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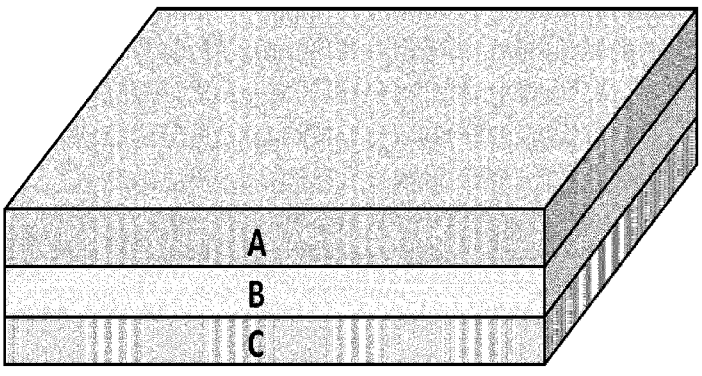

FIGURE 1

(57) Abstract: Multilayer polyethylene (PE) geomembrane liners for unconventional thermal conditions and methods of making them are disclosed. The liners have N co-extruded stacked layers, each layer being made from a PE masterbatch composition comprising a given amount of PE resin and additives, and of a PE metallocene based resin free of acid neutralizer compounds. Also disclosed are customized multilayer PE geomembrane liners of N co-extruded stacked layers, each layer being made from a PE masterbatch comprising a specific additive providing specific behaviour property to the layer; wherein at least two of the N layers comprise a different specific additive in order to provide a geomembrane liner having at least two layers with different behaviour property. The liners have a water-bath aging performance for about 6 months immersion at about 80°C per ASTM D5322 - modified for water, such that about 80% of high pressure OIT value retained per ASTM D5885.

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MULTILAYER POLYETHYLENE GEOMEMBRANE LINERS

FIELD OF THE INVENTION

[0001] The present invention generally relates to geomembrane liners, and more particularly to multilayer polyethylene (PE) geomembrane liners, each layer being made from a specific masterbatch, and to be used under unconventional conditions or applications where regular PE grades liners may not withstand, such as high temperatures.

BACKGROUND OF THE INVENTION

[0002] Due to their ability to minimize advective flow and provide an excellent diffusive barrier to inorganic contaminants, high-density polyethylene (HDPE) geomembranes are extensively used as a part of composite base liner systems in modern landfills. These liner systems often comprise (from top to bottom) a gravel leachate collection layer, a geotextile protection layer, a 1.5 or 2 mm thick HDPE geomembrane, and either a geosynthetic clay liner (GCL) or a compacted clay liner. HDPE geomembranes have been shown to have good chemical resistance to wide range of contaminants found in landfill leachate constituents. The long-term behaviour of geomembranes in landfill base liners is initially controlled by the rate of extraction of antioxidants. This process involves the dissolution or chemical reaction of antioxidants at the surface of the geomembrane and their diffusion from the core structure to the surface due to concentration gradient. The loss of antioxidants leaves the geomembrane vulnerable to the second principal degradation mechanism of oxidative degradation (Rowe R. K. et al.; Journal of geotechnical and geoenvironmental engineering (ASCE) 1090-0241 (2008) 134:1 (68)).

[0003] Multilayered coextruded geomembranes have been developed. U.S. patent no. 5,221,570 (Gokcen et al.) discloses geomembranes The geomembrane consists of three or more polymeric layers with outside layers consisting of high density polyethylene at least 0.930 g/cm^3 and a very low density polyethylene inner core layer less than or equal to 0.920 g/cm^3, providing geomembranes exhibiting enhanced flexibility and ease of handling and welding that is superior to both high density polyethylene and low density polyethylene.

[0004] High temperatures accelerate the degradation of the liners. In U.S. patent application no. US 2014/0364545 A1 (Prachoomdang et al.), a specific high temperature geomembrane liner and masterbatch composition is disclosed. The masterbatch composition disclosed by Prachoomdang et al. is made of very specific additives well known in the art such as: antioxidants (Irganox ™ 1330; Irganox™ 1010; Irgafos™ 168), UV stabilizers (Hindered amine), acid neutralizer (hydrotalcite) and carbon black. These additives are well known for the making of pipes made of polyolefine and resistant to degradation (see for instance PCT application no. WO 2008/040482 by Hastrand et al.); or other polyolefin articles such as geomembranes (see U.S. patent no. 6,774,170 B2 by Webster).

[0005] A first shortcoming of the geomembranes of the prior art is the use of acid neutralizers added to the PE formulation due to the fact that that conventional PE resins comprise some acid residues of the synthesis process such as in Zn-Na catalysts. It has been discovered that by using new generation metallocene catalyzed polyethylene, acid residues are absent and there is not a harmful catalyst residue in the final resin, so there is no need to add an extra additive to neutralize that. New PE metalocene based resins have then been developed to produce new generation of multilayered geomembrane liners.

[0006] Another shortcoming of the prior art is generally mitigated by the use of various unnecessary additives which will increase the cost of the products.

[0007] Another shortcoming is the use of all of the additives in the whole body of the geomembrane because of its single layer structure. In addition in some exposed conditions for this materials, since the contacting liquid or solid will have high temperatures, the presence of an additional radiation heat source i.e. sunlight is not favorable. To diminish the effect of sunlight, application of reflective pigments is preferred.

SUMMARY OF THE INVENTION

[0008] In this invention, a new multilayer structure has been designed to address several problems known in the art such as fast degradation of the membrane under unconventional conditions or applications where regular monolayer PE grades liners cannot withstand, such as high temperatures up to 100 °C.

[0009] The invention is first directed to multilayer polyethylene (PE) geomembrane liner comprising a number N of co-extruded stacked layers with N ≥ 2, preferably with N≥ 3, each layer being made from:

a given amount of a PE masterbatch composition comprising a PE resin and additives, and

a given amount of a PE metallocene based resin; the PE metallocene based resin being free of acid neutralizer compounds.

