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(71) Applicant: **TOTAL RESEARCH & TECHNOLOGY**

FELUY [BE/BE]; Zone Industrielle C, B-7181 Seneffe (BE).

(72) Inventors: **ROUSSEAUX, Dimitri**; Avenue du Monde 10, 1400 NIVELLES (BE). **BOUVY, Claire**; Route de Petit-Roeulx, 233, 7090 Braine-le-Comte (BE).

(74) Agent: **GARCIA MARTIN, Margarita**; Zone Industrielle C, 7181 Seneffe (BE).

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(54) Title: CONDUCTIVE MULTILAYERED PIPES MADE OF POLYETHYLENE, AND PROCESS TO PRODUCE SUCH PIPES

(57) Abstract: The invention relates to a conductive multilayered pipe and to its process of production. The pipe comprises an outer external layer, at least one internal layer and an inner external layer, wherein the inner external layer and the at least one internal layer comprise a polyethylene resin having a melt index MI2 of at most 0.50 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg; the multilayered pipe being characterized in that the outer external layer is made from a second composite material comprising: - from 50 to 99 wt% of a second polyethylene resin as based on the total weight of said second composite material, wherein the second polyethylene resin has a melt index MI2 ranging from 0.8 to 50.0 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg; and - from 0.2 to 10.0 wt% of carbon particles as based on the total weight of said composite material as determined according to ISO 11358 selected from carbon black, nanographenes, carbon nanotubes or any combination thereof.



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CONDUCTIVE MULTILAYERED PIPES MADE OF POLYETHYLENE, AND PROCESS TO PRODUCE SUCH PIPES

Field of the invention

- 5 The present invention relates to conductive multilayered pipes made from polyethylene compositions such as pipes that can be used in mining applications. The invention also relates to a process for the preparation of such conductive pipes.

Background of the invention

- 10 Polymer materials, such as polyethylene (PE), are frequently used for preparing pipes suitable for various purposes, such as fluid transport, *i.e.* transport of liquid or gas, *e.g.* water or natural gas, during which the fluid can be pressurized.

- PE pipes are generally manufactured by extrusion, or by injection moulding. The properties of such conventional PE pipes are sufficient for many purposes, although enhanced properties may be desired, for instance in applications requiring high-pressure resistance, *i.e.* pipes that
15 are subjected to an internal fluid pressure for a long and/or a short period of time.

- According to ISO 9080, PE pipes are classified by their minimum required strength, *i.e.* their capability to withstand different hydrostatic (hoop) stress during 50 years at 20 °C without fracturing. Thereby, pipes withstanding a hoop stress of 8.0 MPa (minimum required strength MRS8.0) are classified as PE 80 pipes, and pipes withstanding a hoop stress of 10.0 MPa
20 (MRS10.0) are classified as PE 100 pipes.

Moreover, the transported fluid may have varying temperatures, thus according to ISO 24033, polyethylene of raised temperature resistance (PE-RT) pipes of type II shall not give any brittle failures indicating the presence of a knee at any temperature up to 110 °C within one year.

- PE 80 pipes, PE 100 pipes and PE-RT pipes are usually prepared from specific polyethylene
25 grades, such as medium density polyethylene and high-density polyethylene. PE 80 pipes and PE 100 pipes are usually produced from a polyethylene resin showing a high viscosity and having, therefore, a melt index MI5 of at most 1.5 g/10 min as determined according to ISO 1133 at 190 °C under a load of 5 kg. PE-RT pipes are usually produced from a polyethylene resin having a melt index MI2 of at most 5.0 g/10 min as determined according to ISO 1133 at
30 190 °C under a load of 2.16 kg.

If conductive pipes are required, such as for mining application, the polyethylene can be then blended with carbon particles such as carbon black. It has been experienced that, in order to achieve the desired electrical properties on the surface of the pipes, the composite material

comprising the polyethylene and the carbon particles should contain at least 15 wt% of carbon particles as based on the total weight of the composite material. Unfortunately, the content of carbon particles directly influences the mechanical properties obtained on the pipe such as the impact failure properties. As a general rule, when a polyethylene is blended with a filler (such as carbon black) the higher the filler content is, the worse the impact properties are.

Thus, there is a need for a solution to achieve good electrical properties (such as good surface resistance) in conductive pipes while keeping at the same time good mechanical properties and in particular good impact properties.

Summary of the invention

It is therefore an object of the present invention to provide conductive pipes, such as pipes suitable for mining applications, the pipes having good mechanical properties and being conductive or at least dissipative, wherein the pipes are produced from composite materials comprising a polyethylene and a low content of carbon particles such as nanographenes or carbon nanotubes (CNT). It is another object of the present invention to provide conductive pipes, such as pipes suitable for mining applications, the pipes having good mechanical properties and being conductive or at least dissipative. It is also an object of the invention to provide a process to produce said pipes having good mechanical properties and being conductive or at least dissipative wherein the pipes are made from a composite material having a low content of carbon particles.

According to a first aspect, the invention relates to a conductive multilayered pipe comprising an outer external layer, at least one internal layer and an inner external layer, wherein the inner external layer and the at least one internal layer comprise a polyethylene resin having a melt index MI2 of at most 0.50 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg; the multilayered pipe being remarkable in that the outer external layer is made from a second composite material comprising:

- from 50 to 99 wt% of a second polyethylene resin as based on the total weight of the said second composite material, wherein the second polyethylene resin has a melt index MI2 ranging from 0.8 to 50.0 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg; and
- from 0.2 to 10.0 wt% of carbon particles as based on the total weight of the said second composite material as determined according to ISO 11358 selected from carbon black, nanographenes, carbon nanotubes or any combination thereof.

Polyethylene resins suitable for pipe applications of the PE 80 and the PE 100 type, and sometimes for the PE-RT grade, have a very low melt index MI2 of below 0.5 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg, to achieve the targeted

mechanical properties on the pipe. This results in difficulties to mix carbon particles homogeneously to render the pipe conductive. Therefore, a high load of carbon particles is necessary to achieve targeted conductive electrical properties.

It has been found by the inventors, that it is possible to achieve the required mechanical properties with the inner external layer and at least one internal layer of the pipe only, wherein both the inner external layer and at least one internal layer comprise a polyethylene resin having a melt index MI2 of at most 0.50 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg. As a consequence, it is possible to use a more fluid polyethylene resin to make the outer external layer, so that a lower content of carbon particles is necessary to achieve the targeted electrical properties in the outer external layer as compared to the inner external layer.

The invention provides a multilayered pipe wherein at least the outer external layer is not made with a polyethylene of a pipe grade having a melt index MI2 of at most 0.50 g/10 min. Therefore, the inventive pipe shows a lower content of carbon particle than a conductive multilayered pipe wherein both the inner external layer and outer external layer are made from pipe grade having a melt index MI2 of at most 0.50 g/10 min. This results in significant cost reduction, said cost reduction being all the more important when carbon particles are carbon nanotubes or nanographenes.

According to a preferred embodiment, the conductive multilayered pipe being remarkable in that:

- a. the inner external layer is made from a first composite material comprising:
 - from 50 to 99 wt% of a first polyethylene resin as based on the total weight of the said first composite material, wherein the first polyethylene resin has a melt index MI2 of at most 0.50 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg; and
 - from 0.2 to 20.0 wt% of carbon particles as based on the total weight of said first composite material as determined according to ISO 11358 selected from carbon black, nanographenes, carbon nanotubes or any combination thereof;
- b. at least one internal layer comprises a third polyethylene resin having a melt index MI2 of at most 0.50 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg;

with preference, the first polyethylene resin and the third polyethylene resin are the same.

In a preferred embodiment, the at least one internal layer is devoid of carbon particles.

In a preferred embodiment, the carbon particles are selected from nanographenes, carbon nanotubes or any combination thereof.

In a preferred embodiment, the inner external layer and/or the outer external layer of the conductive multilayered pipe have a surface resistance of at most $5 \cdot 10^6$ Ohm, preferably of at most $1 \cdot 10^6$ Ohm as measured according to IEC 61340-4-1 with an SRM110 meter.

It has been found by the inventors, that the addition of processing aids and/or of polyethylene glycol (PEG) within the first composite material allows, at similar CNT and/or nanographenes content, better electrical properties compared to articles produced without said processing aids and/or said PEG. In particular, the addition of PEG allows reducing the content of carbon particles within the composite material as compared to a composite material comprising processing aids or being devoid of any processing aids. It is, therefore, possible to achieve the targeted electrical properties, for example on pipes, with a CNT content as low as less than 3 wt%. As the impact properties are directly influenced by the filler content, the invention provides conductive articles with an improved balance of electrical and mechanical properties. Moreover, as the content of carbon particles can be lowered, the invention results, for targeted electrical properties, in less expensive articles with better mechanical properties.

The inventors also found that there was no need of addition of processing aids and/or of polyethylene glycol (PEG) in the second composite material to achieve the targeted electrical properties. Thus, the use of different polyethylene resins in the inner and the outer external conductive layers allows reducing the content of additive to be used in the multilayered pipe and thus the overall cost of the pipe.

With preference one or more of the following embodiments can be used to define the first polyethylene resin and/or the third polyethylene resin:

- The first polyethylene resin and/or the third polyethylene resin have a melt index MI2 of less than 0.45 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg, preferably of less than 0.40 g/10 min, more preferably of less than 0.35 g/10 min.
- The first polyethylene resin and/or the third polyethylene resin have a high load melt index HLMI of at most 60 g/10 min as determined according to ISO 1133 at 190 °C under a load of 21.6 kg, preferably of at most 50 g/10 min, more preferably of at most 20 g/10 min, even more preferably of at most 18 g/10 min, and most preferably of at most 14 g/10 min.
- The first polyethylene resin and/or the third polyethylene resin have a high load melt index HLMI of at least 5 g/10 min as determined according to ISO 1133 at 190 °C under a load of 21.6 kg, preferably of at least 7 g/10 min.

- The first polyethylene resin and/or the third polyethylene resin have a melt index MI5 of at least 0.1 g/10 min as determined according to ISO 1133 at 190 °C under a load of 5 kg, preferably of at least 0.2 g/10 min.
- The first polyethylene resin and/or the third polyethylene resin have a melt index MI5 of at most 5.0 g/10 min as determined according to ISO 1133 at 190 °C under a load of 5 kg, preferably of at most 2.0 g/10 min, more preferably of at most 1.5 g/10 min, even more preferably of at most 1.0 g/10 min, most preferably of at most 0.9 g/10 min, and even most preferably of at most 0.7 g/10 min.
- The first polyethylene resin and/or the third polyethylene resin have a density of at least 0.920 g/cm³ and of at most 0.960 g/cm³ as determined according to ISO 1183 at a temperature of 23 °C; preferably of at least 0.930 g/cm³.

With preference one or more of the following embodiments can be used to define the second polyethylene resin:

- The second polyethylene resin has a melt index MI2 of at least 0.9 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg, preferably of at least 1.0 g/10 min.
- The second polyethylene resin has a melt index MI2 of at most 20 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg, with preference of at most 15 g/10 min.
- The second polyethylene resin has a density of at least 0.920 g/cm³ and of at most 0.960 g/cm³ as determined according to ISO 1183 at a temperature of 23 °C; preferably of at least 0.930 g/cm³.

With preference one or more of the following embodiments can be used to define carbon particles of the first and/or of the second composite material of the inventive conductive multilayered pipe:

- The first composite material and/or the second composite material comprise at least 0.2 wt% of carbon particles as based on the total weight of said composite material as determined according to ISO 11358, the carbon particles being selected from nanographenes, carbon nanotubes (CNT) or any combination thereof, preferably at least 0.5 wt%, more preferably at least 1.0 wt%, even more preferably at least 2.0 wt%; most preferably of at least 2.6 wt% and even most preferably of at least 3.0 wt%.
- The first composite material and/or the second composite material comprise at most 9 wt% of carbon particles as based on the total weight of said composite material as determined according to ISO 11358, the carbon particles being selected from nanographenes, carbon nanotubes (CNT) or any combination thereof, preferably at most 8.5 wt%, and more preferably at most 8 wt%.

- The carbon particles are carbon nanotubes and the first composite material and/or the second composite material comprise from 0.2 to 5.0 wt% of carbon nanotubes as based on the total weight of said composite material as determined according to ISO 11358, preferably the first composite material and/or the second composite material comprise from 0.5 to 4.8 wt%, more preferably from 2.0 to 4.5 wt%, even more preferably from 2.6 to 4.2 wt%, and most preferably from 3.0 to 4.0 wt% of carbon nanotubes as based on the total weight of said composite material.
 - The carbon particles are carbon nanotubes and the second composite material comprises from 0.2 to 5.0 wt% of carbon nanotubes as based on the total weight of said composite material and as determined according to ISO 11358, preferably the second composite material comprises from 0.5 to 4.0 wt%, more preferably from 1.0 to 3.5 wt%, even more preferably from 1.2 to 3.0 wt%, and most preferably from 1.5 to 2.8 wt% of carbon nanotubes as based on the total weight of said composite material.
 - The carbon particles are nanographenes and the first composite material and/or the second composite material comprise from 5.0 to 10.0 wt% of carbon nanographenes as based on the total weight of said composite material as determined according to ISO 11358, preferably the first composite material and/or the second composite material comprise from 6.0 to 9.0 wt% of carbon particles as based on the total weight of said composite material.
- With preference one or more of the following embodiments can be used to define the first composite material of the inner external layer:
- The first composite material of the inner external layer further comprises from 0.10 to 0.48 wt% of polyethylene glycol as based on the total weight of the composite material, and said polyethylene glycol is selected to have a weight average molecular weight Mw of at most 20,000 g/mol.
 - The polyethylene glycol in the first composite material has a weight average molecular weight Mw of at most 12,000 g/mol, preferably at most 10,000 g/mol, more preferably of at most 8,000 g/mol, even more preferably of at most 6,000 g/mol, and most preferably of at most 5,000 g/mol.
 - The polyethylene glycol in the first composite material has a weight average molecular weight Mw of at least 200 g/mol, preferably at least 400 g/mol, more preferably of at least 800 g/mol, even more preferably of at least 1,000 g/mol, most preferably of at least 2,000 g/mol and even most preferably of at least 3,000 g/mol.
 - The polyethylene glycol in the first composite material has a weight average molecular weight Mw of 4,000 g/mol (CAS number 25322-68-3).

