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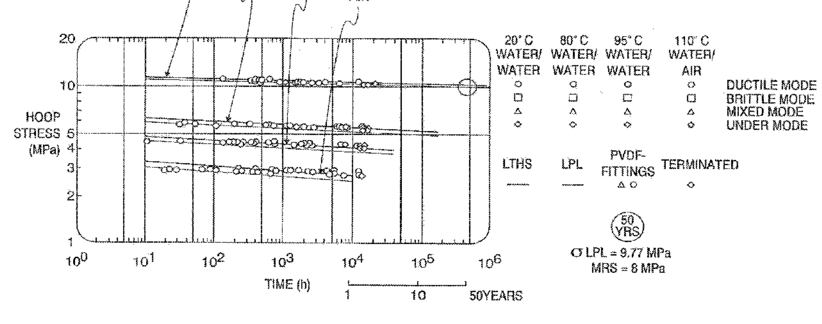
(54) **Title**: HIGH TEMPERATURE GEOMEMBRANE LINERS AND MASTER BATCH COMPOSITIONS

Fig. 1



(57) **Abstract**: Geomembrane liners suitable for use at elevated temperatures up to 100 °C, as well as master batch compositions suitable for preparing such geomembrane liners.

HIGH TEMPERATURE GEOMEMBRANE LINERS AND MASTER BATCH COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This is a non-provisional patent application claiming priority to U.S. Provisional Application Serial No. 61/831,526, filed June 5, 2013, entitled "High Temperature Geomembrane Liners and Master Batch Compositions" and U.S. Serial No. 14/271,011, filed May 6, 2014, entitled "High Temperature Geomembrane Liners and Master Batch Compositions", both of which are hereby incorporated by reference in their entirety.

FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not Applicable.

MICROFICHE/COPYRIGHT REFERENCE

[0003] Not Applicable.

FIELD OF THE INVENTION

[0004] The present invention relates to geomembrane liners, and more specifically to geomembrane liners prepared using a special base resin and a special master batch allowing the geomembrane liners to operate at elevated temperatures up to 100°C.

BACKGROUND OF THE INVENTION

[0005] Polyethylene geomembranes have been successfully used for hazardous waste containments and water reservoirs for more than 30 years. However, because the long service life is a requirement for most applications, their usage is generally limited to those applications that operate at temperature at and below 60 ^{0}C. At higher temperatures, geomembranes are subjected to an accelerated oxidative degradation and creep, thereby shortening their service lives. The mechanism of geomembranes' failure can roughly be divided into three stages.

[0006] Stage 1, "ductile failure," occurs due to stress overload and is a purely mechanical failure.

[0007] Stage 2, "brittle-mechanical failure," occurs due to creeping and depletion of additives.

[0008] Stage 3, "brittle-chemical failure," occurs due to complete consumption of additives; is purely chemical and independent of stress. Stage 3 failure is rapid.

[0009] All three stages are the deciding factors of service life of a geomembrane. Stage 1 is dependent on the number and entanglement of tie-molecules. Resins with higher number of tie-molecules and more entanglements will have a longer ductile mode. At high temperatures, molecules are very active and mobile, which in turn accelerates the creeping mechanism. In addition, the rate of depletion of additives is also increased with the increase of temperature. The combined effects of creep and additives depletion lower the lives of stages 2 and 3.

[0010] Therefore, there is a need in the art for geomembranes that can be utilized at elevated temperatures, such as those above 60 °C.

SUMMARY OF THE INVENTION

[0011] In one aspect of the present invention, a composition for preparing a geomembrane liner for a containment system is provided, wherein said composition is of: 1) a master batch; and 2) a base resin and wherein said composition comprises:

1) about 8-10 wt% of a master batch composition comprising:

a) about 70 to about 80 wt% of one or more of a Linear Low Density Polyethylene (LLDPE), Medium Density Polyethylene (MDPE), High Density Polyethylene (HDPE), or Polyethylene of Raised Temperature (PERT) resin carrier has density from 0.910 to 0.955 g/cm^3;

b) about 1 to about 3 wt% of a primary antioxidant, wherein said primary antioxidant comprises 1,3, trimethyl-2,4,6-tris-(3,5-di-t-butyl-4-hydroxybenzyl) benzene;

c) about 0.1 to about 0.5 wt% of a secondary antioxidant, wherein said secondary antioxidant comprises pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate);

d) optionally, about 0.1 to about 0.5 wt% of tris (2,4-di-tert-butylphenyl) phosphite;

e) about 1 to about 3 wt% of a UV stabilizer, wherein said UV stabilizer comprises a high molecular weight hindered amine light stabilizer;

f) about 0.1 to about 0.5 wt% of an acid neutralizer; and

g) about 20 to about 30 wt% of a carbon black, wherein said carbon black is a furnace carbon black, and wherein the percentages by weight add up to 100% and are based on the total weight of the master batch composition; and

2) about 90 to about 92 wt% of a base resin composition comprising a Polyethylene of Raised Temperature (PERT) base resin, wherein the percentage by weight is based on the total weight of the geomembrane composition.

[0012] It should be understood that the master batch composition by itself is also an aspect of the invention.

[0013] In one form of this aspect of the master batch invention, resin carrier is one or more of a Linear Low Density Polyethylene (LLDPE), Medium Density Polyethylene (MDPE), High Density Polyethylene (HDPE), or Polyethylene of Raised Temperature (PERT). In another form of this aspect of the master batch invention, the high molecular weight hindered amine light stabilizer is 1,3,5-Triazine-2,4,6-triamine,N,N'''-[1,2-ethane-diyl-bis[[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-1,3,5-triazine-2-yl]imino]-3,1-propanediyl]].

[0014] In still another form of this aspect of the master batch invention, the acid neutralizer comprises hydrotalcite.

[0015] In another aspect of the present invention, a geomembrane liner is provided, wherein this geomembrane liner is prepared by letting down the inventive composition (i.e., a master batch) in a base resin.

[0016] In one form of this aspect of the invention, the geomembrane liner comprises about 1100 to about 1400 parts per million (ppm) of said primary antioxidant; about 400 to about 500 ppm of said secondary antioxidant;; about 0 to about 100 ppm of tris (2,4-di-tert-butylphenyl) phosphite; about 1200 to about 1500 ppm of said UV stabilizer; about 300 to about 400 ppm of said acid neutralizer; and about 20,000 to about 25,000 ppm of said carbon black.

[0017] Other objects, features, and advantages of the invention will become apparent from a review of the entire specification, including the appended claims and drawings.

BRIEF DESCRIPTION OF THE FIGURE

[0018] Figure 1 illustrates the results of a hoop stress test of polyethylene of raised temperature (PE-RT) per ISO9080.

DETAILED DESCRIPTION OF THE INVENTION

[0019] In one aspect, the invention provides geomembranes that are resistant to environmental stress crack, have good mechanical properties, and therefore can have long service lives at elevated temperatures of up to 100 °C.

[0020] Base resin used in the inventive geomembranes is Polyethylene of Raised Temperature (PERT), which comprises disproportionately more high molecular weight particles than low molecular weight particles. Thus, it is preferred that most of the co-monomers (side branches) also have a relatively high molecular weight.

[0021] To make a geomembrane, normally a master batch is first prepared. The master batch can then be let down in the resin material to make a geomembrane. It is well within a skill of the art to prepare a final product (e.g., a geomembrane) from a master batch.

[0022] In one aspect, the inventive master batch comprises a resin carrier; a carbon black; a thermal stabilizer which comprises a primary antioxidant, a secondary thermal stabilizer; and optionally, a tertiary antioxidant; a UV stabilizer; and an acid neutralizer.

[0023] Preferably, resin carriers used in the inventive geomembranes comprise either Linear Low Density Polyethylene (LLDPE), Medium Density Polyethylene (MDPE), or High Density Polyethylene (HDPE).

[0024] Even more preferably, the resin carriers comprise Polyethylene of Raised Temperature (PERT).