[0010] The invention is also directed to a method for the making of a multilayer polyethylene (PE) geomembrane liner, the liner comprising a number N of co-extruded stacked layers with N ≥ 2; preferably with N≥ 3, the method comprising the steps of:

a) mixing a given amount of a first PE masterbatch composition of a PE resin and additives, the PE masterbatch composition being free of acid neutralizer compounds with a first PERT metallocene based resin grade to form a first PE formulation;

b) repeating step a) (N-1) times to form (N-1) PE formulations; and

c) co-extruding the N PE formulations formed in steps a) and b) to form the multilayer polyethylene (PE) geomembrane liner.

[0011] The invention is further directed to customized multilayer polyethylene (PE) geomembrane liner comprising a number N of co-extruded stacked layers with N ≥ 2, preferably with N≥ 3, each layer being made from:

a given amount of a PE masterbatch composition comprising a PE resin and additives, and

a given amount of a PE metallocene based resin; the PE metallocene based resin being free of acid neutralizer compounds;

wherein the PE masterbatch composition comprises at least one specific additive providing at least one specific behaviour property to the layer; wherein at least two of the N layers comprise a different specific additive in order to provide a geomembrane liner having at least two layers with different behaviour property.

[0012] The invention is also directed to a method for the making of a customized multilayer polyethylene (PE) geomembrane liner, the liner comprising a number N of co-extruded stacked layers with $N \geq 2$, the method comprising the steps of:

a) mixing a given amount of a PE masterbatch composition comprising a PE resin and additives, with a given amount of polyethylene of raised temperature (PERT) metallocene based resin to form a PE formulation;

b) repeating step a) (N-1) times to form (N-1) PE formulations; and

c) co-extruding the N PE formulations formed in steps a) and b) to form the multilayer polyethylene (PE) geomembrane liner;

wherein at least one of the N PE formulations comprise at least one specific additive presenting a nature and/or a concentration selected in function of a final utility of the geomembrane liner in order to customize the geomembrane liner.

[0013] The invention is also directed to lined containment system comprising at least one customized multilayer polyethylene (PE) geomembrane liners as defined herein or made using the methods as defined herein.

[0014] In accordance with a preferred embodiment, the masterbatch composition disclosed herein can be added to other polyolefin products to get high resistance for aging in oven and liquid immersion.

[0015] The geomembrane liners produced comprising of the above mentioned ingredients can be used but not limited to the unconventional applications such as bioreactors landfills, hot liquid storage, coal seam gas brine ponds, geothermal waste water ponds, or the like.

[0016] The method disclosed herein may be a customized or modular method for providing specific liners in accordance with specific requirements. The adaptable structure of the multilayer liner disclosed herein will allow the manufacturer to design targeted formulations at each layer. For instance, in a 3 layer structure where the outer layers counts for 5% of the thickness, the layer which is not in contact with heat source does not necessarily need to be boosted by high performance additives and regular additives will fulfill the requirements. Also, as an example, the same structure will allow incorporation of reflective pigments on the

layer which fronts onto sunlight and still keep the cost reasonable enough. Other configurations can be provided without departing from the invention as disclosed herein.

[0017] Most of the aging tests introduced so far for the geomembranes are aging in hot air circulating oven. But most of the time, the heat source in contact with the liner is in liquid form. The oxidation behaviour of the geomembranes in a gas or a liquid medium can be totally different. The antioxidants are shown to deplete faster in liquid medium than in air due to various reasons (see e.g. Sangan H. P. et al., Can. Geotech. J., 39: 1221 – 1230 (2002)). In accordance with a preferred embodiment, the multilayer PE geomembrane liner disclosed herein will retain 80% of its high pressure OIT (ASTM 5885) after 6 months and 80% of its selected mechanical properties (ASTM D638) after 6 months immersion in a liquid bath at 80°C (ASTM 5322 modified).

[0018] Other and further aspects and advantages of the present invention will be better understood upon reading of the illustrative embodiments about to be described and various advantages not referred to herein will occur to one skilled in the art upon employment of the invention in practice.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] The above and other aspects, features and advantages of the invention will become more readily apparent from the following description, reference being made to the accompanying drawings in which:

[0020] Figure 1 is a schematic illustration of a multilayer geomembrane liner in accordance with a preferred embodiment of the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0021] A novel multilayer polyethylene geomembrane liner for unconventional conditions will be described hereinafter. Although the invention is described in terms of specific illustrative embodiments, it is to be understood that the embodiments described herein are by way of example only and that the scope of the invention is not intended to be limited thereby.

[0022] The terminology used herein is in accordance with definitions set out below.

[0023] As used herein % or wt.% means weight % unless otherwise indicated. When used herein % refers to weight % as compared to the total weight percent of the phase or composition that is being discussed.

[0024] By "about", it is meant that the value of weight %, time, pH or temperature can vary within a certain range depending on the margin of error of the method or device used to evaluate such weight %, time, pH or temperature. A margin of error of 10% is generally accepted.

[0025] In accordance with a preferred embodiment a multilayer polyethylene (PE) geomembrane liner (hereafter also named "liner") is disclosed. The liner may comprise at least two adjacent layers, each layer being made from different PE masterbatch composition, each PE masterbatch comprising at least one additive providing at least one behaviour property to the layer. As illustrated on Figure 1, the number of layers may be three, but the invention is not limited to a specific number of layers for the making of the liner.

[0026] The multilayer polyethylene (PE) geomembrane liner comprises a number N of co-extruded stacked layers with $N \geq 2$, more preferably N is equals or superior to 3. Each layer is made from:

a given amount of a PE masterbatch composition comprising a PE resin and additives, and

a given amount of a PE metallocene based resin; the PE metallocene based resin being free of acid neutralizer compounds.

[0027] In accordance with a preferred embodiment, at least one of said additives is selected for providing at least one specific behaviour property to the liner. At least two of the N layers may comprise additives different in nature and/or concentration in order to provide a customized geomembrane liner having at least two layers with different behaviour properties. Examples of specific additives and behaviours are given hereinafter.

[0028] In accordance with a preferred embodiment, each layer of the multilayer polyethylene (PE) geomembrane liner may comprise:

- from 5% to 15% of the PE masterbatch composition comprising:
  - from about 50 to about 90 wt.% of a PE resin,
  - from about 0.1 to about 4 wt.% of a phenolic antioxidant, and
  - from about 0.05 to about 3 wt.% of a secondary phosphite antioxidant;
  - from about 0 to 5 wt.% of at least one UV stabilizer, and
  - up to 50 wt.% of at least one specific additive;

  wherein the percentages by weight add up to 100% and are based on the total weight of the PE masterbatch composition; and
- from about 85 to about 95% of a base resin composition comprising polyethylene of raised temperature (PERT) metallocene based resin or its blend with other PE grades;

wherein the percentages by weight add up to 100% and are based on the total weight of the geomembrane composition.