- The first composite material of the inner external layer, further comprises from 0.10 to 0.48 wt% of polyethylene glycol as based on the total weight of the composite material, said polyethylene glycol is selected to have a weight average molecular weight M_w of at most 20,000 g/mol, the carbon particles are carbon nanotubes; and the composite material comprises from 0.2 to 5.0 wt% of carbon particles as based on the total weight of the composite material as determined according to ISO11358, preferably the composite material comprises from 0.5 to 4.8 wt%, more preferably from 1.5 to 4.5 wt%, even more preferably from 1.8 to 4.2 wt%, most preferably from 2.0 to 4.0 wt%, and even most preferably at most 3.5 wt% or at most 3.0 wt%, or at most 2.9 wt% of carbon particles as based on the total weight of the composite material.
- The first composite material of the inner external layer further comprises from 0.01 to 5.0 wt% of one or more processing aids wherein the one or more processing aids are selected from fluoroelastomers, waxes, tristearin, zinc stearate, calcium stearate, magnesium stearate, erucyl amide, oleic acid amide, ethylene-acrylic acid copolymer, ethylene vinyl acetate copolymer, cetyl trimethyl ammonium bromide, polyethylene oxide, polysiloxanes, oleamide, stearamide, behenamide, oleyl palmitamide, ethylene bis-oleamide, ethylene bis(stearamide) (EBS) and any mixture thereof, with preference from 0.01 to 0.48 wt% of one or more processing aids.
- The first composite material of the inner external layer; further comprises from 0.01 to 0.48 wt% of a processing aid as based on the total weight of said composite material, wherein the processing aid is selected from oleamide, stearamide, behenamide, oleyl palmitamide, ethylene bis-oleamide, ethylene bis(stearamide) (EBS) and any mixture thereof.
- The first composite material of the inner external layer; further comprises from 0.01 to 1.0 wt% of an additive composition comprising polyethylene glycol and behenamide, preferably the additive composition comprises a ratio polyethylene glycol:behenamide ranging from 1:1 to 3:1 as based on the total weight of the additive composition.

Without being bound to a theory, it is believed that the high shear resulting from the contact of the extrusion or injection device with the viscous polyethylene leads to the formation of carbon particles composition from the top surface of the article produced up to the centre, such that an insulating layer with very few carbon particles can be found at the extreme surface of the article. Surprisingly, it seems that the addition of PEG having a weight average molecular weight of less than 20,000 g/mol, have a good affinity with carbon particles and therefore migrates with them to the top surface of the article. As a result this addition allows the creation of a carbon particles pattern at the surface of the article.

Preferably, the first composite material of the inner external layer comprises polyethylene glycol and one or more processing aids; wherein the polyethylene glycol and the one or more processing aids form an additive mixture, and further wherein the content of polyethylene glycol in the additive mixture is ranging from 50 wt% to 99 wt% as based on the total weight of the additive mixture, more preferably from 60 wt% to 90 wt%, more preferably from 65 wt% to 85 wt%.

Indeed, as it is shown in the examples, the addition of one or more processing aids to polyethylene glycol further improves the electrical properties of the pipes. However, the best results are obtained when the additive mixture comprising the polyethylene glycol and the one or more processing aids comprises at least 50 wt% of polyethylene glycol.

In a preferred embodiment, the multilayered conductive pipe further comprises an internal steel wire layer, with preference said internal steel wire layer is between two internal layers made from the third polyethylene resin. With preference, the multilayered conductive pipe further comprises adhesive layers arranged between the internal steel wire layer and the two internal layers made from the third polyethylene resin.

In a preferred embodiment, the outer external layer has a thickness ranging from 5 to 25 % based on the total thickness of all the layers forming the conductive multilayered pipe, with preference ranging from 10 to 20 %.

Preferably, the content in weight percent of carbon particles of the second composite material as based on the total weight of the second composite material, is lower than the content in weight percent of carbon particles of the first composite material as based on the total weight of the first composite material, the content of carbon particle being determined according to ISO 11358.

Preferably, the carbon particles are carbon nanotubes and the content in weight percent of carbon nanotubes of the second composite material as based on the total weight of the second composite material, is lower than the content in weight percent of carbon nanotubes of the first composite material as based on the total weight of the first composite material, the content of carbon nanotubes being determined according to ISO 11358.

With preference, the content in weight percent of carbon nanotubes of the second composite material as based on the total weight of the second composite material, is lower than the content in weight percent of carbon nanotubes of the first composite material as based on the total weight of the first composite material, the content of carbon particle being determined according to ISO 11358; and the content of carbon nanotubes of the second composite material as based on the total weight of the second composite material is lower than 3.0 wt%

of carbon nanotubes carbon nanotubes as based on the total weight of said composite material and as determined according to ISO 11358, preferably lower than 2.8 wt%, more preferably ranging from 0.2 to 2.8 wt%.

According to a second aspect, the invention relates to a process to produce a conductive multilayered pipe as defined according to the first aspect of the invention, wherein the process comprises the following steps:

a. providing a first composite material comprising:

- from 50 to 99 wt% of a first polyethylene resin as based on the total weight of the said first composite material, wherein the first polyethylene resin has a melt index MI2 of at most 0.50 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg; and
- from 0.2 to 20.0 wt% of carbon particles as based on the total weight of the said first composite material as determined according to ISO 11358 selected from carbon black, nanographenes, carbon nanotubes or any combination thereof;

b. providing a third polyethylene resin having a melt index MI2 of at most 0.50 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg;

c. coextruding or co-injecting the first composite material and the third polyethylene resin to form a conductive multilayered pipe wherein the first composite material forms the inner external layer of the pipe;

d. providing a second composite material comprising:

- from 50 to 99 wt% of a second polyethylene resin as based on the total weight of the said second composite material, wherein the second polyethylene resin has a melt index MI2 ranging from 0.8 to 50.0 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg; and
- from 0.2 to 10.0 wt% of carbon particles as based on the total weight of said composite material as determined according to ISO 11358 selected from carbon black, nanographenes, carbon nanotubes or any combination thereof;

e. covering the multilayered pipe obtained in step c) with a layer of the second composite material in order to obtain a conductive multilayered pipe wherein the first composite material forms the inner external layer of the pipe, the second composite material forms the outer external layer of the pipe, and the third polyethylene resin forms at least one internal layer in between the inner external layer and the outer external layer of the pipe.

Step e) is performed, for example, by extrusion, in accordance with techniques well-known to the person skilled in the art.

With preference, the carbon particles are selected from carbon nanotubes, nanographenes and mixture thereof, and the first composite material and/or the second composite material are produced by blending the first polyethylene resin and/or the second polyethylene resin respectively, with a masterbatch comprising the blend of a fourth polyethylene resin and at least 5 wt% of carbon particles as based on the total weight of said masterbatch as determined according to ISO 11358; the masterbatch having an HLMI of at least 5 g/10 min and of at most 500 g/10 min as determined according to ISO 1133 at 190 °C under a load of 21.6 kg.

In a preferred embodiment, the carbon particles are selected from carbon nanotubes, nanographenes and mixture thereof; and/or the first composite material comprises polyethylene glycol and/or one or more processing aids.

According to a third aspect, the invention relates to the use of a second composite material comprising:

- from 50 to 99 wt% of a second polyethylene resin as based on the total weight of the said second composite material, wherein the second polyethylene resin has a melt index MI2 ranging from 0.8 to 50.0 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg; and
- from 0.2 to 10.0 wt% of carbon particles as based on the total weight of the said second composite material as determined according to ISO 11358 selected from carbon black, nanographenes, carbon nanotubes or any combination thereof;

in the outer external layer of a conductive multilayered pipe according to the first aspect and/or in a process according to the second aspect.

Detailed description of the invention

For the purpose of the invention the following definitions are given:

As used herein, a "polymer" is a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus embraces the term homopolymer, usually employed to refer to polymers prepared from only one type of monomer, and the terms copolymer and interpolymer as defined below.

As used herein, a "copolymer", "interpolymer" and like terms mean a polymer prepared by the polymerization of at least two different types of monomers. These generic terms include polymers prepared from two or more different types of monomers, e.g. terpolymers, tetrapolymers, etc.

As used herein, "blend", "polymer blend" and like terms refer to a composition of two or more compounds, for example, two or more polymers or one polymer with at least one other compound.

As used herein, the term "melt blending" involves the use of shear force, extensional force, compressive force, ultrasonic energy, electromagnetic energy, thermal energy or combinations comprising at least one of the foregoing forces or forms of energy and is conducted in processing equipment wherein the aforementioned forces are exerted by a single-screw, multiple screws, intermeshing co-rotating or counter-rotating screws, non-intermeshing co-rotating or counter-rotating screws, reciprocating screws, screws with pins, barrels with pins, rolls, rams, helical rotors, or combinations comprising at least one of the foregoing.

As used herein the terms "polyethylene" (PE) and "ethylene polymer" may be used synonymously. The term "polyethylene" encompasses homopolyethylene as well as copolymers of ethylene which can be derived from ethylene and a comonomer such as one or more selected from the group consisting of C₃-C₂₀-alpha-olefins, such as 1-butene, 1-propylene, 1-pentene, 1-hexene, 1-octene.

The term "polyethylene resin" as used herein refers to polyethylene fluff or powder that is extruded, and/or melted and/or pelletized and can be produced through compounding and homogenizing of the polyethylene resin as taught herein, for instance, with mixing and/or extruder equipment. As used herein, the term "polyethylene" may be used as a shorthand for "polyethylene resin".

The terms "fluff" or "powder" as used herein refer to polyethylene material with the hard catalyst particle at the core of each grain and is defined as the polymer material after it exits the polymerization reactor (or the final polymerization reactor in the case of multiple reactors connected in series).

Under normal production conditions in a plant, it is expected that the melt index (MI2, HLMI, MI5) will be different for the fluff than for the polyethylene resin. Under normal production conditions in a plant, it is expected that the density will be slightly different for the fluff, than for the polyethylene resin. Unless otherwise indicated, density and melt index for the polyethylene resin refer to the density and melt index as measured on the polyethylene resin as defined above. The density of the polyethylene resin refers to the polymer density as such, not including additives such as, for example, pigments unless otherwise stated.

The term "carbon particles" as used herein encompasses carbon nanotubes and nanographenes but excludes carbon fibres.

The terms "comprising", "comprises" and "comprised of" as used herein are synonymous with "including", "includes" or "containing", "contains", and are inclusive or open-ended and do not exclude additional, non-recited members, elements or method steps. The terms "comprising", "comprises" and "comprised of" also include the term "consisting of".

The recitation of numerical ranges by endpoints includes all integer numbers and, where appropriate, fractions subsumed within that range (e.g. 1 to 5 can include 1, 2, 3, 4 when referring to, for example, a number of elements, and can also include 1.5, 2, 2.75 and 3.80, when referring to, for example, measurements). The recitation of endpoints also includes the recited endpoint values themselves (e.g. from 1.0 to 5.0 includes both 1.0 and 5.0). Any numerical range recited herein is intended to include all sub-ranges subsumed therein.

The particular features, structures, characteristics or embodiments may be combined in any suitable manner, as would be apparent to a person skilled in the art from this disclosure, in one or more embodiments.

10 The conductive multilayered pipes

The invention provides a conductive multilayered pipe comprising an outer external layer, at least one internal layer and an inner external layer, wherein the inner external layer and at least one internal layer comprise a polyethylene resin having a melt index MI₂ of at most 0.50 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg; the multilayered pipe being characterized in that the outer external layer is made from a second composite material comprising:

- from 50 to 99 wt% of a second polyethylene resin as based on the total weight of the said second composite material, wherein the second polyethylene resin has a melt index MI₂ ranging from 0.8 to 50.0 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg; and
- from 0.2 to 10.0 wt% of carbon particles as based on the total weight of the said second composite material as determined according to ISO 11358 selected from carbon black, nanographenes, carbon nanotubes or any combination thereof.

The conductive articles according to the invention show a lower content of carbon particles than similar articles known from prior art. As the filler content is lower, the articles have a better balance of electrical and mechanical properties. Moreover, the low content of carbon particles makes them less expensive.

The term "pipe" as used herein is meant to encompass pipes in the narrower sense, as well as supplementary parts like fittings, valves and all parts which are commonly necessary for e.g. a hot water piping system.

Pipes according to the invention are multilayer pipes, where for example one or more of the layers is a metal layer and which may include an adhesive layer. Other constructions of pipes, e.g. corrugated pipes, are possible as well.

In a preferred embodiment, the inner external layer and/or the outer external layer of the conductive multilayered pipe have a surface resistance of at most $5 \cdot 10^6$ Ohm, preferably of at most $1 \cdot 10^6$ Ohm as measured according to IEC 61340-4-1 with an SRM110 meter.