[0025] Some non-limiting trade name examples of preferred PERT resins for the purposes of this invention include Dowlex® 2344, Dowlex® 2377, Dowlex® 2388, DGDA-2399, Intrepid^{TM} 2498 NT, Intrepid^{TM} 2499 NT (all products of Dow Chemical, US), Yuclair® DX800 (SK Global Chemical, South Korea), Daelim XP9000 (Daelim, South Korea), Total XRT70 (Total, France), Hostalen 4731B (LyondellBasell, the Netherlands), and Eltex® TUB220-RT (Ineos, Switzerland).

[0026] Certain non-PERT resins also can be used as carriers. However, High Temperature Liner incorporated non-PERT Master batch has an application limit of 90 ^{0}C. Some non-limiting trade name of preferred non-PERT resins for the purposes of this master batch invention include SABIC® LLDPE 0132HS00 (Saudi Basic Industries Corporation, Saudi Arabia), Marlex® K203 (Chevron Phillips Chemical Company, US), and Dowlex® 2342M (Dow Chemical, US).

[0027] Resin carriers used for this master batch invention should have density from 0.910 to 0.955 g/cm^3; and Melt Index (MI) (2.16kg) of less than or equal to 1 dg/min.

[0028] The thermal stabilizer used in the inventive compositions comprises a primary antioxidant, a secondary thermal stabilizer; and optionally, a tertiary antioxidant.

[0029] The primary antioxidant is used for long term stabilization and comprises 1,3, trimethyl-2,4,6-tris-(3,5-di-t-butyl-4-hydroxybenzyl) benzene, CAS No. 1709-70-2. Some non-limiting trade name examples of the primary antioxidant include Irganox 1330 (BASF, Germany), Ethanox 330 (Albemarle Corporation, US), BNX 1330 (Mayzo, US), Songnox 1330 (Songwon, South Korea), and others.

[0030] The secondary antioxidant used in the inventive compositions is a hindered pheonolic antioxidant called pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, CAS No. 6683-19-8. Some non-limiting trade name examples of the secondary antioxidant include Irganox 1010 (BASF, Germany), BNX 1010 (Mayzo, US), Songnox 1010 (Songwon, South Korea), and others.

[0031] The tertiary antioxidant that can optionally be used in the inventive compositions is an organophosphite. In one aspect, this organophosphite is tris (2,4-di-tert-butylphenyl) phosphite, CAS No. 31570-04-4. Some non-limiting trade name examples of the tertiary antioxidant include Irgafos 168 (BASF, Germany), Benefos® 1680 (Mayzo, US), Songnox 1680 (Songwon, South Korea), and others.

[0032] The UV stabilizer used in the inventive compositions comprises a high molecular weight hindered amine light stabilizer (HALS). In one aspect, this HALS is 1,3,5-Triazine-2,4,6-triamine,N,N'''-[1,2-ethane-diyl-bis[[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-1,3,5-triazine-2-yl]imino]-3,1-propanediyl]]. Some non-limiting trade name examples of the UV stabilizer include Chimassorb 119 (BASF, Germany), Sabo® Stab UV 119 (Sabo S.p.A, Italy), Lowilite® 19 (Chemtura, US), and others.

[0033] The acid neutralizer used in the inventive compositions comprises hydrotalcite, CAS No. 11097-59-9. Some non-limiting trade name examples of the acid neutralizer include DHT-4A (Kisuma Chemicals, the Netherlands), DHT-4V (Kisuma Chemicals, the Netherlands), Hycite® 713 (Telko, Finland), and others.

[0034] The carbon black used in the inventive compositions has a particle size smaller than or equal to a particle size of N660 carbon black. Some non-limiting trade name examples of the carbon black include Arosperse 5 (Orion Engineered Carbons, US), Raven® 880 Ultra (Columbian Chemicals, US), Black Pearls® 4060 (Cabot Corporation, US), and others.