[0029] In accordance with a preferred embodiment, the PE resin in the PE masterbatch may have a density of about 0.910 to about 0.960 g/cm^3. Also, the PE resin in the PE masterbatch may be selected from the group consisting Linear Low Density PE (LLDPE), Low Density PE (LDPE), Medium Density PE (MDPE) and High Density PE (HDPE), optionally within a metallocene grade category, and optionally in the PERT family. A primary and secondary antioxidants package and some other additives such as carbon black or TiO_2 can be added for process and long term stabilisation.

[0030] In accordance with a preferred embodiment, the main matrix resin used in this invention is polyethylene of raised temperature (PERT) metallocene based resin. Specific molecular characteristics of this category of polyethylene allow them to maintain their mechanical properties at temperatures as high as 100°C.

[0031] In accordance with a preferred embodiment, geomembrane production out of PE resin is disclosed. The ingredients of each layer of the liner (Fig. 1) may include a master batch of different additives plus the discussed base PERT resin where the master batch is added to the polyethylene resin in an extrusion process.

[0032] In accordance with a preferred embodiment, the main resin used for the making of liners should be a polyethylene of raised temperature (PERT) categorised resin such as Daelim XP9000™ (Daelim. South Korea), LG SP980™ (LG Chemicals, South Korea), etc. Though in certain conditions and in certain layers a blend of regular PE resin can also be incorporated. Obviously the grade content and the layer in which this blend can be used should be determined in a way that it does not deteriorate the mechanical and thermal properties mentioned of the final product.

[0033] In accordance with a preferred embodiment, a stabilizer package may include any combination of one or more of below ingredients:

1) UV stabilizers functioning as free radical scavengers in Hindered Amine Light Stabilizer ("HALS") family (e.g., Chimmasorb 2020™ (BASF, Germany));

2) antioxidants functioning as inhibitors of thermo-oxidative degradation at a broad temperature range for long-term thermal stabilizers in hindered phenolic family (e.g., Irganox 1010™ (BASF, Germany), which is a sterically hindered phenolic antioxidant);

3) process or thermal stabilizers functioning as inhibitors of thermo-oxidative degradation during extrusion process in comprising a phosphite processing stabiliser (e.g., Irgafos 168™ (BASF, Germany)); and/or

4) Carbon black as UV absorber where the Carbon black is a furnace carbon black with particle size equal or below N660; or

5) TiO_2 with particle size of 100 nm and more.

[0034] In accordance with a preferred embodiment, all of the layers comprise at least one of the above mentioned additives.

[0035] Including all of the additives in all layers will escalate the final cost and make it overpriced for some certain applications. To address this problem, in accordance with a preferred embodiment, only the most important layers which are in close proximity of the heat source are fortified by high molecular weight HALS and the rest of the layers are only protected by conventional antioxidants such as Irganox B225™ which is a blend of Irganox 1010™ and Irgafos 168™.

[0036] The use of carbon black in exposed conditions will cause increasing the temperature of the liner under sun. The use of TiO_2 in the outer layer will help the liner retain its Physical-thermal-mechanical properties for longer times due to its light reflection properties.

[0037] In accordance with a preferred embodiment, the composition of the final product will be about 5 to about 15 wt.% of masterbatch and about 85 to about 95 wt.% of main matrix PERT material or its blends in each layer based on the total weight of the geomembrane liner.

[0038] In accordance with a preferred embodiment, the PE masterbatch composition is free of hydrotalcite as acid neutralizer compound.

[0039] In accordance with a preferred embodiment, the liner can be laminated or coextruded with a sub-layer, the sub-layer being adapted to be electrically conductive whereby, in use, integrity of the liner is monitored electrically. The sub-layer may be a coating of the liner using carbon black.

[0040] In accordance with a preferred embodiment, it is also disclosed a formulation for preparing a multilayer polyethylene geomembrane for various applications where each layer comprises of a) a master batch; and b) a base polyethylene resin. Said composition comprises:

i) about 5-15% of a masterbatch composition including all or some of the following components:
   a. about 50-90% of a polyethylene resin (LLDPE, MDPE, HDPE, PERT) with a density of 0.910 to 0.960 g/cm^3;
   b. about 0.1 to about 4 wt % of a phenolic antioxidants, wherein said antioxidant may include pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate);
   c. about 0.05 to about 3 wt % of a secondary phosphite antioxidant such as Tris(2,4-ditert-butylphenyl)phosphite;
   d. about 0.05 to about 5 wt% of a UV stabilizer of high molecular weight hindered amines (HALS) family such as 1,6-Hexanediamine, N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-polymer with 2,4,6-trichloro-1,3,5-triazine, reaction products with N-butyl-1-butanamine and N-butyl-2,2,6,6-tetramethyl-4-piperidinamine; and

e. about 20-50 wt % of a Carbon black, wherein the said carbon black is a furnace carbon black; wherein the percentages by weight add up to 100% and are based on the total weight of the master batch composition; and

ii) about 85 to 95% of a base resin composition comprising polyethylene of raised temperature (PERT) base resin or its blend with other PE grades, wherein the percentages by weight add up to 100% and are based on the total weight of the geomembrane composition.

[0041] The geomembrane liners produced comprising of the above mentioned ingredients can be used but not limited to the unconventional applications such as bioreactors landfills, hot liquid storage, coal seam gas brine ponds, geothermal waste water ponds, or the like.

[0042] As aforesaid, the invention is also a method for the making of a multilayer polyethylene (PE) geomembrane liner. The liner comprising a number N of co-extruded stacked layers with $N \geq 2$; preferably $N \geq 3$. The method comprises at least the following steps of:

a) mixing a given amount of a first PE masterbatch composition of a PE resin and additives, the PE masterbatch composition being free of acid neutralizer compounds with a first PERT metallocene based resin grade to form a first PE formulation;

b) repeating step a) (N-1) times to form (N-1) PE formulations; and

c) co-extruding the N PE formulations formed in steps a) and b) to form the multilayer polyethylene (PE) geomembrane liner.

