer is a thermoplastic copolymer of ethylene or propylene and containing as co-monomers one or more a-olefins having 2-
12 C-atoms, in particular ethylene, isobutene, 1-butene, 1-hexene, 4-methyl-1-pentene
and 1-octene. When ethylene with one or more C2 to C12 a-olefin monomers as co-
monomers is applied, the amount of co-monomer in the copolymer usually is lying between
1 en 50 wt.%, and preferably between 5 and 35 wt. %. In case of ethylene copolymers, the
preferred co-monomer is 1-octene, said co-monomer being in an amount of between 5
wt% and 25 wt%, more preferably between 15 wt% and 20 wt%. In case of propylene
copolymers, the amount of co-monomers and in particular of ethylene co-monomers,
usually lies between 1 en 50 wt.%, and preferably between 2 and 35 wt%, more preferably
between 5 and 20 wt%. Good results were obtained when the density of the plastomer is
between 880 and 920 kg/m³, more preferably between 880 and 910 kg/m³.

The plastomer used in the invention has a good process ability when it
has a DSC peak melting point as measured according to ASTM D3418 of between 70°C
and 120°C, preferably between 75°C and 100°C, more preferably between 80°C and 95°C.

A plastomer manufactured by a single site catalyst polymerization
process and in particular a metallocene plastomer is distinguished from ethylene and
propylene copolymers that have been manufactured with other polymerization techniques,
e.g. Ziegler-Natta catalysation, by its specific density. Said plastomer also differentiates
itself by a narrow molecular weight distribution, Mw/Mn, the values thereof preferably being
between 1.5 en 3 and by a limited amount of long chain branching. The number of long
chain branches preferably amounts at most 3 per 1000 C-atoms. Suitable plastomers that
may be used in the invention and obtained with the metallocene catalyst type are
manufactured on a commercial scale, e.g by Exxon, Mitsui, DEX-Plastomers and DOW
under brand names as Exact, Tafmer, Exceed, Engage, Affinity, Vistamaxx and Versify.
A description of plastomers and in particular of metallocene plastomers as well as an overview of their mechanical and physical properties can be found for instance in Chapter 7.2 of "Handbook of polypropylene and polypropylene composites" edited by Harutun G. Karian (ISBN 0-8247-4064-5) and more in particular in subchapters 7.2.1; 7.2.2; and 7.2.5 to 7.2.7 thereof, which are included herein by reference.

The plastomer used in the invention may also contain various fillers and additives added thereof. Examples of fillers include reinforcing and non-reinforcing materials, e.g. carbon black, calcium carbonate, clay, silica, mica, talc, and glass. Examples of additives include stabilizers, e.g. UV stabilizers, pigments, antioxidants, flame retardants and the like. Preferred flame retardants include aluminum tryhydrates, magnesium dehydrate and ammonium phosphate. The amount of flame retardants is preferably from 1 to 60, more preferably from 1 to 10 by weight percent of the amount of plastomer in the flexible sheet of the invention. Most preferred flame retardant is ammonium phosphate, e.g. Exolit.

As described above rope of the invention contains high modulus polyethylene (HMPE) yarns. Such yarns further contain HMPE fibers. By fiber is herein understood an elongate body, the length dimension of which is much greater that the transverse dimensions of width and thickness. Accordingly, the term fiber includes filament, ribbon, strip, band, tape, and the like having regular or irregular cross-sections. The fibers may have continuous lengths, known in the art as filaments, or discontinuous lengths, known in the art as staple fibers. Staple fibers are commonly obtained by cutting or stretch-breaking filaments. A yarn for the purpose of the invention is an elongated body containing many fibers.

Preferred polyethylene fibers are fibers made of high molecular weight polyethylene (HMWPE) and ultrahigh molecular weight polyethylene (UHMWPE). Said polyethylene fibers may be manufactured by any technique known in the art, preferably by a melt or a gel spinning process.

If a melt spinning process is used to manufacture the HMPE fibers, the polyethylene starting material used for manufacturing thereof preferably has a weight-average molecular weight between 20,000 and 600,000, more preferably between 60,000 and 200,000. An example of a melt spinning process is disclosed in EP 1,350,868 incorporated herein by reference.
Best results are obtained if a yarn of gel spun fibers of high or ultra high molecular weight polyolefin, preferably HMwPE or UHMwPE, is used in the rope, e.g. those sold by DSM Dyneema under the name Dyneema®.