[0035] In one aspect of the present invention, a composition for preparing a geomembrane liner for a containment system is provided, wherein said composition is of: 1) a master batch; and 2) a base resin and wherein said composition comprises:

1) about 8-10 wt% of a master batch composition comprising:

   a) about 70 to about 80 wt% of one or more of a Linear Low Density Polyethylene (LLDPE), Medium Density Polyethylene (MDPE), High Density Polyethylene (HDPE), or Polyethylene of Raised Temperature (PERT) resin carrier has density from 0.910 to 0.955 g/cm^3;

   b) about 1 to about 3 wt% of a primary antioxidant, wherein said primary antioxidant comprises 1,3, trimethyl-2,4,6-tris-(3,5-di-t-butyl-4-hydroxybenzyl) benzene;

   c) about 0.1 to about 0.5 wt% of a secondary antioxidant, wherein said secondary antioxidant comprises pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate);

   d) optionally, about 0.1 to about 0.5 wt% of tris (2,4-di-tert-butylphenyl) phosphite;

   e) about 1 to about 3 wt% of a UV stabilizer, wherein said UV stabilizer comprises a high molecular weight hindered amine light stabilizer;

   f) about 0.1 to about 0.5 wt% of an acid neutralizer; and

   g) about 20 to about 30 wt% of a carbon black, wherein said carbon black is a furnace carbon black, and wherein the percentages by weight add up to 100% and are based on the total weight of the master batch composition; and

2) about 90 to about 92 wt% of a base resin composition comprising a Polyethylene of Raised Temperature (PERT) base resin, wherein the percentage by weight is based on the total weight of the geomembrane composition.

[0036] It should be understood that the master batch composition by itself is also an aspect of the invention.

[0037] In one form of this aspect of the master batch invention, resin carrier is a Linear Low Density Polyethylene (LLDPE), Medium Density Polyethylene (MDPE), High Density Polyethylene (HDPE), or Polyethylene of Raised Temperature (PERT). In still another form of this aspect of the master batch invention, the acid neutralizer comprises hydrotalcite.

[0038] In another aspect of the present invention, a geomembrane liner is provided, wherein this geomembrane liner is prepared by letting down the inventive composition (i.e., a master batch) in a base resin.

[0039] In one form of this aspect of the invention, the geomembrane liner comprises about 1100 to about 1400 ppm of said primary antioxidant; about 400 to about 500 ppm of said secondary antioxidant; about 0 to about 100ppm of tris (2,4-di-tert-butylphenyl) phosphite; about 1200 to about 1500 ppm of said UV stabilizer; about 300 to about 400 ppm of said acid neutralizer; and about 20,000 to about 25,000 ppm of said carbon black.

[0040] The total amount of the primary antioxidant, the secondary antioxidant, tris (2,4-di-tert-butylphenyl) phosphite, the UV stabilizer, and the acid neutralizer is preferably between about 3000 and 3800 ppm.

[0041] Geomembranes of the invention can be used for various purposes known to those skilled in the art. Such purposes include, but are not limited to, lining landfills, hot water containments, underground thermal energy storage, heap leach pad mines, industrial fluid discharges, and the like. This preceding list of possible uses is not limiting and is not intended to limit the applicability of the provided compositions in any way.

[0042] The following Examples are provided solely for illustrative purposes and are not meant to limit the invention in any way.

Examples of the Invention

Example 1

Inventive Master Batch and Geomembrane Composition

[0043] Table 1 lists the ingredients of one of the inventive compositions (an example of a master batch).

[0044] **Table 1**

Masterbatch Formula	%
Dowlex®2344 Carrier	71.45
Carbon Black N330	25.00
Irganox 1330	1.40
Chimassorb 119	1.50
Irganox B225(1:1 Blend of Irganox 1010 and Irgafos 168)	0.25
Hydrotalcite DHT 4A	0.40
Total	100

[0045] Table 2 lists the ingredients of one of the inventive compositions (an example of a geomembrane).

[0046] **Table 2**

Geomembrane Formula	%
Polyethylene of Raised Temperature (PERT) Base Resin	91.5
Inventive Master Batch	8.5
Total	100

Example 2

Oven Aging Testing

[0047] The purpose of this experiment was to determine how the inventive compositions handle heat and to determine their durability.

Experimental Conditions

[0048] First, two inventive geomembranes were prepared: 1) one was prepared from the same master batch composition of Table 1 and 2) the other one was prepared from the geomembrane composition of Table 2 but a different base resin. These two inventive geomembranes are named after their base resin as Dowlex® 2344 Raised Temperature Geomembrane (GMRT 1) and Dowlex® 2377 Raised Temperature Geomembrane (GMRT 2).