5 In a preferred embodiment, the multilayered conductive pipe further comprises an internal steel wire layer, with preference said internal steel wire layer is between two internal layers made from the third polyethylene resin.

10 In a preferred embodiment, the outer external layer has a thickness ranging from 5 to 25 % based on the total thickness of all the layers forming the conductive multilayered pipe, with preference ranging from 10 to 20 %. This thickness distribution is useful to ensure the desired mechanical properties on the pipe.

The first and/or the third polyethylene resins

The conductive multilayered pipe of the invention comprises:

- an inner external layer made of a first composite material comprising a first polyethylene resin and
- 15 - at least one internal layer made of a third polyethylene resin.

The first and the third polyethylene resins may be the same or different, with preference they are the same. In all cases, they are both polyethylene pipe grades selected to be suitable for the application considered, and will be described jointly.

20 Whatever the application considered, the first and/or the third polyethylene resins have preferably a melt index MI2 of less than 0.45 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg, preferably of less than 0.40 g/10 min, more preferably of less than 0.35 g/10 min.

25 Whatever the application considered, the first and/or the third polyethylene resins have preferably a high load melt index HLMI of at most 100 g/10 min as determined according to ISO 1133 at 190 °C under a load of 21.6 kg, preferably of at most 60 g/10 min, and more preferably of at most 50 g/10 min.

Preferably, the first and/or the third polyethylene resins have a high load melt index HLMI of at least 5 g/10 min as determined according to ISO 1133 at 190 °C under a load of 21.6 kg, preferably of at least 6 g/10 min, and more preferably of at least 7 g/10 min.

30 In order to achieve targeted mechanical properties, the first and/or the third polyethylene resins may have a melt index MI5 of at least 0.1 g/10 min as determined according to ISO 1133 at 190 °C under a load of 5 kg, preferably of at least 0.2 g/10 min.

In an embodiment, the first and/or the third polyethylene resins may have a melt index MI5 of at most 5.0 g/10 min as determined according to ISO 1133 at 190 °C under a load of 5 kg, preferably of at most 2.0 g/10 min, more preferably of at most 1.5 g/10 min, even more preferably of at most 1.0 g/10 min, most preferably of at most 0.9 g/10 min, and even most preferably of at most 0.7 g/10 min.

In embodiments requiring the first and/or the third polyethylene resins to be of the PE 80 grade or the PE 100 grade, the first and/or the third polyethylene resins have preferably a high load melt index HLMI of at most 20 g/10 min as determined according to ISO 1133 at 190 °C under a load of 21.6 kg, preferably of at most 18 g/10 min, and more preferably of at most 14 g/10 min.

Polyethylene resins suitable for the invention as first and/or third polyethylene resins (such as pipe grades) are commercially available from TOTAL®. Non-limitative examples are:

- a PE 80 pipe grade is available under the commercial denomination 3802 B. The resin 3802B has a density of 0.948 g/cm³, a melt index MI2 of 0.2 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg, and a melt index MI5 of 0.9 g/10 min as determined according to ISO 1133 at 190 °C under a load of 5 kg;
- a PE 100 pipe grade is available under the commercial denomination XSENE® XCS 50 ORANGE. This product has a density of 0.949 g/cm³ and a melt index MI5 of 0.3 g/10 min as determined according to ISO 1133 at 190 °C under a load of 5 kg;
- a PE-RT pipe grade is available under the commercial denomination XRT 70. This product has a density of 0.947 g/cm³ and a melt index MI5 of 0.7 g/10 min as determined according to ISO 1133 at 190 °C under a load of 5 kg.

The second polyethylene resin

The conductive multilayered pipe according to the invention has an outer external layer made of a second composite material comprising a second polyethylene resin that is more fluid than the first and the third polyethylene resins.

With preference, the second polyethylene resin has a melt index MI2 of at least 0.9 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg, preferably of at least 1.0 g/10 min.

Preferably, the second polyethylene resin has a melt index MI2 of at most 20 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg, with preference of at most 15 g/10 min.

The second polyethylene resin has a density of at least 0.920 g/cm³ and of at most 0.960 g/cm³ as determined according to ISO 1183 at a temperature of 23 °C. Preferably, the second

polyethylene resin has preferably a density of at least 0.925 g/cm^3 as determined according to ISO 1183 at a temperature of 23°C , more preferably of at least 0.930 g/cm^3 , and even more preferably of at least 0.935 g/cm^3 .

Polyethylene resins suitable for the invention as second polyethylene resin are commercially available from TOTAL®. Non-limitative examples are:

- a metallocene polyethylene available under the commercial denomination M3581. The resin M3581 has a density of 0.934 g/cm^3 , a melt index MI2 of 8.0 g/10 min as determined according to ISO 1133 at 190°C under a load of 2.16 kg ;
- a metallocene copolymer of ethylene and hexane, available under the commercial denomination M4040. This product has a density of 0.940 g/cm^3 and a melt index MI2 of 4.0 g/10 min as determined according to ISO 1133 at 190°C under a load of 2.16 kg .

Each of the polyethylene resin used in the invention (*i.e.* the first, the second and/or the third polyethylene resins) may have a molecular weight distribution M_w/M_n of at least 2 and of at most 30, M_w being the weight average molecular weight and M_n being the number average molecular weight.

Each of the polyethylene resin may have a monomodal molecular weight distribution or a bimodal molecular weight distribution, preferably the first polyethylene resin has a bimodal molecular weight distribution.

As used herein, the term “monomodal polyethylene” or “polyethylene with a monomodal molecular weight distribution” refers to polyethylene having one maximum in their molecular weight distribution curve, which is also defined as a unimodal distribution curve. As used herein, the term “polyethylene with a bimodal molecular weight distribution” or “bimodal polyethylene” refers to polyethylene having a distribution curve being the sum of two unimodal molecular weight distribution curves, and refers to a polyethylene product having two distinct but possibly overlapping populations of polyethylene macromolecules each having different weight average molecular weights. As used herein, the term “polyethylene with a multimodal molecular weight distribution” or “multimodal polyethylene” refers to polyethylene with a distribution curve being the sum of at least two, preferably more than two unimodal distribution curves, and refers to a polyethylene product having two or more distinct but possibly overlapping populations of polyethylene macromolecules each having different weight average molecular weights. The multimodal polyethylene resin of the article can have an “apparent monomodal” molecular weight distribution, which is a molecular weight distribution curve with a single peak and no shoulder. In an embodiment, said polyethylene resin having a multimodal, preferably bimodal, molecular weight distribution can be obtained by physically blending at least two polyethylene fractions. In a preferred embodiment, said polyethylene resin having a

multimodal, preferably bimodal, molecular weight distribution can be obtained by the chemical blending of at least two polyethylene fractions, for example by using at least 2 reactors connected in series.

5 The polyethylene resin used as first, second and third polyethylene resins can be produced by polymerizing ethylene and one or more optional comonomers, optionally hydrogen, in the presence of a catalyst being a metallocene catalyst, a Ziegler-Natta catalyst or a chromium catalyst.

In an embodiment, at least one of the first, second or third polyethylene resin is a Ziegler-Natta catalyzed polyethylene resins, preferably having a bimodal molecular weight distribution.

10 In an embodiment, at least one of the first, second or third polyethylene resin is a chromium catalyzed polyethylene resin, preferably having a monomodal molecular weight distribution.

The term "chromium catalysts" refers to catalysts obtained by deposition of chromium oxide on a support, e.g. a silica or aluminium support. Illustrative examples of chromium catalysts comprise but are not limited to CrSiO_2 or CrAl_2O_3 .

15 In an embodiment, at least one of the first, second or third polyethylene resin is obtained in the presence of a single site catalyst, preferably a metallocene catalyst. Preferably, at least one of the first, second or third polyethylene resin has a bimodal molecular weight distribution.

At least one of the first, second or third polyethylene resin may be a polyethylene copolymer, which is a copolymer of ethylene and at least one comonomer selected from C_3 - C_{20} alpha-olefin. As used herein, the term "comonomer" refers to olefin comonomers which are suitable for being polymerized with ethylene monomers. Comonomers may comprise but are not limited to aliphatic C_3 - C_{20} alpha-olefins. Examples of suitable aliphatic C_3 - C_{20} alpha-olefins include propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. Preferably, the
20 comonomer is 1-hexene.
25

Where at least one of the first, second or third polyethylene resin is a polyethylene copolymer, it preferably has a comonomer content of at least 1 wt% and at most 5 wt% as based on the total weight of the polyethylene copolymer.

The carbon particles

30 In all embodiments, the carbon particles of the first and/or second composite materials are a carbonaceous material. In a preferred embodiment, the carbon particles of the first and/or second composite materials are nanoparticles. The nanoparticles used in the present invention can generally be characterized by having a size from 1 nm to 5 μm . In the case of, for example,

nanotubes, this definition of size can be limited to two dimensions only, *i.e.* the third dimension may be outside of these limits. Preferably, the carbon particles are selected from the group of carbon nanoparticles. In an embodiment, the carbon particles are selected from the group comprising carbon black, carbon nanotubes, carbon nanofibers, nanographenes, nanographites, and blends thereof. Preferably, the carbon particles are selected from the group comprising carbon black, carbon nanotubes, carbon nanofibers, nanographenes and blends thereof. More preferred, the carbon particles are carbon nanotubes, nanographenes, and blends of these. Most preferred, the carbon particles are carbon nanotubes.

The invention provides a conductive multilayered pipe produced from two different composite materials having a reduced content of carbon particles compared to prior art. Thus preferably, the first and/or second composite materials comprise at most 9 wt% of carbon particles as based on the total weight of said composite material as determined according to ISO 11358 selected from nanographenes, carbon nanotubes (CNT) or any combination thereof, preferably at most 8.5 wt%, and more preferably at most 8 wt%.

With preference, the first and/or second composite materials comprise at least 0.2 wt% of carbon particles as based on the total weight of said composite material as determined according to ISO 11358 selected from nanographenes, carbon nanotubes (CNT) or any combination thereof, preferably at least 0.5 wt%, and more preferably at least 1.0 wt%.

Should the carbon particles be nanographenes, the first and/or second composite materials may advantageously comprise from 5 to 10 wt% of carbon particles as based on the total weight of said composite material as determined according to ISO 11358, preferably the first and/or second composite materials comprise from 6 to 9 wt% of nanographenes as based on the total weight of the composite material.

The content of carbon particles can be further lowered by selecting carbon nanotubes instead or in addition to nanographenes.

In an embodiment, the carbon particles are carbon nanotubes and the first and/or second composite materials comprises from 0.2 to 5.0 wt% of carbon particles as based on the total weight of the composite material as determined according to ISO 11358, preferably the first and/or second composite materials comprise from 0.5 to 4.8 wt% of carbon particles.

In a preferred embodiment, the content in weight percent of carbon particles of the second composite material as based on the total weight of the second composite material, is lower than the content in weight percent of carbon particles of the first composite material as based on the total weight of the first composite material, the content of carbon particle being determined according to ISO 11358.

Suitable carbon nanotubes used in the present invention can generally be characterized by having a size from 1 nm to 5 μm , this definition of size can be limited to two dimensions only, *i.e.* the third dimension may be outside of these limits.

5 Suitable carbon nanotubes also referred to as “nanotubes” herein, can be cylindrical in shape and structurally related to fullerenes, an example of which is Buckminsterfullerene (C_{60}). Suitable carbon nanotubes may be open or capped at their ends. The end cap may, for example, be a Buckminster-type fullerene hemisphere. Suitable carbon nanotubes used in the present invention can comprise more than 90%, more preferably more than 95%, even more preferably more than 99% and most preferably more than 99.9% of their total weight in carbon.
10 However, minor amounts of other atoms may also be present.

Carbon nanotubes can exist as single-walled nanotubes (SWNT) and multi-walled nanotubes (MWNT). In single-walled carbon nanotubes a one atom thick sheet of atoms, for example, a one atom thick sheet of graphite (also called graphene), is rolled seamlessly to form a cylinder. Multi-walled carbon nanotubes consist of a number of such cylinders arranged concentrically.
15 The arrangement, in multi-walled carbon nanotubes, can be described by the so-called Russian doll model, wherein a larger doll opens to reveal a smaller doll.

In an embodiment, the carbon nanotubes are single-walled nanotubes characterized by an outer diameter of at least 0.5 nm, more preferably of at least 1 nm, and most preferably of at least 2 nm. Preferably their outer diameter is at most 50 nm, more preferably at most 30 nm
20 and most preferably at most 10 nm. Preferably, the length of single-walled nanotubes is at least 0.1 μm , more preferably at least 1 μm , even more preferably at least 10 μm . Preferably, their length is at most 50 μm , more preferably at most 25 μm .

In an embodiment, the carbon nanotubes are single-walled carbon nanotubes, preferably having an average L/D ratio of at least 1000.

25 In an embodiment, the carbon nanotubes are multi-walled carbon nanotubes, more preferably multi-walled carbon nanotubes having on average from 5 to 15 walls.

Multi-walled carbon nanotubes are preferably characterized by an outer diameter of at least 1 nm, more preferably of at least 2 nm, 4 nm, 6 nm or 8 nm, and most preferably of at least 9 nm. The preferred outer diameter is at most 100 nm, more preferably at most 80 nm, 60 nm or
30 40 nm, and most preferably at most 20 nm. Most preferably, the outer diameter is in the range from 10 nm to 20 nm. The preferred length of the multi-walled nanotubes is at least 50 nm, more preferably at least 75 nm, and most preferably at least 100 nm. In an embodiment, the multi-walled carbon nanotubes have an average outer diameter in the range from 10 nm to 20 nm or an average length in the range from 100 nm to 10 μm or both. In an embodiment, the

average L/D ratio (length/diameter ratio) is at least 5, preferably at least 10, preferably at least 25, preferably at least 50, preferably at least 100, and more preferably higher than 100.