[0043] In accordance with a preferred embodiment, the method may further comprise the step of laminating or coextruding the liner with a sub-layer, the sub-layer being adapted to be electrically conductive whereby, in use, integrity of the liner is monitored electrically. Preferably, the sub-layer may be formed by coating the liner using carbon black. Other coating known in the art can be used.

[0044] Additionally, in accordance with a preferred embodiment, the multilayer geomembrane liners disclosed herein can also be textured. The most widely spread technology to manufacture textured geomembranes involves co-extrusion of the polyethylene in three layers, wherein :

- in the central layer, the polymer is extruded in a similar manner than a smooth geomembrane, which gives the material its key functional properties such as watertightness or low gas permeability;

- on the outer layers, a mixture of polyethylene and nitrogen is extruded. When this melted mixture comes out of the die, the nitrogen is expulsed out of the polyethylene, making 'bubbles' that will create the texture of the geomembrane as they solidify.

[0045] In accordance with a preferred embodiment, it is thus possible to control the asperity height of the geomembrane – and thus the friction properties – at the time of manufacture by controlling various extrusion parameters such as the percentage of nitrogen in the mixture or the temperature of the polymer / of the air in the vicinity of the die.

[0046] As aforesaid, the present invention also concerns a customized multilayer polyethylene (PE) geomembrane liner. By "customized", it is understood that the final liner will be adapted to the final use which can be dictated by several conditions (geography, weather conditions; nature of the liquids to be retained by the liner, etc).

[0047] The customized multilayer polyethylene (PE) geomembrane liner according to the invention comprises a number N of co-extruded stacked layers with $N \geq 2$. Each layer are made from a given amount of a PE masterbatch composition comprising a PE resin and additives, and a given amount of a PE metallocene based resin; the PE metallocene based resin being free of acid neutralizer compounds. The PE masterbatch composition comprises at least one specific additive providing at least one specific behaviour property to the layer; wherein at least two of the N layers comprise a different specific additive in order to provide a geomembrane liner having at least two layers with different behaviour property.

[0048] A method for the making of a customized multilayer polyethylene (PE) geomembrane liner is also disclosed. The liner comprises a number N of co-extruded stacked layers with $N \geq 2$, and the method comprises at least the following steps of:

a) mixing a given amount of a PE masterbatch composition comprising a PE resin and additives, with a given amount of polyethylene of raised temperature (PERT) metallocene based resin to form a PE formulation;

b) repeating step a) (N-1) times to form (N-1) PE formulations; and

c) co-extruding the N PE formulations formed in steps a) and b) to form the multilayer polyethylene (PE) geomembrane liner;

wherein at least one of the N PE formulations comprise at least one specific additive presenting a nature and/or a concentration selected in function of a final utility of the geomembrane liner in order to customize the geomembrane liner.

[0049] In accordance with a preferred embodiment, $N \geq 3$ and at least two of the N layers comprise different specific additives.

[0050] Apparatus for the mixing and extrusion steps are those known in the art of making co-extruded membranes. It is also understood that the preferred embodiments detailed herein above apply for the customized liner and method for making the same.

[0051] Lined containment systems comprising at least one customized or un-customized multilayer polyethylene (PE) geomembrane liner are also part of the present invention. The different liners are assembled in accordance with techniques known in the art of lined containment systems.

EXAMPLES

[0052] An example of a multilayer geomembrane structure is illustrated on Figure 1, where three different layers identified as layers A, B and C are disclosed, each layers can have different thickness and different formulations. Different ranges of thickness percentages are mentioned in Table 1 below, but the invention cannot be limited to any specific layer thicknesses. Also the total thickness of each multilayer geomembrane liner may vary in function of its use for unconventional applications.

[0053] The geomembrane liners disclosed herein have a water-bath aging performance for 6 months immersion at 80°C per ASTM D5322 (modified) such that 80% of high pressure OIT value retained per ASTM D5885. ASTM D5322 is the standard practice for immersion procedure for evaluating the chemical resistance of geosynthetics to liquids. By "modified", it

is understood that the standard is performed using water instead of chemicals. Details for the Standard ASTM D5322 are available at http://www.astm.org/Standards/D5322.htm, the content of which is incorporated herewith by reference. The geomembrane liners disclosed herein have also a water-bath aging performance for 6 months immersion at 80°C per ASTM D5322 (modified) such that 80% of tensile properties per ASTM D638.

Example 1:

[0054] The ingredients to be used in the three masterbatches (see Table 1) for the geomembrane in Figure 1 are as follow:

TABLE 1

Masterbatch ingredients	**Layer C wt %**	**Layer B wt %**	**Layer A wt %**
PE metallocene grade (LG Lucene™ SP980)	65.75	64.5	64.5
Carbon Black N 550	31.25	31.25	0
TiO_2 (Ti-pure© by Dupont)	0	0	31.25
Irganox™ 1010	1.5	1.5	1.5
Irgafos 168	1.5	1.5	1.5
Chimmasorb 2020	0	1.25	1.25
Thickness (%)	**1-10**	**80-98**	**1-10**

TABLE 2

Geomembrane ingredients	**wt %**
PERT resin (Daelim™ XP9020)	92
Masterbatch formula for each layer	8

[0055] Blending each masterbatch A, B and C of Table 1 with a PERT resin in accordance with the proportions of Table 2 followed by extrusion of the same, will result in a three layer geomembrane according to one example of the present invention.

Example 2: Water immersion testing

[0056] In this test, the geomembrane was prepared according to the masterbatch formulation of Table 1 and the geomembrane composition of Table 2 with Daelim^{TM} XP9020 as the base PERT resin (GMB-U).

[0057] For the purpose of comparison, another commercial geomembrane of the same thickness has been prepared (GMB-R) (regular HD geomembrane of Solmax based on the GRI GM13 standard). Both of these geomembranes were immersed in a water bath at 80 °C (or 176 °F) according to ASTM D 5322 for 180 days. Since the HP_OIT test is an indicator of the protective antioxidants necessary to protect the geomembrane in its service life, the HP-OIT (ASTM D5885-6) of these products were measured before and after this period. Percent retention of this property will show the remaining amount of the antioxidants and light stabiliser additives in the geomembrane (Table 3).