[0049] Second, two comparative geomembranes were made from the same PERT base resins, but from the Standard Supplier Masterbatch (SSMB) (conventional master batch) used for preparation of conventional geomembranes.

[0050] Then, the inventive and comparative geomembrane samples were tested for Oxidative Induction Time (OIT) and High Pressure OIT (HPOIT). The OIT was tested in accordance with ASTM D3895, while the HPOIT was performed according to ASTM D5885.

[0051] Two comparative geomembranes were incubated in an air-circulating oven at 85°C for 90 days as per ASTM D5721. GSE High Temperature geomembranes were incubated under the same environment conditions for 1 year. OIT/HPOIT tests were performed after oven aging. Percentage retained of OIT and HPOIT showed that the inventive geomembranes have an acceptable retention after 1 year incubation, while comparative geomembranes failed within 90 days of incubation.

[0052] Test results are shown in Table 3 to Table 6.

[0053] **Table 3, GMRT 1/ 85^{0}C Oven Aging**

Test Conditions	Baseline	After 90 days	% Retained	After 375 days	% Retained
Dowlex®2344 Raised Temperature Geomembrane (GMRT 1)					
150^{0}C, 500 psi Oxygen pressure (OIT-minute)	987	813	82%	901	92%
200°C, Atmospheric Oxygen pressure (OIT-minute)	201	184	91%	90	45%

[0054] **Table 4, GMRT 2/ 85^{0} Oven Aging**

Test Conditions	Baseline	After 90 days	% Retained	After 375 days	% Retained
Dowlex®2377 Raised Temperature Geomembrane (GMRT 2)					
150°C, 500 psi Oxygen pressure (OIT-minute)	846	755	89%	811	95%
200°C, Atmospheric Oxygen pressure (OIT-minute)	187	187	100%	93	50%

[0055] **Table 5, Dowlex®2344 Conventional Formulation / 85^{0}C Oven Aging**

Test Conditions	Baseline	After 60 days	% Retained
Dowlex®2344 Based Comparative Geomembrane			
150°C, 500 psi Oxygen pressure (HP OIT- minute)	315	216	69%
200°C, Atmospheric Oxygen pressure (OIT - minute)	116	82	71%

[0056] **Table 6, Dowlex®2377 Conventional Formulation / 85^{0}C Oven Aging**

Test Conditions	Baseline	After 60 days	% Retained
Dowlex®2377 Based Comparative Geomembrane			
200°C, Atmospheric Oxygen pressure (OIT - minute)	120	88	73%

[0057] Industry standard specifications for performance of geomembrane in oven aging test are listed in GRI GM13. The durability requirements of this standard require 80% retention rate of HP OIT and 55% retention rate of OIT after 90 days oven exposure. These results show that the inventive compositions GMRT1 and GMRT2, handle heat well and were durable, while the comparative compositions failed HP OIT within 90 days of incubation, and cannot compete with inventive compositions in OIT retention.

Example 3

UV Resistance Testing

[0058] The purpose of this experiment was to determine the resistance of the inventive compositions to UV.

Experimental Conditions

[0059] The inventive and comparative geomembrane samples described in Example 2 were subjected to UV Exposure in QUV with the cycle of 75^{0}C for 20 UV hours, 60^{0}C for 4 Condensation hours, and with the irradiance of 0.72 W/m^2.nm(±10%) at 340 nm. The UV irradiance from 295 nanometer to 400 nanometer is 39W/ m^2 (±10%). Exposed samples were then tested for the OIT Retained. Retention of 50% after 5,000 hours of UV Exposure is considered acceptable. Test results are shown in Table 7 and Table 8.