In an embodiment, the carbon nanotubes having an average L/D ratio of at least 1000 and the composite material comprises from 0.2 to 5.0 wt% of carbon particles as based on the total weight of the composite material as determined according to ISO 11358, preferably the composite material comprises from 0.5 to 4.8 wt%.

In another embodiment, the carbon particles are carbon nanotubes having an average L/D ratio of at most 500 and the composite material comprises from 1.0 to 5.0 wt% of carbon particles as based on the total weight of the composite material as determined according to ISO 11358, preferably the composite material comprises from 2.0 to 4.8 wt%, more preferably from 2.6 to 4.5 wt%, even more preferably from 2.8 to 4.2 wt%, and most preferably from 3.0 to 4.0 wt% of carbon particles as based on the total weight of the composite material.

In a preferred embodiment, the carbon particles are carbon nanotubes and the second composite material comprises from 0.2 to 5.0 wt% of carbon nanotubes as based on the total weight of said composite material as determined according to ISO 11358, preferably the second composite material comprises from 0.5 to 4.0 wt%, more preferably from 1.0 to 3.5 wt%, even more preferably from 1.2 to 3.0 wt%, and most preferably from 1.5 to 2.8 wt% of carbon nanotubes as based on the total weight of said composite material.

Preferably, the carbon particles are carbon nanotubes and the content in weight percent of carbon nanotubes of the second composite material as based on the total weight of the second composite material, is lower than the content in weight percent of carbon nanotubes of the first composite material as based on the total weight of the first composite material, the content of carbon nanotubes being determined according to ISO 11358.

With preference, the content in weight percent of carbon nanotubes of the second composite material as based on the total weight of the second composite material, is lower than the content in weight percent of carbon nanotubes of the first composite material as based on the total weight of the first composite material, the content of carbon particle being determined according to ISO 11358; and the content of carbon nanotubes of the second composite material as based on the total weight of the second composite material is lower than 3.0 wt% of carbon nanotubes carbon nanotubes as based on the total weight of said composite material and as determined according to ISO 11358, preferably lower than 2.8 wt%, more preferably ranging from 0.2 to 2.8 wt%.

With preference, the content in weight percent of carbon nanotubes of the second composite material as based on the total weight of the second composite material, is lower than the

content in weight percent of carbon nanotubes of the first composite material as based on the total weight of the first composite material, the content of carbon particle being determined according to ISO 11358; and:

- 5 - the content of carbon nanotubes of the second composite material as based on the total weight of the second composite material is lower than 3.0 wt% of carbon nanotubes carbon nanotubes as based on the total weight of said composite material and as determined according to ISO 11358, preferably lower than 2.8 wt%, more preferably ranging from 0.2 to 2.8 wt%; and
- 10 - the content of carbon nanotubes of the first composite material as based on the total weight of the second composite material is lower than 5.0 wt% of carbon nanotubes carbon nanotubes as based on the total weight of said composite material and as determined according to ISO 11358, preferably lower than 4.5 wt%, more preferably ranging from 2.5 to 5.0 wt%, and most preferably ranging from 2.9 to 4.5 wt%.

Suitable carbon nanotubes to be used in the present invention can be prepared by any method known in the art. Non-limiting examples of commercially available multi-walled carbon nanotubes are Graphistrength™ 100 available from Arkema, Nanocyl™ NC 7000 available from Nanocyl, FloTube™ 9000 available from CNano Technology.

Nanocyl™ NC 7000 available from Nanocyl are carbon nanotubes having an average L/D ratio of at most 500.

20 The polyethylene glycol and the processing aids

In a preferred embodiment, the first composite material comprises from 0.10 to 0.48 wt% of polyethylene glycol as based on the total weight of the composite material, and in that said polyethylene glycol is selected to have a weight average molecular weight Mw of at most 20,000 g/mol.

25 The invention encompasses the embodiments wherein the polyethylene glycol in the composite material is a mixture of polyethylene glycol of different molecular weight. In such a case, the molecular weight to be taken into consideration is the weight average molecular weight of the mixture.

In an embodiment, the polyethylene glycol has a weight average molecular weight Mw of at most 12,000 g/mol, preferably at most 10,000 g/mol, more preferably of at most 8,000 g/mol, even more preferably of at most 6,000 g/mol, and most preferably of at most 5,000 g/mol.

With preference, the polyethylene glycol has a weight average molecular weight Mw of at least 200 g/mol, preferably at least 400 g/mol, more preferably of at least 800 g/mol, even more

preferably of at least 1,000 g/mol, most preferably of at least 2,000 g/mol and even most preferably of at least 3,000 g/mol.

In a preferred embodiment, the polyethylene glycol is selected to have a weight average molecular weight Mw of 4,000 g/mol (CAS number 25322-68-3).

- 5 With preference, the first composite material comprises at least 0.15 wt% of polyethylene glycol as based on the total weight of the first composite material, preferably at least 0.20 wt%, more preferably at least 0.25 wt% and even more preferably at least 0.30 wt%.

In an embodiment, the first composite material comprises at most 0.45 wt% of polyethylene glycol as based on the total weight of the first composite material, preferably at most 0.42 wt%.

- 10 In a preferred embodiment, the first composite material further comprises from 0.01 to 5.0 wt% of one or more processing aids as based on the total weight of said first composite material, wherein the one or more processing aids are selected from fluoroelastomers, waxes, tristearin, zinc stearate, calcium stearate, magnesium stearate, erucyl amide, oleic acid amide, ethylene-acrylic acid copolymer, ethylene vinyl acetate copolymer, cetyl trimethyl ammonium bromide,
15 polyethylene oxide, polysiloxanes, oleamide, stearamide, behenamide, oleyl palmitamide, ethylene bis-oleamide, ethylene bis(stearamide) (EBS) and any mixture thereof.

The polyethylene oxide, in accordance to the invention, is a polyoxyethylene having a weight average molecular weight Mw of at least 20,000 g/mol, preferably of at least 25,000 g/mol.

- 20 With preference, the first composite material further comprises at most 3.0 wt% of one or more processing aids as based on the total weight of said first composite material, preferably at most 1.5 wt%, more preferably at most 1.0 wt%, even more preferably at most 0.8 wt%, most preferably at most 0.5 wt%, and even most preferably at most 0.48 wt% or 0.45 wt% or 0.42 wt%.

- 25 With preference, the first composite material comprises at least 0.15 wt% of one or more processing aids as based on the total weight of the first composite material, preferably at least 0.20 wt%, more preferably at least 0.25 wt% and even more preferably at least 0.30 wt%.

Preferably, the one or more processing aids are selected from oleamide, stearamide, behenamide, oleyl palmitamide, ethylene bis-oleamide, ethylene bis(stearamide) (EBS) and any mixture thereof.

- 30 Preferably, the first composite material comprises both polyethylene glycol and one or more processing aids, and the polyethylene glycol and the one or more processing aids form an additive mixture, and the content of polyethylene glycol in the additive mixture is ranging from

50 wt% to 99 wt% as based on the total weight of the additive mixture, more preferably from 60 wt% to 90 wt%, more preferably from 65 wt% to 85 wt%.

In a preferred embodiment, the second composite material is devoid of polyethylene glycol, and/or is devoid of any processing aids selected from fluoroelastomers, waxes, tristearin, zinc stearate, calcium stearate, magnesium stearate, erucyl amide, oleic acid amide, ethylene-acrylic acid copolymer, ethylene vinyl acetate copolymer, cetyl trimethyl ammonium bromide, polyethylene oxide, polysiloxanes, oleamide, stearamide, behenamide, oleyl palmitamide, ethylene bis-oleamide, ethylene bis(stearamide) (EBS) and any mixture thereof.

In all embodiments of the invention, the first and/or the second composite materials may further comprise one or more additives different from the listed processing aids, the one or more additive being selected from the group comprising an antioxidant, an antiacid, a UV-absorber, an antistatic agent, a light stabilizing agent, an acid scavenger, a lubricant, a nucleating/clarifying agent, a colorant or a peroxide. An overview of suitable additives may be found in *Plastics Additives Handbook*, ed. H. Zweifel, 5th edition, 2001, Hanser Publishers, which is hereby incorporated by reference in its entirety.

In all embodiments of the invention, the first and/or the second composite materials, and/or the third polyethylene resin, may comprise from 0% to 45% by weight of one or more filler based on the total weight of the composite material, preferably from 1% to 35 % by weight. The one or more filler being selected from the group consisting of talc, calcium carbonate, calcium hydroxide, barium sulphate, mica, calcium silicate, clay, kaolin, silica, alumina, wollastonite, magnesium carbonate, magnesium hydroxide, titanium oxide, zinc oxide, zinc sulphate, natural fibres, glass fibres. With preference, the filler is talc.

The invention also encompasses the pipe as described herein wherein the first and/or the second composite materials, and/or the third polyethylene resin, comprises from 0% to 10% by weight of at least one additive such as antioxidant, based on the total weight of said composite material or resin. In a preferred embodiment, the first and/or the second composite materials, and/or the third polyethylene resin, comprise less than 5% by weight of additive, based on the total weight of said composite material, for example from 0.1 to 3% by weight of additive, based on the total weight of said composite material.

In an embodiment, the first and/or the second composite materials, and/or the third polyethylene resin, comprise an antioxidant. Suitable antioxidants include, for example, phenolic antioxidants such as pentaerythritol tetrakis[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate] (herein referred to as Irganox 1010), tris(2,4-ditert-butylphenyl) phosphite (herein referred to as Irgafos 168), 3DL-alpha-tocopherol, 2,6-di-tert-butyl-4-methylphenol, dibutylhydroxyphenylpropionic acid stearyl ester, 3,5-di-tert-butyl-4-

hydroxyhydrocinnamic acid, 2,2'-methylenebis(6-tert-butyl-4-methyl-phenol), hexamethylene bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], benzenepropanamide, N,N'-1,6-hexanediyl bis[3,5-bis(1,1-dimethylethyl)-4-hydroxy] (Antioxidant 1098), Diethyl 3,5-Di-Tert-Butyl-4-Hydroxybenzyl Phosphonate, Calcium bis[monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate], Triethylene glycol bis(3-tert-butyl-4-hydroxy-5-methylphenyl)propionate (Antioxidant 245), 6,6'-di-tert-butyl-4,4'-butylidenedi-m-cresol, 3,9-bis(2-(3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy-1,1-dimethylethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butane, (2,4,6-trioxo-1,3,5-triazine-1,3,5(2H,4H,6H)-triyl)triethylene tris[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, Tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate, ethylene bis[3,3-bis(3-tert-butyl-4-hydroxyphenyl)butyrate], and 2,6-bis[[3-(1,1-dimethylethyl)-2-hydroxy-5-methylphenyl]octahydro-4,7-methano-1H-indenyl]-4-methyl-phenol. Suitable antioxidants also include, for example, phenolic antioxidants with dual functionality such 4,4'-Thio-bis(6-tert-butyl-m-methyl phenol) (Antioxidant 300), 2,2'-Sulfanediylbis(6-tert-butyl-4-methylphenol) (Antioxidant 2246-S), 2-Methyl-4,6-bis(octylsulfanylmethyl)phenol, thiodiethylene bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino)phenol, N-(4-hydroxyphenyl)stearamide, bis(1,2,2,6,6-pentamethyl-4-piperidyl) [[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]methyl]butylmalonate, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxy-benzoate, 2-(1,1-dimethylethyl)-6-[[3-(1,1-dimethylethyl)-2-hydroxy-5-methylphenyl] methyl]-4-methylphenyl acrylate, and CAS 128961-68-2 (Sumilizer GS). Suitable antioxidants also include, for example, aminic antioxidants such as N-phenyl-2-naphthylamine, poly(1,2-dihydro-2,2,4-trimethyl-quinoline), N-isopropyl-N'-phenyl-p-phenylenediamine, N-Phenyl-1-naphthylamine, CAS 68411-46-1 (Antioxidant 5057), and 4,4-bis(alpha,alpha-dimethylbenzyl)diphenylamine (Antioxidant KY 405). Preferably, the antioxidant is selected from pentaerythritol tetrakis[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) propionate] (herein referred to as Irganox 1010), tris(2,4-ditert-butylphenyl) phosphite (herein referred to as Irgafos 168), or a mixture thereof.

30 The process to produce the conductive multilayered pipe

The invention also provides a process to produce the conductive multilayered pipe as described above, wherein the process comprises the following steps:

a. providing a first composite material comprising:

- from 50 to 99 wt% of a first polyethylene resin as based on the total weight of the said first composite material, wherein the first polyethylene resin has a melt index

MI2 of at most 0.50 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg; and

- from 0.2 to 20.0 wt% of carbon particles as based on the total weight of the said first composite material as determined according to ISO 11358 selected from carbon black, nanographenes, carbon nanotubes or any combination thereof;

b. providing a third polyethylene resin having a melt index MI2 of at most 0.50 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg;

c. coextruding or co-injecting the first composite material and the third polyethylene resin to form a conductive multilayered pipe wherein the first composite material forms the inner external layer of the pipe;

d. providing a second composite material comprising:

- from 50 to 99 wt% of a second polyethylene resin as based on the total weight of the said second composite material, wherein the second polyethylene resin has a melt index MI2 ranging from 0.8 to 50.0 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg; and

- from 0.2 to 10.0 wt% of carbon particles as based on the total weight of the said second composite material as determined according to ISO 11358 selected from carbon black, nanographenes, carbon nanotubes or any combination thereof;

e. covering the multilayered pipe obtained in step c) with a layer of the second composite material in order to obtain a conductive multilayered pipe wherein the first composite material forms the inner external layer of the pipe, the second composite material forms the outer external layer of the pipe, and the third polyethylene resin forms at least one internal layer in between the inner external layer and the outer external layer of the pipe.