Table 3

Geomembrane	*HPOIT Initial (min)*	*HPOIT After 180 days (min) Aging at water bath at 80°C*	*% Retained*
GMB-U	1100	1045	95
GMB-R	965	625	65%

[0058] In most of the geomembrane applications, the liner is in contact with a liquid phase at various temperatures. Since it is known that the aging phenomenon is different in air and in liquid medium, this test is of more value for real service life calculation of the geomembranes than the regular GRI-GM13 oven aging tests. Today there are some complementary test methods such as EPA 9090 which are designed for testing the compatibility of the liners in

different liquid media. The inventive geomembrane demonstrated better retention in a liquid medium than the conventional geomembranes.

[0059] While illustrative and presently preferred embodiments of the invention have been described in detail hereinabove, it is to be understood that the inventive concepts may be otherwise variously embodied and employed and that the appended claims are intended to be construed to include such variations except insofar as limited by the prior art.

WHAT IS CLAIMED IS:

1. A multilayer polyethylene (PE) geomembrane liner comprising a number N of co-extruded stacked layers with $N \geq 2$, each layer being made from:

a given amount of a PE masterbatch composition comprising a PE resin and additives, and

a given amount of a PE metallocene based resin; the PE metallocene based resin being free of acid neutralizer compounds.

2. The multilayer polyethylene (PE) geomembrane liner of claim 1, wherein $N \geq 3$.

3. The multilayer polyethylene (PE) geomembrane liner of claim 1 or 2, wherein at least one of said additives is selected for providing at least one specific behaviour property to the liner.

4. The multilayer polyethylene (PE) geomembrane liner of claim 3, wherein at least two of the N layers comprise additives different in nature and/or concentration in order to provide a customized geomembrane liner having at least two layers with different behaviour properties.

5. The multilayer polyethylene (PE) geomembrane liner of any one of claims 1 to 4, wherein each layer comprises:

- from 5% to 15% of the PE masterbatch composition comprising:
  - from about 50 to about 90 wt.% of a PE resin,
  - from about 0.1 to about 4 wt.% of a phenolic antioxidant, and
  - from about 0.05 to about 3 wt.% of a secondary phosphite antioxidant.
  - from about 0 to 5 wt.% of at least one UV stabilizer, and
  - up to 50 wt.% of at least one specific additive;

wherein the percentages by weight add up to 100% and are based on the total weight of the PE masterbatch composition; and

- from about 85 to about 95% of a base resin composition comprising polyethylene of raised temperature (PERT) metallocene based resin or its blend with other PE grades;

wherein the percentages by weight add up to 100% and are based on the total weight of the geomembrane composition.

6. The multilayer polyethylene (PE) geomembrane liner of claim 5, wherein the PE resin in the PE masterbatch has a density of about 0.910 to about 0.960 g/cm^3.

7. The multilayer polyethylene (PE) geomembrane liner of claim 5 or 6, wherein the PE resin in the PE masterbatch is selected from the group consisting of Linear Low Density PE (LLDPE), Low Density PE (LDPE), Medium Density PE (MDPE) and High Density PE (HDPE), optionally within a metallocene grade category, and optionally in the PERT family.

8. The multilayer polyethylene (PE) geomembrane liner of any one of claims 5 to 7, wherein the metallocene resin is a Metallocene – Medium Density Polyethylene resin having a density of about 0.941 g/cm^3 according to the test method ASTM D1505, also known as DAELIM^{TM} XP-9020.

9. The multilayer polyethylene (PE) geomembrane liner of any one of claims 5 to 7, wherein the metallocene resin is a Metallocene – Medium Density Polyethylene resin having a density of about 0.938 g/cm^3 according to the test method ASTM D1505, also known as LUCENE^{TM} SP980.

10. The multilayer polyethylene (PE) geomembrane liner of any one of claims 5 to 9, wherein the phenolic antioxidant comprises pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), also known as Irganox 1010™.

11. The multilayer polyethylene (PE) geomembrane liner of any one of claims 5 to 10, wherein the secondary phosphite antioxidant is Tris(2,4-ditert-butylphenyl)phosphite, also known as Irgafos^{TM} 168.

12. The multilayer polyethylene (PE) geomembrane liner of any one of claims 5 to 11, wherein the UV stabilizer is selected from high molecular weight hindered amines (HALS).

13. The multilayer polyethylene (PE) geomembrane liner of claim 12, wherein the HALS is 1,6-hexanediamine, N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-polymer with 2,4,6-trichloro-1,3,5-triazine, reaction products with N-butyl-1-butanamine and N-butyl-2,2,6,6-tetramethyl-4-piperidinamine, also known as Chimmasorb^{TM} 2020.

14. The multilayer polyethylene (PE) geomembrane liner of any one of claims 5 to 13, wherein the at least one specific additive is selected from Carbon black or TiO_2 particles.

15. The multilayer polyethylene (PE) geomembrane liner of claim 14, wherein the carbon black is a furnace carbon black with a particle size equal or below N660.

16. The multilayer polyethylene (PE) geomembrane liner of claim 14 or 15, wherein TiO_2 particle size is about 100 nm and more.

17. The multilayer polyethylene (PE) geomembrane liner of any one of claims 1 to 16, wherein said geomembrane liner has a water-bath aging performance for about 6 months immersion at about 80°C per ASTM D5322 - modified for water, such that about 80% of high pressure oxidative induction time (OIT) value retained per ASTM D5885.

18. The multilayer polyethylene (PE) geomembrane liner of any one of claims 1 to 17, wherein the PE masterbatch composition is free of hydrotalcite as acid neutralizer compound.

19. The multilayer polyethylene (PE) geomembrane liner of any one of claims 1 to 18, wherein the liner is laminated or coextruded with a sub-layer, the sub-layer being adapted to be electrically conductive whereby, in use, integrity of the liner is monitored electrically.

20. The multilayer polyethylene (PE) geomembrane liner of claim 19, wherein the sub-layer is a coating of the liner using carbon black.