[0060] **Table 7, GMRT 1, UV Exposure**

Test Conditions	Baseline	After 1220 hours UV Exposure	After 6360 hours UV Exposure
Dowlex®2344 Raised Temperature Geomembrane (GMRT 1)			
150°C, 500 psi Oxygen pressure (OIT- minute)	987	866(87% retained)	693(70% retained)

[0061] **Table 8, GMRT 2, UV Exposure**

Test Conditions	Baseline	After 1642 hours UV Exposure	After 6382 hours UV Exposure
Dowlex®2377 Raised Temperature Geomembrane (GMRT 2)			
150°C, 500 psi Oxygen pressure (OIT- minute)	846	783(92% retained)	694(82% retained)

[0062] Industry standard specifications for performance of geomembrane in UV aging test are listed in GRI GM13. The durability requirements of this standard require 50% retention rate of HP OIT after 1600 UV exposure. These results show that the inventive compositions are resistant to UV exposure.

Example 4

Mechanical Performance/Creep Resistance

[0063] The purpose of this experiment was to determine mechanical performance/creep resistance of the inventive compositions.

Experimental Conditions

[0064] GMRT 1 and GMRT 2 samples were tested for the Environmental Stress Crack Resistance by Single Point Notched Constant Tensile Load (SP-NCTL) Method according to ASTM D5397 (modified) at 3.4 MPa(500 psi) Tensile Stress in 80 ^{0}C solution of 10 w% Igepal CA-720 and water. The time to failure of 500 hours or greater is acceptable. Test results are shown in Table 9.

[0065] **Table 9, GMRT 1 and GMRT 2 in 10 w% Igepal CA-720 Water Solution**

Geomembrane Sample	Temperature ^{0}C	Tensile Stress MPa (psi)	Failure Time hour
Dowlex®2344 Raised Temperature Geomembrane (GMRT 1)	80	3.4 (500)	≥ 500
Dowlex®2377 Raised Temperature Geomembrane (GMRT 2)	80	3.4 (500)	≥ 500

[0066] Industry standard specifications for performance of geomembrane in oven aging test are listed in GRI GM13. The creep resistance requirements of this standard require at least 300 hours of testing @ 50°C. These results show that the inventive compositions have strong creep resistance.

Example 5

Mechanical Performance/Solid State Integrity

[0067] The purpose of this experiment was to determine mechanical performance/solid state integrity of the inventive compositions.

Experimental Conditions

[0068] GMRT 1 and GMRT 2 samples were tested for tensile properties according to ISO 527-1, 2. Young's Modulus of 35 MPa, Tensile Yield Stress of 4 MPa, and Break Tensile Elongation of 400% are arbitrarily chosen as minimum values to assure integrity of solid state property of Geomembrane at an elevated temperature. Results are shown in Table 10 and Table 11.

[0069] **Table 10, Tensile Properties, GMRT 1**

Test Temperature (°C)	Young' Modulus MPa (ksi)	Yield Stress MPa (psi)	Break Elongation (%)
60	130 (19)	11 (1600)	≥ 400
80	75 (10)	7 (1000)	≥ 400
100	38 (5.5)	5 (700)	≥400

[0070] **Table 11, Tensile Properties, GMRT 2**

Test Temperature (°C)	Young' Modulus MPa (ksi)	Yield Stress MPa (psi)	Break Elongation (%)
60	175 (25)	13 (1900)	≥ 400
80	90 (13)	9 (1300)	≥ 400
100	50 (7.2)	6 (850)	≥400

[0071] These results show that the inventive compositions have good solid state properties.

[0072] Additionally, various test results of PE-RT resin and on the inventive geomembrane compositions further illustrate the suitability of the geomembrane compositions according to present invention.

[0073] PE-RT (Polyethylene of Raised Temperature) resin used as the base resin for the high temperature liner has a history of successful field service for high temperature pressure pipes applications. Fig. 1 illustrates the results of a USO9080 hoop stress test of PE-RT. Such hoop stress test is a typical test method to evaluate the creep resistance of pressure pipes, and gives an extrapolating method of linear regression analysis to estimate the lifespan of a resin in pipe form. In Fig. 1, the PE-RT was tested for hoop stress test at four temperatures: 20, 80, 95, and 110°C. At 110°C testing temperature, no creep failure was observed after 10,000 hours (over 1 year) testing. Through the extrapolating method, the resin is determined to have over 25 years creep resistance at 80°C.