In a preferred embodiment, the carbon particles are selected from carbon nanotubes, nanographenes and mixture thereof, and the first composite material is produced by blending the first polyethylene resin with a masterbatch comprising the blend of a fourth polyethylene resin and at least 5 wt% of carbon particles as based on the total weight of said masterbatch as determined according to ISO 11358; the masterbatch having an HLMI of at least 5 g/10 min and of at most 500 g/10 min as determined according to ISO 1133 at 190 °C under a load of 21.6 kg.

With preference, the first composite material comprises polyethylene glycol and/or one or more processing aids. The polyethylene glycol and/or one or more processing aids can be added by any known method. In an embodiment, the polyethylene glycol and/or one or more processing aids can be provided with a masterbatch.

In another embodiment, alternative or complementary to the preceding one, the polyethylene glycol and/or the optional processing aids are added pure in the extruder in the main feeder but it is preferably added via a side-feeder during the preparation of the first composite material.

- 5 In a preferred embodiment, the carbon particles are selected from carbon nanotubes, nanographenes and mixture thereof, and the second composite material is produced by blending the second polyethylene resin with a masterbatch comprising the blend of a fourth polyethylene resin and at least 5 wt% of carbon particles as based on the total weight of said masterbatch as determined according to ISO 11358; the masterbatch having an HLMI of at
10 least 5 g/10 min and of at most 500 g/10 min as determined according to ISO 1133 at 190 °C under a load of 21.6 kg.

As used herein, the term “masterbatch” refers to concentrates of carbon particles (such as carbon nanotubes (CNT) or nanographenes) and the optional polyethylene glycol and/or processing aids in a polymer, which are intended to be subsequently incorporated into another
15 polymer miscible with the polymer already contained in the masterbatches. Use of masterbatches makes processes more easily to adapt to industrial scale, compared to direct incorporation of the carbon particles into the polyethylene composition. In accordance with the invention, two polymers are said miscible when they are of the same nature, for instance when both are polyethylene.

- 20 In all embodiments, the masterbatch preferably comprises the blend of a fourth polyethylene resin and from 5 to 25 wt% of carbon particles as based on the total weight of said masterbatch as determined according to ISO 11358, the carbon particles being selected from nanographenes, carbon nanotubes or any combination thereof; preferably from 6 to 15 wt% of carbon particles.

- 25 With preference, the masterbatch is produced by blending together a fourth polyethylene resin having a melting temperature T_m as measured according to ISO 11357-3, carbon particles, optional polyethylene glycol and optional processing aids, in an extruder comprising a transport zone and a melting zone maintained at a temperature comprised between $T_m + 1\text{ °C}$ and $T_m + 50\text{ °C}$, preferably comprised between $T_m + 5\text{ °C}$ and $T_m + 30\text{ °C}$.

- 30 Preferably, the fourth polyethylene resin has a melt flow index ranging from 5 to 250 g/10 min as measured according to ISO 1133 at 190 °C under a load of 2.16 kg.

In an embodiment, the process for the preparation of the masterbatch according to the present invention comprises the steps of:

- i. providing carbon particles;

- ii. providing a fourth polyethylene resin having a melting temperature, T_m , measured according to ISO 11357-3, and wherein said fourth polyethylene resin has a melt flow index preferably comprised between 5 and 250 g/10 min measured according to ISO 1133 at 190 °C under a load of 2.16 kg;
- 5 iii. blending together said carbon particles and said fourth polyethylene resin by extrusion in an extruder comprising a transport zone and a melting zone maintained at a temperature comprised between $T_m + 1$ °C and $T_m + 50$ °C, preferably between $T_m + 5$ °C and $T_m + 30$ °C; and
- iv. forming a masterbatch through a die, said masterbatch,
- 10 • comprising at least 5 wt% of carbon particles based on the total weight of the masterbatch as determined according to ISO 11358, and
- having a high load melt index, HLMI, of from 2 g/10 min to 1000 g/10 min, preferably ranging from 10 to 1000 g/10 min, determined according to ISO 1133 at 190 °C under a load of 21.6 kg.

15 In a preferred embodiment, the process further comprises the step of blending, with the fourth polyethylene resin and the carbon particles in step iii, from 0.1 to 20.0 wt% of polyethylene glycol as based on the total weight of the masterbatch, preferably from 0.5 to 10.0 wt%, more preferably from 0.8 to 5.0 wt%, even more preferably from 1.0 to 4.0 wt%, most preferably from 1.2 to 3.0 wt% and even more preferably from 1.5 to 2.5 wt%, wherein the polyethylene glycol

20 is selected to have a weight average molecular weight M_w of at most 20,000 g/mol.

In another embodiment, the process further comprises the step of blending, with the fourth polyethylene resin and the carbon particles in step iii, from 0.01 to 20 wt% one or more processing aids based on the total weight of the masterbatch, preferably from 0.01 to 10 wt%, more preferably from 0.01 to 4.0 wt%.

25 In a preferred embodiment, step iii of blending is carried out on co-rotating twin-screw extruder at a screw speed of at least 300 rpm, preferably at least 500 rpm.

In a preferred embodiment, the temperature of the masterbatch at the extruder's outlet ranges from the crystallization temperature and the melting temperature of the masterbatch polymer.

In a preferred embodiment, the fourth polyethylene resin is a polyethylene homopolymer or a

30 copolymer of ethylene with C_3 - C_{20} olefins; and the temperature within the transport and melting zone of the extruder, preferably over the entire length of the extruder, ranges from 140 °C to 180 °C, preferably from 140 °C to 170 °C, more preferably from 140 °C to 160 °C, most preferably from 150 °C to 160 °C. Preferably, the temperature of the masterbatch at the extruder's outlet may range from the crystallization temperature and the melting temperature

35 of the polyethylene homopolymer or of the copolymer of ethylene with C_3 - C_{20} olefins.

A homopolymer according to this invention has less than 0.2 wt%, preferably less than 0.1 wt%, more preferably less than 0.05 wt% and most preferably less than 0.005 wt%, of alpha-olefins other than ethylene in the polymer. Most preferred, no other alpha-olefins are detectable. Accordingly, when the polyethylene of the invention is a homopolymer of ethylene,
5 the comonomer content in the polyethylene is less than 0.2 wt%, more preferably less than 0.1 wt%, even more preferably less than 0.05 wt% and most preferably less than 0.005 wt% based on the total weight of the polyethylene.

Step a) of providing a first composite material

With preference, in all embodiments, the step a) of providing a first composite material and the
10 step of preparing a first composite material are performed together in a single extrusion apparatus or in a single injection apparatus. Thus, the different components of the first composite material are dry blended together and directly provided to the extrusion apparatus or to the injection apparatus. The different components of the first composite material are not melt blended nor chopped into pellets before the shaping step (by extrusion or by injection) to
15 form a pipe.

This embodiment encompasses cases wherein the carbon particles are provided with a masterbatch so that the blending of the masterbatch with the first polyethylene resin and their shaping into a conductive multilayered pipe is done in a single step and in a single extrusion or injection moulding device. The inventive process allows obtaining further enhanced
20 electrical properties on the pipe compared with processes comprising a first step of compounding the masterbatch with the first polyethylene resin to obtain a first composite material and a subsequent step of shaping the composition to form the pipe.

Preferably, in step a) of the present process, the blending is a dry blending of the masterbatch and the first polyethylene resin.

25 In a preferred embodiment, step d) and e) are performed together, in a single step.

Pipes according to the invention can be produced by first plasticizing the composite material, or its components, in an extruder at temperatures in the range of from 200 °C to 250 °C and then extruding it through an annular die and cooling it.

Preferably, step c) of the present process is carried out in a twin-screw extruder with a screw
30 rotation speed comprised between 5 to 1000 rpm, preferably between 10 and 750 rpm, more preferably between 15 and 500 rpm, most preferably between 20 and 400 rpm, in particular between 25 and 300 rpm. Twin-screw extruders are preferred to carry out step e) of the present process since high shear stress is generated which favours the enhancement of the electrical properties.

The extruders for producing the pipes can be single-screw extruders or twin-screw extruders or extruder cascades of homogenizing extruders (single-screw or twin-screw). To produce pellets from the fluff (when homogenizing and introducing the additives), a single-screw extruder can be used, preferably with an L/D ratio of 20 to 40, or twin-screw extruders, preferably with an L/D ratio of 20 to 40, preferably an extruder cascade is used. In some embodiments, supercritical CO₂ or water is used during extrusion to help homogenization. Variations could be considered like the use of supercritical CO₂ to help homogenization, and use of water during extrusion. Optionally, a melt pump and/or a static mixer can be used additionally between the extruder and the ring die head. Ring-shaped dies with diameters ranging from approximately 16 to 2000 mm and even greater are possible.

The melt arriving from the extruder can be first distributed over an annular cross-section via conically arranged holes and then fed to the core/die combination via a coil distributor or screen. If necessary, restrictor rings or other structural elements for ensuring uniform melt flow may additionally be installed before the die outlet.

After leaving the annular die, the pipe can be taken off over a calibrating mandrel, usually accompanied by cooling of the pipe by air cooling and/or water cooling, optionally also with inner water cooling.

The masterbatch comprising polyethylene glycol

The invention provides a masterbatch for use in a process according to the invention, to produce the first composite material.

With preference, the polyethylene glycol is present in the masterbatch. The masterbatch comprises the blend of a fourth polyethylene resin and at least 5 wt% of carbon particles as based on the total weight of said masterbatch as determined according to ISO 11358, the carbon particles being selected from nanographenes, carbon nanotubes or any combination thereof; the masterbatch having a HLMI of at least 5 g/10 min and of at most 500 g/10 min as determined according to ISO 1133 at 190 °C under a load of 21.6 kg; and from 0.1 to 20.0 wt% of polyethylene glycol as based on the total weight of the masterbatch, wherein the polyethylene glycol is selected to have a weight average molecular weight Mw of at most 20,000 g/mol.

The masterbatch optionally comprises from 0.01 to 5.0 wt% of a processing aid based on the total weight of the masterbatch, said processing aid being selected from fluoroelastomers, waxes, tristearin, zinc stearate, calcium stearate, magnesium stearate, erucyl amide, oleic acid amide, ethylene-acrylic acid copolymer, ethylene vinyl acetate copolymer, cetyl trimethyl ammonium bromide, polyethylene oxide, polysiloxanes, oleamide, stearamide, behenamide,

oleyl palmitamide, ethylene bis-oleamide, ethylene bis(stearamide) (EBS) and any mixture thereof.

Preferably, the fourth polyethylene resin has a melt flow index MI₂ ranging from 5 to 250 g/10 min as measured according to ISO 1133 at 190 °C under a load of 2.16 kg.

- 5 In a preferred embodiment, the masterbatch comprises from 0.5 to 10.0 wt% of polyethylene glycol as based on the total weight of the masterbatch, preferably from 0.8 to 5.0 wt%, more preferably from 1.0 to 4.0 wt%, even more preferably from 1.2 to 3.0 wt% and most preferably from 1.5 to 2.5 wt%.

With preference, the polyethylene glycol has a weight average molecular weight (M_w):

- 10 • of at most 12,000 g/mol, preferably at most 10,000 g/mol, more preferably of at most 8,000 g/mol, even more preferably of at most 6,000 g/mol, and most preferably of at most 5,000 g/mol; and/or
- of at least 200 g/mol, preferably at least 400 g/mol, more preferably of at least 800 g/mol, even more preferably of at least 1,000 g/mol, most preferably of at least 2,000 g/mol and
- 15 even most preferably of at least 3,000 g/mol.

In a preferred embodiment, the polyethylene glycol has a weight average molecular weight (M_w) of 4,000 g/mol (CAS number 25322-68-3).

- With preference, the masterbatch comprises both the polyethylene glycol and the one or more processing aids, wherein the polyethylene glycol and the one or more processing aids form an
- 20 additive mixture, and further wherein the content of polyethylene glycol in the additive mixture is ranging from 50 wt% to 99 wt% as based on the total weight of the additive mixture, preferably from 60 wt% to 90 wt%, more preferably from 65 wt% to 85 wt%.

- When polyethylene glycol is present, and when the carbon particles are carbon nanotubes; the composite material may comprise from 0.2 to 5.0 wt% of carbon nanotubes as based on the
- 25 total weight of the composite material as determined according to ISO11358, preferably the composite material comprises from 0.5 to 4.8 wt%, more preferably from 1.5 to 4.5 wt%, even more preferably from 1.8 to 4.2 wt%, most preferably from 2.0 to 4.0 wt%, and even most preferably at most 3.5 wt% or at most 3.0 wt%, or at most 2.9 wt% of carbon nanotubes as based on the total weight of the composite material.

30 **Test methods**

The melt flow index (MI_{2PE}) of the polyethylene is determined according to ISO 1133 at 190 °C under a load of 2.16 kg.

The melt flow index (MI_{5PE}) of the polyethylene is determined according to ISO 1133 at 190 °C under a load of 5 kg.

The high load melt flow index (HLMI) of the polyethylene is determined according to ISO 1133 at 190 °C under a load of 21.6 kg.