21. A method for the making of a multilayer polyethylene (PE) geomembrane liner, the liner comprising a number N of co-extruded stacked layers with N ≥ 2; the method comprising the steps of:

a) mixing a given amount of a first PE masterbatch composition of a PE resin and additives, the PE masterbatch composition being free of acid neutralizer compounds with a first PERT metallocene based resin grade to form a first PE formulation;

b) repeating step a) (N-1) times to form (N-1) PE formulations; and

c) co-extruding the N PE formulations formed in steps a) and b) to form the multilayer polyethylene (PE) geomembrane liner.

22. The method of claim 21, wherein N ≥ 3.

23. The method of claim 21 or 22, wherein at least one of said additives is selected for providing at least one specific behaviour property to the liner.

24. The method of claim 23, wherein at least two of the N layers comprise additives different in nature and/or concentration in order to provide a customized geomembrane liner having at least two layers with different behaviour properties.

25. The method of any one of claims 21 to 24, wherein each of said N layer is made:

- from 5% to 15% of the PE masterbatch composition comprising:
  - from about 50 to about 90 wt.% of a PE resin,
  - from about 0.1 to about 4 wt.% of a phenolic antioxidant, and
  - from about 0.05 to about 3 wt.% of a secondary phosphite antioxidant.
  - from about 0 to 5 wt.% of at least one UV stabilizer, and
  - up to 50 wt.% of at least one specific additive;

wherein the percentages by weight add up to 100% and are based on the total weight of the PE masterbatch composition; and

- mixed with from about 85 to about 95% of a base resin composition comprising polyethylene of raised temperature (PERT) metallocene based resin or its blend with other PE grades;

wherein the percentages by weight add up to 100% and are based on the total weight of the geomembrane composition.

26. The method of claim 25, wherein the PE metallocene resin has a density of about 0.910 to about 0.960 g/cm^3.

27. The method of claim 25 or 26, wherein the PE resin is selected from the group consisting of Linear Low Density PE (LLDPE), Low Density PE (LDPE), Medium Density PE (MDPE) and High Density PE (HDPE), optionally within a metallocene grade category, and optionally in the PERT family.

28. The method of any one of claims 25 to 27, wherein the metallocene resin is a Metallocene – Medium Density Polyethylene resin having a density of about 0.941 g/cm^3 according to the test method ASTM D1505, also known as DAELIM^{TM} XP-9020.

29. The method of any one of claims 25 to 27, wherein the metallocene resin is a Metallocene – Medium Density Polyethylene resin having a density of about 0.938 g/cm^3 according to the test method ASTM D1505, also known as LUCENE^{TM} SP980.

30. The method of any one of claims 25 to 29, wherein the phenolic antioxidant comprises pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), also known as Irganox 1010™.

31. The method of any one of claims 25 to 30, wherein the secondary phosphite antioxidant is Tris(2,4-ditert-butylphenyl)phosphite, also known as Irgafos^{TM} 168.

32. The method of any one of claims 25 to 31, wherein the UV stabilizer is selected from high molecular weight hindered amines (HALS).

33. The method of claim 32, wherein the HALS is 1,6-hexanediamine, N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-polymer with 2,4,6-trichloro-1,3,5-triazine, reaction products with N-butyl-1-butanamine and N-butyl-2,2,6,6-tetramethyl-4-piperidinamine, also known as Chimmasorb^{TM} 2020.

34. The method of any one of claims 25 to 33, wherein the at least one specific additive is selected from Carbon black or TiO_2 particles.

35. The method of claim 34, wherein the carbon black is a furnace carbon black with a particle size equal or below N660.

36. The method of claim 34 or 35, wherein TiO_2 particle size is about 100 nm and more.

37. The method of any one of claims 21 to 36, wherein said geomembrane liner has a water-bath aging performance for about 6 months immersion at about 80°C per ASTM D5322 - modified for water, such that about 80% of high pressure oxidative induction time (OIT) value retained per ASTM D5885.

38. The method of any one of claims 21 to 37, wherein the N PE masterbatch compositions are free of hydrotalcite as acid neutralizer compound.

39. The method of claims 21 to 38, further comprising the step of laminating or coextruding the liner with a sub-layer, the sub-layer being adapted to be electrically conductive whereby, in use, integrity of the liner is monitored electrically.

40. The method of claim 39, wherein the sub-layer is formed by coating the liner using carbon black.

41. A lined containment system comprising at least one multilayer polyethylene (PE) geomembrane liner as defined in any one of claims 1 to 20 or formed using the method as defined in any one of claims 21 to 40.

42. A customized multilayer polyethylene (PE) geomembrane liner comprising a number N of co-extruded stacked layers with $N \geq 2$, each layer being made from:

a given amount of a PE masterbatch composition comprising a PE resin and additives, and

a given amount of a PE metallocene based resin; the PE metallocene based resin being free of acid neutralizer compounds;

wherein the PE masterbatch composition comprises at least one specific additive providing at least one specific behaviour property to the layer; wherein at least two of the N layers comprise a different specific additive in order to provide a geomembrane liner having at least two layers with different behaviour property.

43. The customized multilayer polyethylene (PE) geomembrane liner of claim 42, wherein $N \geq 3$ and at least two of the N layers comprise different specific additives.

44. The customized multilayer polyethylene (PE) geomembrane liner of claim 42 or 43, wherein each layer comprises:

- from 5% to 15% of the PE masterbatch composition comprising:
  from about 50 to about 90 wt.% of a PE resin with a density of about 0.910 to about 0.960 g/cm^3,
  from about 0.1 to about 4 wt.% of a phenolic antioxidant,
  from about 0.05 to about 3 wt.% of a secondary phosphite antioxidant,
  from 0 to 5 wt.% of at least one UV stabilizer, and
  up to 50 wt.% of the at least one specific additive;

  wherein the percentages by weight add up to 100% and are based on the total weight of the PE masterbatch composition; and
- from about 85 to about 95% of a base resin composition comprising polyethylene of raised temperature (PERT) metallocene based resin or its blend with other PE grades;

wherein the percentages by weight add up to 100% and are based on the total weight of the geomembrane composition.