The gel spinning process is described in for example GB-A-2042414, GB-A-2051667, EP 0205960 A and WO 01/73173 A 1. This process essentially comprises the preparation of a solution of a polyolefin of high intrinsic viscosity, spinning the solution to filaments at a temperature above the dissolving temperature, cooling down the filaments below the gelling temperature so that gelling occurs and drawing the filaments before, during or after removal of the solvent.

The shape of the cross-section of the filaments may be selected here through selection of the shape of the spinning aperture.

Preferably HMwPE is used with an intrinsic viscosity of at least 3 dl/g, determined in decalin at 135°C, more preferably at least 4 dl/g, most preferably at least 5 dl/g. Preferably the IV is at most 40 dl/g, more preferably at most 25 dl/g, more preferably at most 15 dl/g.

The intrinsic viscosity is determined according to PTC-179 (Hercules Inc. Rev. Apr. 29, 1982) at 135°C, the dissolution time being 16 hours, the anti-oxidant is DPBC, in an amount of 2 g/l solution, and the viscosity is measured at different and is extrapolated to zero concentration.

Preferably, the UHMWPE has less than 1 side chain per 100 C atoms, more preferably less than 1 side chain per 300 C atoms.

Preferably, the polyethylene fibers have deniers per filament in the range of from 0.1 to 50, more preferably from 0.5 to 20, most preferably from 1 to 10 dpf. The polyethylene yarns preferably are preferably from 200 to 50,000, more preferably from 500 to 10,000, most preferably from 800 to 4800 denier.

The tensile strength of the polyethylene fibers utilized in the present invention as measured according to ASTM D2256 is preferably at least 1.2 GPa, more preferably at least 2.5 GPa, most preferably at least 3.5 GPa. The tensile modulus of the polyethylene fibers as measured according to ASTM D2256 is preferably at least 30 GPa, more preferably at least 50 GPa, most preferably at least 60 GPa.

Other fibers that may be used in combination with the polyethylene fibers to construct the rope of the invention include but are not limited to fibers manufactured...
from polyamides and 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®); poly(hexamethyleneadipamide) (known as nylon 6,6), poly(4-aminobutyric acid) (known as nylon 6); polyesters, e.g. poly(ethylene terephthalate), poly(butylene terephthalate), and poly(1,4 cyclohexylenedimethylene terephthalate); polyvinyl alcohols; thermotropic liquid crystal polymers (LCP) as known from e.g. US 4,384,016; but also polyolefins other than polyethylene e.g. homopolymers and copolymers of polypropylene. Also combinations of fibers manufactured from the above referred polymers can be used in the rope of the invention. Preferred other fibers however are fibers of polyaramides and/or LCP.

In order to fully have the advantage of the use of the plastomer on the rope containing HMPE yarns, it is preferred that the core contains at least 60 wt%, based of the total weight of the core, of HMPE yarns. More preferably the core contains at least 70 wt.% of even at least 80 wt.% HMPE yarns. The remaining weight of the core may consist of yarns manufactured from other polymers as enumerated hereinabove.

Before applying the coating of plastomer on the rope, the rope may be coated by other coatings known in the art. Such coatings can, as an example, comprise polyurethane, silicone oil, bitumen or combinations thereof. An example of a suitable coating is ICO-N-Dure from I-Coats. The rope may contain this coating of 2.5-35 wt% in a dried state. In particular, the rope contains 10-25 wt% of such a non-plastomer coating.

It is also possible to use HMPE yarns that have a coating applied thereon to make the rope. Such coatings comprise overlay finishes known in the art, which can also be polyurethane, silicone, cross-linked silicone, etc.

The plastomer coating of the invention can be applied as a single layer, i.e. in one extrusion step, but also more than one layer, e.g. two layers of the plastomer coating can be envisaged.

Further to the plastomer coating, other coatings can be applied on top of the plastomer coating, e.g. by co-extrusion. Such a further coating or coatings could be used to increase abrasion resistance. Examples of such coatings are polyurethane or nylon coatings.
Also, a cover can be applied on the rope coated with the plastomer of the invention. Such a cover can be a braided or woven cover of materials known in the art, such as HMPE yarns, but also polyester or nylon yarns.

The rope of the invention may have any construction known for synthetic ropes. The core may have a plaited, a braided, a laid, a twisted or a parallel construction, or combinations thereof. Preferably the core has a laid or a braided construction, or a combination thereof.