- 5 Molecular weights are determined by Size Exclusion Chromatography (SEC) at high temperature (145 °C). A 10 mg polyethylene sample is dissolved at 160 °C in 10 mL of trichlorobenzene (technical grade) for 1 hour. Analytical conditions for the GPC-IR from Polymer Char are:
- Injection volume: +/- 0.4 mL;
 - 10 • Automatic sample preparation and injector temperature: 160 °C;
 - Column temperature: 145 °C;
 - Detector temperature: 160 °C;
 - Column set: 2 Shodex AT-806MS and 1 Styragel HT6E;
 - Flow rate: 1 mL/min;
 - 15 • Detector: IR5 Infrared detector (2800-3000 cm⁻¹);
 - Calibration: Narrow standards of polystyrene (commercially available);
 - Calculation for polyethylene: Based on Mark-Houwink relation ($\log_{10}(M_{PE}) = 0.965909 \log_{10}(M_{PS}) - 0,28264$); cut off on the low molecular weight end at $M_{PE} = 1000$.

20 The molecular weight averages used in establishing molecular weight/property relationships are the number average (M_n), weight average (M_w) and z average (M_z) molecular weight. These averages are defined by the following expressions and are determined from the calculated M_i :

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} = \frac{\sum_i W_i}{\sum_i W_i / M_i} = \frac{\sum_i h_i}{\sum_i h_i / M_i}$$

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \frac{\sum_i W_i M_i}{\sum_i M_i} = \frac{\sum_i h_i M_i}{\sum_i M_i}$$

$$M_z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2} = \frac{\sum_i W_i M_i^2}{\sum_i W_i M_i} = \frac{\sum_i h_i M_i^2}{\sum_i h_i M_i}$$

Here N_i and W_i are the number and weight, respectively, of molecules having molecular weight M_i . The third representation in each case (farthest right) defines how one obtains these averages from SEC chromatograms. h_i is the height (from baseline) of the SEC curve at the i_{th} elution fraction and M_i is the molecular weight of species eluting at this increment.

5 The molecular weight distribution (MWD) is then calculated as M_w/M_n .

10 The ^{13}C -NMR analysis is performed using a 400 MHz or 500 MHz Bruker NMR spectrometer under conditions such that the signal intensity in the spectrum is directly proportional to the total number of contributing carbon atoms in the sample. Such conditions are well known to the skilled person and include for example sufficient relaxation time etc. In practice, the
15 intensity of a signal is obtained from its integral, *i.e.* the corresponding area. The data is acquired using proton decoupling, 2000 to 4000 scans per spectrum with 10 mm room temperature through or 240 scans per spectrum with a 10 mm cryoprobe, a pulse repetition delay of 11 seconds and a spectral width of 25000 Hz ($\pm$ 3000 Hz). The sample is prepared by dissolving a sufficient amount of polymer in 1,2,4-trichlorobenzene (TCB, 99%,
20 spectroscopic grade) at 130 °C and occasional agitation to homogenise the sample, followed by the addition of hexadeuterobenzene (C_6D_6 , spectroscopic grade) and a minor amount of hexamethyldisiloxane (HMDS, 99.5+ %), with HMDS serving as internal standard. To give an example, about 200 mg to 600 mg of polymer are dissolved in 2.0 mL of TCB, followed by addition of 0.5 mL of C_6D_6 and 2 to 3 drops of HMDS.

20 Following data acquisition, the chemical shifts are referenced to the signal of the internal standard HMDS, which is assigned a value of 2.03 ppm.

25 The comonomer content of a polyethylene is determined by ^{13}C -NMR analysis of pellets according to the method described by G.J. Ray et al. in *Macromolecules*, vol. 10, n° 4, 1977, p. 773-778.

25 Melting temperatures T_m were determined according to ISO 3146 on a DSC Q2000 instrument by TA Instruments. To erase the thermal history the samples are first heated to 200 °C and kept at 200 °C for a period of 3 minutes. The reported melting temperatures T_m are then determined with heating and cooling rates of 20 °C/min.

30 The density is determined according to ISO 1183 at a temperature of 23 °C.

30 The content of carbon particles, such as carbon nanotubes in percentage by weight in blends (%CNT) can be determined by thermal gravimetric analysis (TGA) according to ISO 11358, using a Mettler Toledo STAR TGA/DSC 1 apparatus. Prior to the determination of the content of carbon nanotubes in % by weight in blends (%CNT), the carbon content of the carbon nanotubes in % by weight (%C-CNT) was determined as follows: 2 to 3 milligrams of carbon

nanotubes were placed into a TGA. The material was heated at a rate of 20 °C/min from 30 °C to 600 °C in nitrogen (100 ml/min). At 600 °C, the gas was switched to air (100 ml/min), and the carbon oxidized, yielding the carbon content of the carbon nanotubes in % by weight (%C-CNT). The %C-CNT value was the average of 3 measurements. For the content of carbon nanotubes % by weight in blends (%CNT), 10 to 20 milligrams of sample was placed into a TGA. The material was heated at a rate of 20 °C/min from 30 °C to 600 °C in nitrogen (100 ml/min). At 600 °C, the gas was switched to air (100 ml/min), and the carbon oxidized, yielding to the carbon content of carbon nanotubes in the sample (%C-sample). The %C-sample value was the average of 3 measurements. The content of carbon nanotubes in % by weight in the sample (%CNT) was then determined by dividing the carbon content of carbon nanotubes in % by weight in samples (%C-sample) by the carbon content of the carbon nanotubes in % by weight (%C-CNT) and multiplying by 100.

$$\%CNT = \%C\text{-sample} / \%C\text{-CNT} * 100$$

The surface resistance and resistivity (SR) of the article were measured by the following silver ink method using a 2410 SourceMeter® apparatus. Conditions which were used were those described in the CEI 60167 test methods. The surface resistivity (SR) was measured on the article. The resistance measurement was performed using an electrode system made of two conductive paint lines using silver ink and an adhesive mask presenting 2 parallel slits 25 mm long, 1 mm wide and 2 mm apart. The samples were conditioned at 23 °C/50% RH for minimum 4 hours before running the test. The measure of the resistance in Ohm was reported to a square measurement area and expressed in Ohm/square using the following equation: $SR = (R \times L) / d$, wherein: SR is the average resistance reported to a square measurement area, conventionally called surface resistivity (expressed in Ohm/sq), R is the average of the resistance measurements (Ohm), L is the paint line length (cm), d is the distance between the electrodes (cm). L = 2 cm and d = 0.2 cm and $SR = R \times 10$. The surface resistivity (SR) value was the average of 3 measurements.

Alternatively, surface resistance (Ohm) was measured according to IEC 61340-4-1 with an SRM110 meter. The SRM110 is a surface resistance tester. Its internal parallel electrodes comply with DIN EN 100 015/1. IEC electrodes were externally connected for tests according to IEC 61340-4-1.

The following non-limiting examples illustrate the invention.

Examples:

Example 1: Preparation of a masterbatch comprising carbon nanotubes

The carbon nanotubes used were multi-walled carbon nanotubes Nanocyl™ NC 7000, commercially available from Nanocyl. These CNTs have a surface area of 250-300 m²/g (measured by BET method), a carbon purity of about 90 % by weight (measured by thermal gravimetric analysis), an average diameter of 9.5 nm and an average length of 1.5 µm (as measured by transmission electron microscopy).

The fourth polyethylene resin used was polyethylene PE4 with a melt flow index of 16 g/10 min as measured according to ISO 1133 H (190 °C-2.16kg), a density of 0.935 g/cm³ (ISO 1183) and a T_m of 125 °C (ISO 11357-3).

The masterbatch M1a was prepared by blending polyethylene PE4 and carbon nanotubes, using classical twin-screw extrusion process. Carbon nanotubes powder and polyethylene were introduced into the extruder such as to obtain a CNT content of about 10 % by weight based on the total weight of the masterbatch. The masterbatch M1a was blended on Leitztriz co-rotating twin-screw extruder with an L/D ratio of 52 (D=60), the barrel temperature was set at 90-100 °C, to have a melt temperature of about 160 °C.

M1b was produced in the same conditions except that the barrel temperature was slightly lower.

The properties of the polyethylene based masterbatches are provided in below table 1.

Table 1 – Properties of the PE masterbatch

PE Masterbatch	M1a	M1b
PE4 (wt%)	90	90
PE4 MFI (g/10 min)	16	16
Processing aids (wt%)	-	-
CNT (wt%)	10	10
Screw speed (RPM)	500	500
Throughput (kg/h)	90-100	150
Barrel temperature (°C)	135-140	80-95
HLMI (g/10 min.)	26.2	31.0
Surface resistance ⁽¹⁾ , R _s (Ohm)	2.7x10 ⁰	4.2 x10 ⁰
Surface resistivity ⁽¹⁾ , ρ _s (Ohm/sq)	2.7x10 ¹	4.2 x10 ¹

(1) as measured on compression moulded plaque/square from pellets according to ASTM D-257-07, the surface resistivity is done with an accuracy of +/- 1.0x10¹. The silver ink method was used for determination of the surface resistance and resistivity.

Example 2: Influence of the viscosity of the polyethylene on electrical properties

Extruded blends were prepared by mixing the masterbatch M1a with different polyethylene resins commercially available from TOTAL®, having a different melt index, under the following procedure.

- 5 Dry-blend of 15% of masterbatch-CNT and 85% PE resin were introduced in the feed zone through the hopper and then extruded on twin-screw extruder (screw diameter 18 mm) at a melt temperature of 230°C (barrel temperature profile from the hopper to die: 220-230-230-230-220°C) at 80 rpm screw speed and 2kg/h throughput. No additives were added.

- 10 Surface resistivity was measured with resistance meter using silver ink electrodes painted on compressed moulded plates (CMP) made from CPD pellets at 230°C during 4 min then cooled down to 30°C at 20°C/min. The results are reported on the below table 2.

Table 2

Resin	MI2 of the resin before blending (190°C/2.16kg)	MI5 of the resin before blending (190°C/5kg)	HLMI of the resin before blending (190°C/ 21.6kg)	Density of the resin before blending	Surface resistivity ⁽¹⁾ (Ohm/square) of the extruded blend
PE1	0.3	0.7	15	947	$> 1 \times 10^{10}$
PE5	1	Nd	26	918	7×10^4
PE6	1.2	Nd	33	956	2×10^4
PE2b	4	Nd	86	940	2×10^3

(1) as measured with the silver ink method on compressed moulded square

Nd = not determined

- 15 From the results, it can be seen the influence of the melt index of the polyethylene resin on the possibility to obtain a surface resistivity of below 5×10^6 .

- 20 PE1 is commercially available from TOTAL® under the tradename XRT 70. PE1 has an MI5 of 0.7 g/10 min as measured according to ISO 1133 (190 °C- 5kg), a density of 0.949 g/cm³ (ISO 1183), an HLMI of 12 g/10 min as measured according to ISO 1133 (190 °C- 21.6 kg). PE1 can be used as first polyethylene resin as well as third polyethylene resin according to the invention in order to produce the inner external layer and the internal layer. Because of its low melt index (MI2 is below 0.5 g/10 min), an additive mixture comprising processing aids is to be added together with the CNT when preparing the inner external layer.

PE2b is commercially available from TOTAL® under the tradename M4040. PE5 is commercially available from TOTAL® under the tradename LL1810. PE6 is commercially available from TOTAL® under the tradename M5510 EP. For example, PE6 can be used as a second polyethylene resin in order to produce the outer external layer.

5 Example 3 - Production of a conductive pipe – presence of processing aids

The masterbatch M1a was dry blended with a first polyethylene resin PE1 and extruded to form a pipe.

The first polyethylene resin used was polyethylene PE1 commercially available from TOTAL® under the tradename XRT 70. PE1 has an MI5 of 0.7 g/10 min as measured according to ISO 1133 (190 °C- 5kg), a density of 0.949 g/cm³ (ISO 1183), an HLMI of 12 g/10 min as measured according to ISO 1133 (190 °C- 21.6 kg).

Pipe 1 is comparative, Pipe 2 is inventive. In all cases, the temperature at the outlet was 260 °C, the screw speed was 40 rpm. In pipe 2 the processing aid selected to produce the sample was Dynamar FX5922 commercially available from 3M.

15 The properties of the conductive pipes are provided in below table 3.

Table 3 – Properties of the conductive pipes

	Pipe 1	Pipe 2
Masterbatch	M1a	M1a
Masterbatch (wt%)	40	40
PE1 (wt%)	60	59,7
PE1 MI2 (g/10 min)	0.3	0.3
Processing aid (wt%)	-	0.3
CNT (wt%) ⁽²⁾	4	4
Screw speed (RPM)	40	40
Draw rate (m/min)	0.5	0.5
barrel temperature (°C)	260	260
Surface resistivity ⁽¹⁾ of the pipe, ρ_s (Ohm/sq)	1×10^8	1×10^5

⁽¹⁾ as determined according to the method silver ink method described above the surface resistivity is done with an accuracy of +/- 1.0×10^1

⁽²⁾ The CNTs are originated from the masterbatch.

From the results, it can be clearly seen that improved surface resistivity is achieved on the inventive pipe, at same CNT content. The composite material of pipe 2 can be used to form the inner external layer of the conductive multilayered pipe according to the invention.