45. The customized multilayer polyethylene (PE) geomembrane liner of claim 44, wherein the PE resin in the masterbatch having a density of about 0.910 to about 0.960 g/cm^3 is selected from the group consisting of Linear Low Density PE (LLDPE), Low Density PE (LDPE), Medium Density PE (MDPE) and High Density PE (HDPE), optionally within a metallocene grade category, and optionally in the PERT family.

46. The customized multilayer polyethylene (PE) geomembrane liner of claim 44 or 45, wherein the PE resin having a density of about 0.910 to about 0.960 g/cm^3 is a PE metallocene resin.

47. The customized multilayer polyethylene (PE) geomembrane liner of claim 46, wherein the metallocene resin is a Metallocene – Medium Density Polyethylene resin having a density of about 0.941 g/cm^3 according to the test method ASTM D1505, also known as DAELIM^{TM} XP-9020.

48. The customized multilayer polyethylene (PE) geomembrane liner of claim 46, wherein the metallocene resin is a Metallocene – Medium Density Polyethylene resin having a density of about 0.938 g/cm^3 according to the test method ASTM D1505, also known as LUCENE^{TM} SP980.

49. The customized multilayer polyethylene (PE) geomembrane liner of any one of claims 46 to 48, wherein said geomembrane liner is free of acid neutralizer.

50. The customized multilayer polyethylene (PE) geomembrane liner of any one of claims 46 to 49, wherein said geomembrane liner is free of hydrotalcite as acid neutralizer.

51. The customized multilayer polyethylene (PE) geomembrane liner of any one of claims 44 to 50, wherein the phenolic antioxidant comprises pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), also known as Irganox 1010™.

52. The customized multilayer polyethylene (PE) geomembrane liner of any one of claims 44 to 51, wherein the secondary phosphite antioxidant is Tris(2,4-ditert-butylphenyl)phosphite, also known as Irgafos^{TM} 168.

53. The customized multilayer polyethylene (PE) geomembrane liner of any one of claims 44 to 52, wherein the PE masterbatch composition comprises from about 0.05 to about 5 wt% of the at least one UV stabilizer selected from high molecular weight hindered amines (HALS).

54. The customized multilayer polyethylene (PE) geomembrane liner of claim 53, wherein the HALS is 1,6-hexanediamine, N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-polymer with 2,4,6-trichloro-1,3,5-triazine, reaction products with N-butyl-1-butanamine and N-butyl-2,2,6,6-tetramethyl-4-piperidinamine, also known as Chimmasorb™ 2020.

55. The customized multilayer polyethylene (PE) geomembrane liner of any one of claims 42 to 54, wherein the at least one specific additive is Carbon black or TiO_2 particles.

56. The customized multilayer polyethylene (PE) geomembrane liner of claim 55, wherein the carbon black is a furnace carbon black with a particle size equal or below N660.

57. The customized multilayer polyethylene (PE) geomembrane liner of claim 55 or 56, wherein TiO_2 particle size is about 100 nm and more.

58. The customized multilayer polyethylene (PE) geomembrane liner of any one of claims 42 to 57, wherein said geomembrane liner has a water-bath aging performance for about 6 months immersion at about 80°C per ASTM D 5322 - modified for water, such that about 80% of high pressure oxidative induction time (OIT) value retained per ASTM 5885.

59. A method for the making of a customized multilayer polyethylene (PE) geomembrane liner, the liner comprising a number N of co-extruded stacked layers with $N \geq 2$, the method comprising the steps of:

a) mixing a given amount of a PE masterbatch composition comprising a PE resin and additives, with a given amount of polyethylene of raised temperature (PERT) metallocene based resin to form a PE formulation;

b) repeating step a) (N-1) times to form (N-1) PE formulations; and

c) co-extruding the N PE formulations formed in steps a) and b) to form the multilayer polyethylene (PE) geomembrane liner;

wherein at least one of the N PE formulations comprise at least one specific additive presenting a nature and/or a concentration selected in function of a final utility of the geomembrane liner in order to customize the geomembrane liner.

60. The method of claim 59, wherein N ≥ 3.

61. The method of claim 59 or 60, wherein each of said N layer is made with:

- from 5% to 15% of the PE masterbatch composition comprising:
  - from about 50 to about 90 wt.% of a PE resin having a density of from about 0.910 to about 0.960 g/cm^3,
  - from about 0.1 to about 4 wt.% of a phenolic antioxidant, and
  - from about 0.05 to about 3 wt.% of a secondary phosphite antioxidant.
  - from about 0 to 5 wt.% of at least one UV stabilizer, and
  - up to 50 wt.% of at least one specific additive;

  wherein the percentages by weight add up to 100% and are based on the total weight of the PE masterbatch composition; and
- mixed with from about 85 to about 95% of a base resin composition comprising polyethylene of raised temperature (PERT) metallocene based resin or its blend with other PE grades;

wherein the percentages by weight add up to 100% and are based on the total weight of the geomembrane composition.

62. The method of claim 61, wherein the PE resin of the masterbatch is selected from the group consisting of Linear Low Density PE (LLDPE), Low Density PE (LDPE), Medium Density PE (MDPE) and High Density PE (HDPE); optionally within a metallocene grade category, and optionally in the PERT family.

63. The method of claim 61 or 62, wherein the PE resin is a PE metallocene resin.

64. The method of claim 63, wherein the metallocene resin is a Metallocene – Medium Density Polyethylene resin having a density of about 0.941 g/cm^3 according to the test method ASTM D1505, also known as DAELIM^{TM} XP-9020.

65. The method of claim 63, wherein the metallocene resin is a Metallocene – Medium Density Polyethylene resin having a density of about 0.938 g/cm^3 according to the test method ASTM D1505, also known as LUCENE^{TM} SP980.

66. The method of any one of claims 63 to 65, wherein the N PE masterbatch compositions are free of acid neutralizer compound.

67. The method of any one of claims 63 to 66, wherein the N PE masterbatch compositions are free of hydrotalcite as acid neutralizer compound.

68. The method of any one of claims 61 to 67, wherein the phenolic antioxidant comprises pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), also known as Irganox 1010™.

69. The method of any one of claims 61 to 68, wherein the secondary phosphite antioxidant is Tris(2,4-ditert-butylphenyl)phosphite, also known as Irgafos™ 168.