[0074] Additionally, aging tests have also shown excellent aging properties, with excellent antioxidants retention at elevated temperatures and superb UV protection, as shown in Table 12.

[0075] **Table 12. High Temperature Liner Aging Test Results vs. Industry Regulation**

Property	GRI GM13	GSE High Temperature Liner
^{1}High Pressure Oxidant Induction Time (HPOIT)	400min	≥ 700min
<u>Oven Aging</u>		
^{1,2}HPOIT Retained after 90 Days 85°C Exposure	80%	≥ 85%
^{1,2}HPOIT Retained after 90 Days 100°C Exposure	-	≥ 80%
^{1,2}HPOIT Retained after 1 year 85°C Exposure	-	≥ 80%
<u>UV Aging</u>		
^{1,3}HPOIT Retained after 1600hrs QUV Exposure	50%	≥ 70%
^{1,3}HPOIT Retained after 6000hrs QUV Exposure	-	≥ 60%

[1] High Pressure OIT Test Procedure per ASTM D5885

[2] Oven Aging Procedure per ASTM D5721

[3] UV Exposure Procedure per ASTM D7238

UV exposure conditions:

Per GRI GM13, ASTM D7238

<u>Exposure cycle</u>: 20 h UV cycle at 75°C followed by 4 h condensation at 60°C

<u>UV lamp</u>: UVA-340

<u>Irradiance level</u>: 0.72 W/(m^2.nm) at 340 nm

[0076] Tensile properties of the high temperature liners are shown in Table 13 and 14. Table 13 compares the tensile properties at room temperature of the high temperature liners (60 mil) versus industry regulation (GRI GM13) per ASTM D6693, and Table 14 (discussed below) shows the advantageous tensile properties at high temperatures of the inventive high temperature liners (60 mil) per ISO 527.

[0077] **Table 13. High Temperature Liner Tensile Properties vs. Industry Regulation**

Tensile Properties @ Room Temperature 23°C	GRI GM13	GSE High Temperature Liner
Yield Strength (psi)	126	140
Yield Elongation (%)	12	15
Break Strength (psi)	228	300
Break Elongation (%)	700	700

[0078] A higher start up value of yield/break strength at room temperature usually brings a higher strength level at elevated temperatures.)

[0079] Still further, a geomembrane meeting the following criteria will function well as a solid barrier by assuring the integrity of its solid state property at an elevated temperature:

I. Yield Stress ≥ 4Mpa (580psi);
II. Elastic Modulus ≥ 35Mpa (5000psi);
III. Break Tensile Elongation ≥ 400%

[0080] As shown in Table 14, the high temperature liner far exceeds such desirable tensile strengths. Elastic modulus, also known as tensile modulus, is a measure of the stiffness of materials. Coupled with yield stress and break tensile elongation, it tells the mechanical integrity of the geomembrane at the test temperature. For example, Elastic Modulus of the high temperature Liner at 100°C is higher than 38 MPa (5,500 psi). This value is comparable to those of VLDPE and TPO roofing membranes at room temperature.

[0081] **Table 14. High Temperature Liner Tensile Properties at elevated temperature**

Test Temperature °C	Yield Strength Mpa (psi)	Break Elongation %	Elastic Modulus Mpa (psi)
40	≥ 16 (2320)	≥ 400*	≥ 270 (39,000)
60	≥ 11 (1600)	≥ 400*	≥ 130 (19,000)
80	≥ 7 (1000)	≥ 400*	≥ 75 (10,000)
100	≥ 5 (700)	≥ 400*	≥ 38 (5,500)

** Due to the configuration of the test frame and temperature chamber, the maximum strain that could be measured was limited @ 400%.*

[0082] Environmental stress crack resistance is also illustrated by the Notched Constant Tensile Load (NCTL) Test per ASTM D5397. As shown in Table 15, whereas standard NCTL testing temperature is 50°C, even at an elevated test temperature of 80°C, no failure was observed after 1000 testing hours.