Example 4: Production of bars - influence of the presence of PEG in the additive composition

- 5 The masterbatch M1a was dry blended with a first polyethylene resin PE1 and extruded to form a bar. Extrusion trials were conducted on Gottfert single-screw extruder with a rectangular die of 50x20 mm. The Gottfert single-screw extruder had a screw diameter = 30 mm, and a length/diameter ratio (L/D ratio) of 35. In all cases, the barrel temperature was 250 °C, the screw speed was 120 rpm.
- 10 The first polyethylene resin used was polyethylene PE1 commercially available from TOTAL® under the tradename XRT 70. PE1 has an MI5 of 0.7 g/10 min as measured according to ISO 1133 (190 °C- 5kg), a density of 0.949 g/cm³ (ISO 1183), an HLMI of 12 g/10 min as measured according to ISO 1133 (190 °C- 21.6 kg).

The following samples have been tested and results are reported in the below table 4:

- 15 - Bar 1 is a comparative sample, wherein the composite material is devoid of polyethylene glycol and of processing aids.
- Bar 2 is a comparative sample using processing aid, the processing aid selected to produce the sample was Dynamar FX5922 commercially available from 3M.
- Bar 3 is a comparative sample using processing aid, the processing aid selected to produce the sample was behenamide. The behenamide (CAS number: 3061-75-4) was commercially available from CRODA under the commercial name Crodamide BR.
- 20 - Bar 4 is an inventive sample using polyethylene glycol (PEG). The PEG selected had an Mw of 4000 g/mol (CAS number: 25322-68-3) and is commercially available from ALFA AESAR.
- 25 - In Bars 5 to 7, the additive used was a mixture of Polyethylene Glycol (PEG) and behenamide at different ratios. The PEG selected had an Mw of 4000 g/mol (CAS number: 25322-68-3) and is commercially available from ALFA AESAR. The behenamide (CAS number: 3061-75-4) was commercially available from CRODA under the commercial name Crodamide BR.

30 Table 4 – Properties of the bars produced

	Bar 1	Bar 2	Bar 3	Bar 4	Bar 5	Bar 6	Bar 7
Masterbatch	M1a	M1a	M1a	M1a	M1a	M1a	M1a
Masterbatch (wt%)	20	20	20	20	20	20	20
PE1 (wt%)	80	79.4	79.7	79.7	79.4	79.4	79.4

PE1 MI2 (g/10 min)	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Dynamar FX5922 (wt%)	-	0.6	-	-	-	-	-
PEG 4000 (wt%)	-	-	-	0.3	0.3	0.4	0.5
Behenamide (wt%)	-	-	0.3	-	0.3	0.2	0.1
CNT (wt%) ⁽²⁾	2	2	2	2	2	2	2
Screw speed (RPM)	120	120	120	120	120	120	120
barrel temperature (°C)	250	250	250	250	250	250	250
Surface resistance ⁽¹⁾ of the bar ρ_s (Ohm)	1×10^{12}	1×10^7	1×10^{12}	1×10^6	1×10^6	1×10^5	1×10^8

⁽¹⁾ Surface resistance was determined at 20 °C according to IEC 61340-4-1 with an SRM110 meter.

⁽²⁾ The CNTs are originated from the masterbatch.

- 5 From the results, it can be seen a clear influence of the addition of a small quantity of PEG of low molecular weight on the surface resistance, as compared to the other additives tested on bars 1 to 3. The additive mixture between PEG and processing aids provides also good results as far as the content of PEG is below the threshold of 0.5 wt%.

10 The results showed that the ratio of PEG/behenamide in the additive mixture has also an influence on the surface resistance achieved on the bars. An improvement, compared to the reference bar produced with processing aids, is obtained with an additive composition comprising 2/3 PEG and 1/3 behenamide.

15 It is to be noted that Dynamar FX5922 is an additive blend comprising from 60 to 70 wt% of polyethylene oxide (PEO) and from 25 to 35 wt% of vinylidene fluoride-hexafluoropropylene polymer.

20 PEG and PEO are both polyoxyethylenes differing from their molecular weight. Indeed, PEG refers to oligomers and polymers with a molecular weight below 20,000 g/mol, whereas PEO to polymers with a molecular weight above 20,000 g/mol. Comparison between bar 2 and bar 4 shows the improvement in using polyoxyethylenes having a molecular weight below 20,000 g/mol compared to polyoxyethylenes having a molecular weight above 20,000 g/mol as additives in the composite material.

The composite material of the inventive samples can be used in the inner external layer of the conductive multilayered pipe according to the invention.

Example 5: Production of bars - influence of the presence of PEG in the additive composition and of the CNT content

Further tests were conducted with Masterbatch M1a. The masterbatch M1a was dry blended with a first polyethylene resin PE1 and extruded to form a bar. Extrusion trials were conducted on Gottfert single-screw extruder with a rectangular die of 50x20 mm. The Gottfert single-screw extruder had a screw diameter = 30 mm, and a length/diameter ratio (L/D ratio) of 35. In all cases, the barrel temperature was 250 °C, the screw speed was 120 rpm.

The first polyethylene resin used was polyethylene PE1 commercially available from TOTAL® under the tradename XRT 70. PE1 has an MI5 of 0.7 g/10 min as measured according to ISO 1133 (190 °C- 5kg), a density of 0.949 g/cm³ (ISO 1183), an HLMI of 12 g/10 min as measured according to ISO 1133 (190 °C- 21.6 kg).

The following samples have been tested, and results are reported in the below table 5:

- Bar 8 is a comparative sample with a CNT content of 2.0 wt%, the processing aid selected was Viton Z100 commercially available from the Chemours Company.
- Bar 9 is a comparative sample with a CNT content of 2.5 wt%, the processing aid selected was Viton Z100 commercially available from the Chemours Company.
- Bar 10 is a comparative sample with a CNT content of 2.0 wt%, the processing aid was a blend of PEO and behenamide. The PEO was POLYOX™ WSR-301 (molecular weight 4,000,000 g/mol) commercially available from Dow®. The behenamide (CAS number: 3061-75-4) was commercially available from CRODA under the commercial name Crodamide BR.
- Bar 11 is a comparative sample with a CNT content of 2.5 wt%, the processing aid was a blend of PEO and behenamide. The PEO was POLYOX™ WSR-301 (molecular weight Mw 4,000,000 g/mol) commercially available from Dow®. The behenamide (CAS number: 3061-75-4) was commercially available from CRODA under the commercial name Crodamide BR.
- Bar 12 (Bar 6 was repeated) is an inventive sample with a CNT content of 2.0 wt%, the processing aid was a blend of PEG and behenamide. The PEG selected had an Mw of 4000 g/mol (CAS number: 25322-68-3) and is commercially available from ALFA AESAR. The behenamide (CAS number: 3061-75-4) is commercially available from CRODA under the commercial name Crodamide BR.
- Bar 13 is an inventive sample with a CNT content of 2.0 wt%, the processing aid was a blend of PEG and Ethylene-bis-stearamide (EBS). The PEG selected had an Mw of 4000 g/mol (CAS number: 25322-68-3) and is commercially available from ALFA

AESAR. The EBS (CAS number: 110-30-5) is commercially available from CRODA under the commercial name Crodamide EBS.

Table 5 – Properties of the bars produced

	Bar 8	Bar 9	Bar 10	Bar 11	Bar 12	Bar 13
Masterbatch	M1a	M1a	M1a	M1a	M1a	M1a
Masterbatch (wt%)	20	25	20	25	20	20
PE1 (wt%)	79.4	74.4	79.4	74.4	79.4	79.4
PE1 MI2 (g/10 min)	0.3	0.3	0.3	0.3	0.3	0.3
Viton Z100 (%wt)	0.6	0.6	-	-	-	-
POLYOX™ WSR-301 (%wt)	-	-	0.4	0.4	-	-
PEG (%wt)	-	-	-	-	0.4	0.4
Behenamide (%wt)	-	-	0.2	0.2	0.2	-
EBS (%wt)	-	-	-	-	-	0.2
Eurucamide (%wt)	-	-	-	-	-	-
CNT (wt%) ⁽²⁾	2	2.5	2	2.5	2	2
Screw speed (RPM)	120	120	120	120	120	120
barrel temperature (°C)	250	250	250	250	250	250
Surface resistance ⁽¹⁾ of the bar ρ_s (Ohm)	1×10^9	1×10^7	1×10^{12}	1×10^{11}	1×10^5	1×10^6

⁽¹⁾ Surface resistance was determined at 20 °C according to IEC 61340-4-1 with an SRM110 meter.

⁽²⁾ The CNTs are originated from the masterbatch.

It is to be noted that Ziton 100 is an additive blend comprising less than 50 wt% of polyethylene oxide (PEO) and more than 5 wt% of vinylidene fluoride-hexafluoropropylene polymer.

The inventive composite material can be used to produce the inner external layer of the conductive multilayered pipe according to the invention.

Example 6: Production of pipes

Samples of pipes have been produced with masterbatch M1. Two different lots of masterbatch were used, M1a and M1b. Masterbatch M1a is the same that was used in examples 1 to 5.

Masterbatch M1b showed slightly lower properties than M1a. Thus, to compensate, the content of CNT in the composite material has been increased from 2 to 2.5 wt%.

The masterbatches M1a and M1b were dry blended with a first polyethylene resin PE1 and extruded to form a pipe. The first polyethylene resin used was polyethylene PE1 with an MI5 of 0.3 g/10 min as measured according to ISO 1133 (190 °C- 5kg), a density of 0.949 g/cm³ (ISO 1183), a HLMI of 12 g/10 min as measured according to ISO 1133 (190 °C- 21.6 kg). In all cases, the temperature at the outlet was 235 °C, the screw speed was 40 rpm, except for pipe 5. The results are provided in table 6.

Pipes 3, 7 and 8 were devoid of polyethylene glycol. Pipes 4 to 6 comprise polyethylene glycol:

- Pipe 3 is a comparative sample using processing aids, the processing aid selected to produce the sample was Dynamar FX5922 commercially available from 3M.
- In pipes 4 to 8, the additive used was a mixture of polyethylene glycol (PEG) and behenamide. The PEG selected had an Mw of 4000 g/mol (CAS number: 25322-68-3) and is commercially available from ALFA AESAR. The behenamide (CAS number: 3061-75-4) was commercially available from CRODA under the commercial name Crodamide BR.
- Pipe 9 is a comparative sample using processing aids, the processing aid selected to produce the sample was Incroslip Q commercially available from Croda.
- Pipe 10 is a comparative sample using processing aids, the processing aid selected to produce the sample was glycerol monostearate (GMS) (CAS number: 123-94-4).

Table 6 – Properties of the pipes produced

	Pipe 3	Pipe 4	Pipe 5	Pipe 6	Pipe 7	Pipe 8	Pipe 9	Pipe 10
Masterbatch	M1a	M1a	M1b	M1b	M1b	M1b	M1b	M1b
Masterbatch (wt%)	20	20	25	25	25	27,5	25	25
PE1 (wt%)	79.5	79.4	74.4	74.4	74.4	71.9	74.4	74.4
PE1 MI2 (g/10 min)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Dynamar FX5922 (wt%)	0.5	-	-	-	-	-	-	-
PEG 4000 (wt%)	-	0.4	0.4	0.4	0.4	0.4	-	-
Behenamide (wt%)	-	0.2	0.2	0.2	0.2	0.2	-	-
Incroslip Q (wt%)	-	-	-	-	-	-	0.60	-
GMS (wt%)	-	-	-	-	-	-	-	0.60
CNT (wt%) ⁽²⁾	2	2	2.5	2.5	2.5	2.75	2.5	2.5
Screw speed (RPM)	40	40	20	40	40	40	40	40

Draw rate (m/min)	1.5	1.5	1	1.4	1.8	1.2	2.4	1.8
barrel temperature (°C)	235	235	235	235	235	235	235	235
Surface resistance (⁽¹⁾ of the pipe ρ_s (Ohm)	1×10^{11}	1×10^6	1×10^{12}	1×10^{12}	1×10^6	1×10^6	1×10^{12}	1×10^{10}

(⁽¹⁾) Surface resistance was determined at 20 °C according to IEC 61340-4-1 with an SRM110 meter.

(⁽²⁾) The CNTs are originated from the masterbatch.

From the results, it can be seen that the addition of PEG allows to achieve a surface resistance of 1.10^6 Ohm on pipes, with a CNT content below 3 wt%. Pipes 5 and 6 are comparative and produced with the masterbatch M1b. The results showed that initial failure to obtain the targeted resistance properties may be solved by adapting the processing conditions (screw speed and draw rate) or by increasing the CNT content.

Example 7: Production of bars – composite material for the external layer

Further tests were conducted with Masterbatch M1a. The masterbatch M1a was dry blended with second polyethylene resins PE2 and PE2b and extruded to form a bar. Extrusion trials were conducted on Gottfert single-screw extruder with a rectangular die of 50x20 mm. The Gottfert single-screw extruder had a screw diameter = 30 mm, and a length/diameter ratio (L/D ratio) of 35. In all cases, the barrel temperature was 250 °C, the screw speed was 120 rpm.

PE2a commercially available from TOTAL® under the tradename M3581. PE2a has an MI2 of 8.0 g/10 min as measured according to ISO 1133 (190 °C- 2.16 kg), a density of 0.934 g/cm³ (ISO 1183).

PE2b commercially available from TOTAL® under the tradename M4040. PE2b has an MI5 of 4.0 g/10 min as measured according to ISO 1133 (190 °C- 2.16 kg), a density of 0.940 g/cm³ (ISO 1183).

The following samples have been tested and results are reported in the below tables 7a and 7b.

Table 7a – Properties of the bars produced

	Bar 15	Bar 16	Bar 17
Masterbatch	M1a	M1a	M1a
Masterbatch (wt%)	15	10	7

PE2a (wt%)	85	90	93
PE2a MI2 (g/10 min)	6	6	6
CNT (wt%) ⁽²⁾	1,5	1	0,7
Screw speed (RPM)	120	120	120
barrel temperature (°C)	190	190	190
Surface resistance of the bar ρ_s (Ohm)	1×10^4	1×10^5	1×10^6

⁽¹⁾ Surface resistance was determined at 20 °C according to IEC 61340-4-1 with an SRM110 meter.