70. The method of any one of claims 61 to 69, wherein the UV stabilizer is selected from high molecular weight hindered amines (HALS).

71. The method of claim 70, wherein the HALS is 1,6-hexanediamine, N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-polymer with 2,4,6-trichloro-1,3,5-triazine, reaction products with N-butyl-1-butanamine and N-butyl-2,2,6,6-tetramethyl-4-piperidinamine, also known as Chimmasorb™ 2020.

72. The method of any one of claims 61 to 71, wherein the at least one specific additive is selected from Carbon black or TiO_2 particles.

73. The method of claim 72, wherein the carbon black is a furnace carbon black with a particle size equal or below N660.

74. The method of claim 72 or 73, wherein TiO_2 particle size is about 100 nm and more.

75. The method of any one of claims 59 to 74, wherein said geomembrane liner has a water-bath aging performance for about 6 months immersion at about 80°C per ASTM D5322 - modified for water, such that about 80% of high pressure oxidative induction time (OIT) value retained per ASTM D5885.

76. The method of claims 59 to 75, further comprising the step of laminating or coextruding the liner with a sub-layer, the sub-layer being adapted to be electrically conductive whereby, in use, integrity of the liner is monitored electrically.

77. The method of claim 76, wherein the sub-layer is formed by coating the liner using carbon black.

78. A lined containment system comprising at least one customized multilayer polyethylene (PE) geomembrane liner as defined in any one of claims 42 to 58 or made using the method as defined in any one of claims 59 to 77.

* * *

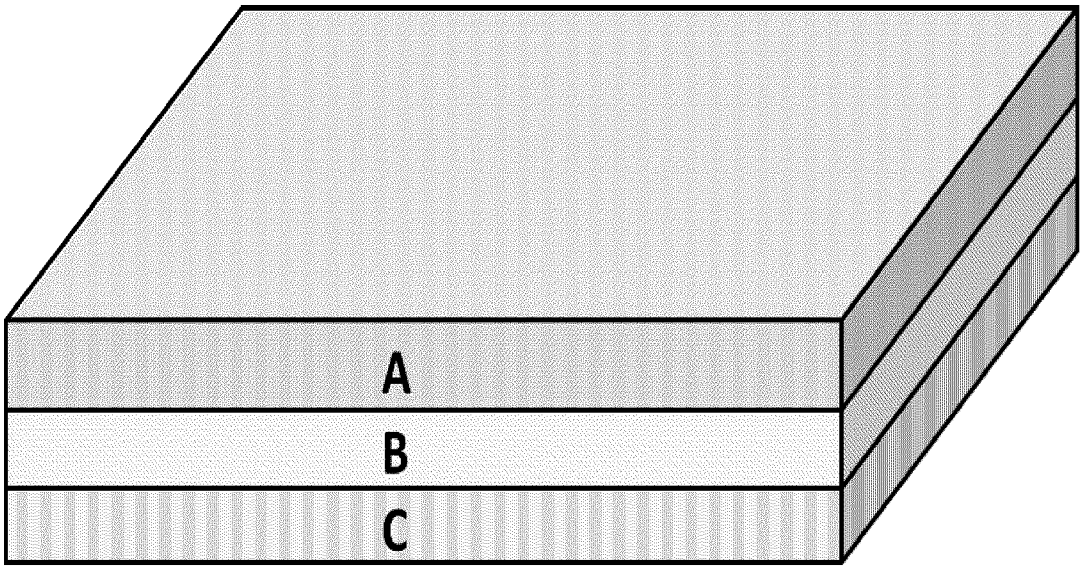

FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2016/050051

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***B32B 27/18*** (2006.01), ***B32B 27/32*** (2006.01), ***B32B 37/00*** (2006.01), *C08J 3/22* (2006.01)

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 27/18 (2006.01), ***B32B 27/32*** (2006.01), ***B32B 37/00*** (2006.01), *C08J 3/22* (2006.01)

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

B32B, C08J

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)

Questel Orbit: metallocene, geomembrane, polyethylene
Google: metallocene, PE-RT,

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US20140364545 (PRACHOOMDANG ET AL.) 11 December 2014 (2014-12-11) ** see paragraphs [0011]-[0022], [0030], [0059] and claims**	1-78
Y	INEOS Metallocene Product Family, Ineos Olefins & Polymers Europe, October 2013. http://www.ineos.com/globalassets/ineos-group/businesses/ineos-olefins-and-polymers-europe/brochures/metallocene-teaser.pdf	1-78
Y	EP2133367 (INEOS MANUFACTURING) 16 December 2009 (2009-12-16)	1-78
Y	"A Guide to Polymeric Membranes: A Practical Approach" (SCHEIRS, JOHN) 27 August 2009 (2009-08-27), John Wiley & Sons, page 77	1-78

☐ Further documents are listed in the continuation of Box C.

☑ See patent family annex.

*	Special categories of cited documents:
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier application or patent but published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search 2 March 2016 (02-03-2016)	Date of mailing of the international search report 22 March 2016 (22-03-2016)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 819-953-2476	Authorized officer Amanda Livingston (819) 639-8502

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2016/050051

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US2014364545A1	11 December 2014 (11-12-2014)	US2014364545A1	11 December 2014 (11-12-2014)
		AU2014275335A1	10 December 2015 (10-12-2015)
		CA2915688A1	11 December 2014 (11-12-2014)
		KR20160017057A	15 February 2016 (15-02-2016)
		US2014083793A1	27 March 2014 (27-03-2014)
		WO2014197197A1	11 December 2014 (11-12-2014)
		WO2014197197A8	07 January 2016 (07-01-2016)
EP2133367A1	16 December 2009 (16-12-2009)	EP2133367A1	16 December 2009 (16-12-2009)
		CN102112498A	29 June 2011 (29-06-2011)
		CN102112498B	13 August 2014 (13-08-2014)
		EP2285843A2	23 February 2011 (23-02-2011)
		EP2285843B1	31 December 2014 (31-12-2014)
		ES2534240T3	20 April 2015 (20-04-2015)
		US2011086191A1	14 April 2011 (14-04-2011)
		WO2010000557A2	07 January 2010 (07-01-2010)
		WO2010000557A3	04 March 2010 (04-03-2010)