In such rope constructions, the ropes are made up of strands. The strands are made up of rope yarns, which contain synthetic fibers. Methods of forming yarns from fiber, strands from yarn and ropes from strands are known in the art.

In embodiments comprising a mixture of HMPE fibers and further synthetic fibers as described above, the mixture of the fibers may be at all levels. The mixture may be at rope yarns made from fibers, at strands made from rope yarns, and/or at the final rope made from strands.

The number of strands in the core rope may also vary widely, but is generally at least 3 and preferably at most 16, to arrive at a combination of good performance and ease of manufacture.

When the rope is a braided rope, there is a variety of braid types known, each generally distinguished by the method that forms the rope. Suitable constructions include soutache braids, tubular braids, and flat braids. Tubular or circular braids are the most common braids for rope applications and generally consist of two sets of strands that are intertwined, with different patterns possible. The number of strands in a tubular braid may vary widely. Especially if the number of strands is high, and/or if the strands are relatively thin, the tubular braid may have a hollow core; and the braid may collapse into an oblong shape.

The number of strands in a braided rope according to the invention is preferably at least 3. An increasing number of strands tends to lower the strength efficiency of the rope. The number of strands is therefore preferably at most 16, depending on the type of braid. Particularly suitable are ropes of an 8- or 12-strand plaited or braided construction. Such ropes provide a favourable combination of tenacity and resistance to bend fatigue, and can be made economically on relatively simple machines.
The rope according to the invention can be of a construction wherein the lay length (the length of one helix of a strand in a laid construction) or the braiding period (that is the length of one helix of a strand in a plaited or braided rope) is adapted to the outer steel wire strands to assure a mutual tension sharing over the working area of a rope and also at break to failure.

Suitable braiding periods are in the range of from 4 to 20. A higher braiding period may result in a more loose rope having higher strength efficiency, but which is less robust and more difficult to splice. Too low a braiding period would reduce tenacity too much. Preferably therefore, the braiding period is about 5 - 15, more preferably 6 - 10. In all cases the lay length or braiding period can be adapted to the steel wire type and construction in such a way that both products work best together with respect to load sharing (strength) and/or fatigue performance in the working area of the rope and the break to failure.

In the rope according to the invention the construction of the strands, also referred to as primary strands, is not specifically critical. The skilled person can select suitable constructions like laid or braided strands, and twist factor or braiding period respectively, such that a balanced and torque-free rope results and an optimum cooperation with the outer steel wire strands is achieved with regard to load sharing.

The rope of the invention can have any known thickness, depending on the ultimate use of the hybrid rope. Generally the core will have a diameter from 1 mm to 300 mm. Preferably the core has a diameter from 5 mm to 200 mm.

The rope of the invention can be "heat-set". This means that the method of manufacturing the rope can also comprise a step of post-stretching the primary strands before constructing the rope, or alternatively a step of post-stretching the rope. Such stretching step is preferably performed at elevated temperature but below the melting point of the (lowest melting) filaments in the stands (also called heat-stretching or heat-setting); preferably at temperatures in the range 80-150°C. Such a post-stretching step is described in EP 398843 B1 or US 5901632. Heat setting can be performed both before and after application of the coating on the rope.

The rope of the invention can be coated with the plastomer by methods known in the art. For example the rope of the invention can be coated with the plastomer by known extrusion-coating processes, also known as jacket-extrusion, where the rope is
extruded together with the molten plastomer through a die and then cooled below the melting temperature of the plastomer.

The temperature in the extruder to process the plastomer is from 70 to 200 °C. Too low a temperature will result in the plastomer not melting properly, too high a temperature may result in decomposition of the plastomer. The skilled person will be able to determine the optimal temperature based on the material and equipment used.

The plastomer coating can be deposited on the exterior of the rope of the invention as a layer having an average thickness of at least 0.1 mm, more preferably at least 0.5 mm. Preferably said thickness is at most 20 mm, more preferably at most 15 mm.

The average thickness can be measured with methods known in the art, e.g. with an optical microscope on cross-section of said rope and averaging at least 10 measurements. It is preferred that the layer of plastomer coats substantially the whole surface of the core, i.e. the layer of plastomer coats the entire core, but for instance both ends of the rope can be left uncoated.