⁽²⁾ The CNTs are originated from the masterbatch.

Table 7b – Properties of the bars produced

	Bar 18	Bar 19	Bar 20
Masterbatch	M1a	M1a	M1a
Masterbatch (wt%)	15	10	7
PE2b (wt%)	85	90	93
PE2b MI2 (g/10 min)	4	4	4
CNT (wt%) ⁽²⁾	1,5	1	0,7
Screw speed (RPM)	120	120	120
barrel temperature (°C)	190	190	190
Surface resistance of the bar ρ_s (Ohm)	1×10^5	1×10^5	1×10^7

⁽¹⁾ Surface resistance was determined at 20 °C according to IEC 61340-4-1 with an SRM110 meter.

⁽²⁾ The CNTs are originated from the masterbatch.

From the results, it is possible to see again the influence of the viscosity of the polyethylene resin on the electrical properties. It can be also seen that it is possible to achieve a surface resistance of 1×10^6 Ohms with a content of CNT being less than 1 wt% (see bar 17). Thus, lower carbon particles content is needed in the second composite material as compared to the first composite material.

CLAIMS

1. Conductive multilayered pipe comprising an outer external layer, at least one internal layer and an inner external layer, wherein the inner external layer and the at least one internal layer comprise a polyethylene resin having a melt index MI2 of at most 0.50 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg; the multilayered pipe being characterized in that the outer external layer is made from a second composite material comprising:
- from 50 to 99 wt% of a second polyethylene resin as based on the total weight of the said second composite material, wherein the second polyethylene resin has a melt index MI2 ranging from 0.8 to 50.0 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg; and
 - from 0.2 to 10.0 wt% of carbon particles as based on the total weight of the said second composite material as determined according to ISO 11358 selected from carbon black, nanographenes, carbon nanotubes or any combination thereof.
2. The conductive multilayered pipe according to claim 1, characterized in that:
- a) the inner external layer is made from a first composite material comprising:
 - from 50 to 99 wt% of a first polyethylene resin as based on the total weight of the said first composite material, wherein the first polyethylene resin has a melt index MI2 of at most 0.50 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg, and
 - from 0.2 to 20.0 wt% of carbon particles as based on the total weight of the said first composite material as determined according to ISO 11358 selected from carbon black, nanographenes, carbon nanotubes or any combination thereof;
 - b) at least one internal layer comprises a third polyethylene resin having a melt index MI2 of at most 0.50 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg;
- with preference, the first polyethylene resin and the third polyethylene resin are the same.
3. The conductive multilayered pipe according to claim 1 or 2, characterized in that the inner external layer and/or the outer external layer have a surface resistance of at most $5 \cdot 10^6$ Ohm, preferably of at most $1 \cdot 10^6$ Ohm as measured according to IEC 61340-4-1 with an SRM110 meter.

4. The conductive multilayered pipe according to any one of claim 1 to 3, the inner external layer being made from a first composite material, the pipe being characterized in that:
- the carbon particles are carbon nanotubes, and in that the first composite material and/or the second composite material comprise from 0.2 to 5.0 wt% of carbon nanotubes as based on the total weight of said composite material as determined according to ISO 11358, preferably the first composite material and/or the second composite material comprise from 0.5 to 4.8 wt% of carbon particles as based on the total weight of said composite material; or
 - the carbon particles are nanographenes, and in that the first composite material and/or the second composite material comprise from 5.0 to 10.0 wt% of carbon nanographenes as based on the total weight of said composite material as determined according to ISO 11358, preferably the first composite material and/or the second composite material comprise from 6.0 to 9.0 wt% of carbon particles as based on the total weight of said composite material.
5. The conductive multilayered pipe according to claim 4, the first composite material of the inner external layer; further comprises from 0.10 to 0.48 wt% of polyethylene glycol as based on the total weight of the composite material, and in that said polyethylene glycol is selected to have a weight average molecular weight M_w of at most 20,000 g/mol, preferably of at most 10,000 g/mol.
6. The conductive multilayered pipe according to claim 4 or 5, characterized in that the first composite material of the inner external layer; further comprises from 0.01 to 5.0 wt% of one or more processing aids wherein the one or more processing aids are selected from fluoroelastomers, waxes, tristearin, zinc stearate, calcium stearate, magnesium stearate, erucyl amide, oleic acid amide, ethylene-acrylic acid copolymer, ethylene vinyl acetate copolymer, cetyl trimethyl ammonium bromide, polyethylene oxide, polyethylene oxide, polysiloxanes, oleamide, stearamide, behenamide, oleyl palmitamide, ethylene bis-oleamide, ethylene bis(stearamide) (EBS) and any mixture thereof.
7. The conductive multilayered pipe according to claim 5 and 6, characterized in that the first composite material of the inner external layer comprises polyethylene glycol and one or more processing aids; wherein the polyethylene glycol and the one or more processing aids form an additive mixture, and further wherein the content of polyethylene glycol in the additive mixture is ranging from 50 wt% to 99 wt% as based

on the total weight of the additive mixture, more preferably from 60 wt% to 90 wt%, more preferably from 65 wt% to 85 wt%.

8. The conductive multilayered pipe according to any one of claims 1 to 7, characterized in that the first and/or the third polyethylene resins have a melt index MI2 of less than 0.40 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg, and/or an HLMI of at most 60 g/10 min as determined according to ISO 1133 at 190 °C under a load of 21.6 kg, preferably of at most 50 g/10 min.

9. The conductive multilayered pipe according to any one of claims 1 to 8, characterized in that the second polyethylene resin has a melt index MI2 of at least 1.0 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg, and/or has a melt index MI2 of at most 20 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg, with preference of at most 15 g/10 min.

10. The conductive multilayered pipe according to any one of claims 1 to 9, characterized in that the multilayered conductive pipe further comprises an internal steel wire layer, with preference said internal steel wire layer is between two internal layers made from the third polyethylene resin.

11. The conductive multilayered pipe according to any one of claims 1 to 10, characterized in that the outer external layer has a thickness ranging from 5 to 25 % based on the total thickness of all the layers forming the conductive multilayered pipe, with preference ranging from 10 to 20 %.

12. The conductive multilayered pipe according to any one of claims 2 to 11, characterized in that the content in weight percent of carbon particles of the second composite material as based on the total weight of the second composite material, is lower than the content in weight percent of carbon particles of the first composite material as based on the total weight of the first composite material, the content of carbon particle being determined according to ISO 11358.

13. Process to produce a conductive multilayered pipe as defined according to any one of claims 1 to 12, wherein the process comprises the following steps:

- a. providing a first composite material comprising:
 - from 50 to 99 wt% of a first polyethylene resin as based on the total weight of the said first composite material, wherein the first polyethylene resin has a

melt index MI2 of at most 0.50 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg, and

- from 0.2 to 20.0 wt% of carbon particles as based on the total weight of said composite material as determined according to ISO 11358 selected from carbon black, nanographenes, carbon nanotubes or any combination thereof;
- b. providing a third polyethylene resin having a melt index MI2 of at most 0.50 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg;
- c. coextruding or co-injecting the first composite material and the third polyethylene resin to form a conductive multilayered pipe wherein the first composite material forms the inner external layer of the pipe;
- d. providing a second composite material comprising:
 - from 50 to 99 wt% of a second polyethylene resin as based on the total weight of the said second composite material, wherein the second polyethylene resin has a melt index MI2 ranging from 0.8 to 50.0 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg; and
 - from 0.2 to 10.0 wt% of carbon particles as based on the total weight of the said second composite material as determined according to ISO 11358 selected from carbon black, nanographenes, carbon nanotubes or any combination thereof;
- e. covering the multilayered pipe obtained in step c) with a layer of the second composite material in order to obtain a conductive multilayered pipe wherein the first composite material forms the inner external layer of the pipe, the second composite material forms the outer external layer of the pipe, and the third polyethylene resin forms at least one internal layer in between the inner external layer and the outer external layer of the pipe.

14. The process according to claim 13, characterised in that the carbon particles are selected from carbon nanotubes, nanographenes and mixture thereof, and the first composite material and/or the second composite material are produced by blending the first polyethylene resin and/or the second polyethylene resin respectively, with a masterbatch comprising the blend of a fourth polyethylene resin and at least 5 wt% of carbon particles as based on the total weight of said masterbatch as determined according to ISO 11358; the masterbatch having an HLMI of at least 5 g/10 min and of at most 500 g/10 min as determined according to ISO 1133 at 190 °C under a load of 21.6 kg.

15. Use of a second composite material comprising:

- from 50 to 99 wt% of a second polyethylene resin as based on the total weight of the said second composite material, wherein the second polyethylene resin has a melt index MI2 ranging from 0.8 to 50.0 g/10 min as determined according to ISO 1133 at 190 °C under a load of 2.16 kg; and

- 5
- from 0.2 to 10.0 wt% of carbon particles as based on the total weight of the said second composite material as determined according to ISO 11358 selected from carbon black, nanographenes, carbon nanotubes or any combination thereof;

in the outer external layer of a conductive multilayered pipe according to any one of claims 1 to 12 and/or in a process according to claim 13 or 14.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/077163

A. CLASSIFICATION OF SUBJECT MATTER
INV. B32B27/20 B32B27/32 B32B1/08 F16L9/12 B32B27/08
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B32B F16L

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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DATABASE WPI Week 201733 Thomson Scientific, London, GB; AN 2017-209941 XP002778829, -& CN 106 523 810 A (OIL RES INST GEN LOGISTIC DEPT PLA) 22 March 2017 (2017-03-22) claim 7; examples -----	1-15
Y	WO 2016/142545 A1 (TOTAL RES & TECHNOLOGY FELUY [BE]) 15 September 2016 (2016-09-15) claims 1, 5, 6,8,9, 10-13, 14 -----	1-15
Y	WO 2016/142544 A1 (TOTAL RES & TECHNOLOGY FELUY [BE]) 15 September 2016 (2016-09-15) claims ----- -/-	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Derz, Thomas

INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2015/162212 A1 (TOTAL RES & TECHNOLOGY FELUY [BE]) 29 October 2015 (2015-10-29) claims -----	1-15
Y	DE 44 33 626 A1 (POLI FILM VERWALTUNGS GMBH [DE]) 31 August 1995 (1995-08-31) column 1, line 25 - column 2, line 39; claims 1-3 -----	1-15
A	US 2005/170121 A1 (BONNET ANTHONY [FR] ET AL) 4 August 2005 (2005-08-04) paragraphs [0023] - [0024], [0069], [0072]; claim 19; example 3 -----	1-15
A	US 2004/191440 A1 (FUNAKI ATSUSHI [JP] ET AL) 30 September 2004 (2004-09-30) paragraph [0122] - paragraphs [0106], [0033] - [0034], [0073]; claims 1,8-11 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2018/077163

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
CN 106523810	A	22-03-2017	NONE	
WO 2016142545	A1	15-09-2016	BR 112017019477 A2 CA 2976851 A1 CN 107428951 A EP 3268415 A1 JP 2018513230 A KR 20170127528 A PH 12017501599 A1 SG 11201707174Y A US 2018273703 A1 WO 2016142545 A1	15-05-2018 15-09-2016 01-12-2017 17-01-2018 24-05-2018 21-11-2017 12-02-2018 30-10-2017 27-09-2018 15-09-2016
WO 2016142544	A1	15-09-2016	BR 112017019417 A2 CA 2976850 A1 CN 107428952 A EP 3268416 A1 JP 2018507940 A KR 20170129178 A PH 12017501600 A1 SG 11201707175X A US 2018044485 A1 WO 2016142544 A1	02-05-2018 15-09-2016 01-12-2017 17-01-2018 22-03-2018 24-11-2017 12-02-2018 30-10-2017 15-02-2018 15-09-2016
WO 2015162212	A1	29-10-2015	AU 2015250852 A1 BR 112016024693 A2 CA 2946458 A1 CN 106459289 A EA 201691948 A1 EP 3077714 A1 JP 2017519946 A KR 20160147888 A PH 12016502069 A1 SG 11201608689S A US 2017058063 A1 WO 2015162212 A1	17-11-2016 15-08-2017 29-10-2015 22-02-2017 28-02-2017 12-10-2016 20-07-2017 23-12-2016 09-01-2017 29-11-2016 02-03-2017 29-10-2015
DE 4433626	A1	31-08-1995	NONE	
US 2005170121	A1	04-08-2005	AT 382469 T CA 2487080 A1 CN 1623764 A DE 602004011101 T2 EP 1537989 A1 EP 1690673 A2 ES 2299136 T3 ES 2529672 T3 JP 4224857 B2 JP 2005207582 A KR 20050053026 A KR 20070032970 A MY 139176 A TW 1273087 B US 2005170121 A1	15-01-2008 01-06-2005 08-06-2005 02-01-2009 08-06-2005 16-08-2006 16-05-2008 24-02-2015 18-02-2009 04-08-2005 07-06-2005 23-03-2007 28-08-2009 11-02-2007 04-08-2005
US 2004191440	A1	30-09-2004	BR 0302454 A CN 1534228 A EP 1470910 A1	05-04-2005 06-10-2004 27-10-2004

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		ES 2312690 T3	01-03-2009
		JP 4619624 B2	26-01-2011
		JP 2004301247 A	28-10-2004
		US 2004191440 A1	30-09-2004