According to the second embodiment of the invention, the HMPE yarns of the core are impregnated with the plastomer. For an efficient impregnation of the core it is desirable that the plastomer is deposited between and around the fibers of the rope. This may be achieved for example by guiding the fibers through a bath containing a solution or a dispersion of the plastomer in a suitable solvent. A more preferred impregnation method is by using pressure and temperature to force the molten plastomer into the rope as exemplified in GB 1,296,339 included herein by reference. It has been suggested therein to make use of a pressure impregnation, wherein the rope is moved through a treating chamber to which an impregnation agent, e.g. the plastomer, is supplied under pressure.

A further preferred impregnation method comprises the steps:

(i) providing tapes or shreds of the plastomer obtained by splitting or shredding a plastomer film;

(ii) mixing said tapes or shreds of plastomer with the polyethylene fibers and forming strands thereof;

(iii) forming a rope from the strands obtained at step (ii); and

(iv) heating the rope of step (iii) at a temperature between the melting temperature of the plastomer and the melting temperature of the polyethylene fibers while
Example 1

First the rope of HMPE yarn was produced. In a first step a 12 strand braided first core part was produced, each strand consisting of 8*1760 dTex Dyneema® SK78 yarn. The first core part has a diameter of 6.5 mm. This first core part is overbraided with 12 strands of 4*1760 dTex Dyneema® yarn. The total diameter of the so obtained core is 8 mm.

In a next step a coating of a plastomer EXACT™ 0230 was extruded on the core as manufactured above using a Collin™ 45 mm single screw extruder with the following processing conditions:
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CLAIMS

1. A rope containing high modulus polyethylene (HMPE) yarns wherein the rope is coated with a plastomer, the plastomer being a semi-crystalline copolymer of ethylene or propylene and one or more C2 to C12 α-olefin co-monomers and the plastomer having a density as measured according to IS01 183 of between 870 and 930 kg/m³.

2. A rope containing high modulus polyethylene (HMPE) yarns containing HMPE fibers, the HMPE fibers being impregnated with a plastomer deposited between and around the fibers, the plastomer being a semi-crystalline copolymer of ethylene or propylene and one or more C2 to C12 α-olefin co-monomers and the plastomer having a density as measured according to IS01 183 of between 870 and 930 kg/m³.

3. The rope according to claim 1 or 2, wherein the plastomer is manufactured by a single site catalyst polymerization process.

4. The rope according to any of the preceding claims wherein the plastomer is a thermoplastic copolymer of ethylene or propylene and contains as co-monomers one or more α-olefins having 2-12 C-atoms.

5. The rope according to any of the preceding claims wherein the plastomer has a density of between 880 and 910 kg/m³.

6. The rope according to any of the preceding claims wherein the plastomer has a peak melting point of between 70°C and 120°C.

7. The rope according to any of the preceding claims wherein the HMPE yarns contain fibers which are gel spun fibers of ultrahigh molecular weight polyethylene (UHMWPE).

8. The rope according to any of the preceding claims, wherein the HMPE yarns contain fibers of HMWPE having an intrinsic viscosity of at least 3 dl/g determined in decalin at 135 °C.

9. The rope according to any of the preceding claims, wherein the HMPE yarns contain fibers having a tensile modules of at least 30 GPa.
### A. CLASSIFICATION OF SUBJECT MATTER

INV. D07B1/02 D07B1/16

ADD.

According to International Patent Classification (IPC) into both national classification and IPC

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D07B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<td>EP 0 091 547 A1 (ALLIED CORP [US]) 19 October 1983 (1983-10-19) page 13, line 26 - page 14, line 4 page 7, line 14</td>
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<td>A</td>
<td>US 6 083 243 A (POKROPSKII HENRY [US] ET AL) 4 July 2000 (2000-07-04) column 1, line 53 column 2, line 4 - line 5; claim 1 column 3, line 14 - line 17</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
  
  * "A" document defining the general state of the art which is not considered to be of particular relevance
  
  * "E" earlier document but published on or after the international filing date
  
  * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  
  * "O" document referring to an oral disclosure, use, exhibition or other means
  
  * "P" document published prior to the international filing date but later than the priority date claimed
  
  * "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  
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  * "A" document member of the same patent family

Date of the actual completion of the international search

2 November 2011

Date of mailing of the international search report

09/11/2011

Name and mailing address of the ISA/

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NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer

Uhlig, Robert
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