[0083] **Table 15. Notched Constant Temperature Load Test of High Temperature Liner at elevated temperatures**

Property	GRI GM13	GSE High Temperature Liner
NCTL @ 50°C	300 hrs	≥ 2000 hrs
NCTL @ 80°C	-	≥ 1000 hrs

Still other aspects, objects, and advantages of the present invention can be obtained from a study of the specification and the appended claims. It should be understood, however, that the present invention could be used in alternate forms where less than all of the objects and advantages of the present invention and preferred embodiment as described above would be obtained.

CLAIMS

1. A composition for preparing a geomembrane liner for a containment system, wherein said composition is of: 1) a master batch; and 2) a base resin and wherein said composition comprises:

i) about 8-10 wt% of a master batch composition comprising

a) about 70 to about 80 wt% of a Linear Low Density Polyethylene (LLDPE), Medium Density Polyethylene (MDPE), High Density Polyethylene (HDPE), or Polyethylene of Raised Temperature (PERT) resin carrier has density from 0.910 to 0.955 g/cm3.

b) about 1 to about 3 wt% of a primary antioxidant, wherein said primary antioxidant comprises 1,3, trimethyl-2,4,6-tris-(3,5-di-t-butyl-4-hydroxybenzyl) benzene;

c) about 0.1 to about 0.5 wt% of a secondary antioxidant, wherein said secondary antioxidant comprises pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate);

d) optionally, about 0.1 to about 0.5 wt% of tris (2,4-di-tert-butylphenyl) phosphite;

e) about 1 to about 3 wt% of a UV stabilizer, wherein said UV stabilizer comprises a high molecular weight hindered amine light stabilizer;

f) about 0.1 to about 0.5 wt% of an acid neutralizer; and

g) about 20 to about 30 wt% of a carbon black, wherein said carbon black is a furnace carbon black, and wherein the percentages by weight add up to 100% and are based on the total weight of the master batch composition; and

ii) about 90 to about 92 wt% of a base resin composition comprising Polyethylene of Raised Temperature (PERT) base resin, wherein the percentage by weight is based on the total weight of the geomembrane composition.

2. The composition of master batch in claim 1, wherein said resin carrier is LLDPE, MDPE, HDPE or polyethylene of raised temperature (PERT).

3. The composition of claim 1, wherein said high molecular weight hindered amine light stabilizer is 1,3,5-Triazine-2,4,6-triamine,N,N'''-[1,2-ethane-diyl-bis[[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-1,3,5-triazine-2-yl]imino]-3,1-propanediyl]].

4. The composition of claim 1, wherein said acid neutralizer is hydrotalcite.

5. The geomembrane liner of claim 1, wherein said geomembrane liner has an oven aging performance for 1 year incubation @ 85°C per ASTM D5721 such that 90% of high pressure OIT value retained per ASTM D5885.

6. The geomembrane liner of claim 1, wherein said geomembrane liner has an UV aging performance for 1 year UV exposure such that 70% of high pressure OIT value retained according to ASTM D5885.

7. The geomembrane liner of claim 1, wherein said geomembrane liner has a creep resistance according to modified ASTM D 5397 such that no failure occurred within 500 hours testing at 80°C.

8. The geomembrane liner of claim 1, wherein said geomembrane liner has an adequate solid state property at 100°C such that a Young's Modulus of at least 38Mpa according to ISO 527-1,2.

9. A master batch composition comprising

a) about 70 to about 80 wt% of a Linear Low Density Polyethylene (LLDPE), Medium Density Polyethylene (MDPE), High Density Polyethylene (HDPE), or Polyethylene of Raised Temperature (PERT) resin carrier has density from 0.910 to 0.955 g/cm^3;

b) about 1 to about 3 wt% of a primary antioxidant, wherein said primary antioxidant comprises 1,3, trimethyl-2,4,6-tris-(3,5-di-t-butyl-4-hydroxybenzyl) benzene;

c) about 0.1 to about 0.5 wt% of a secondary antioxidant, wherein said secondary antioxidant comprises pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate);

d) optionally, about 0.1 to about 0.5 wt% of tris (2,4-di-tert-butylphenyl) phosphite;

e) about 1 to about 3 wt% of a UV stabilizer, wherein said UV stabilizer comprises a high molecular weight hindered amine light stabilizer;

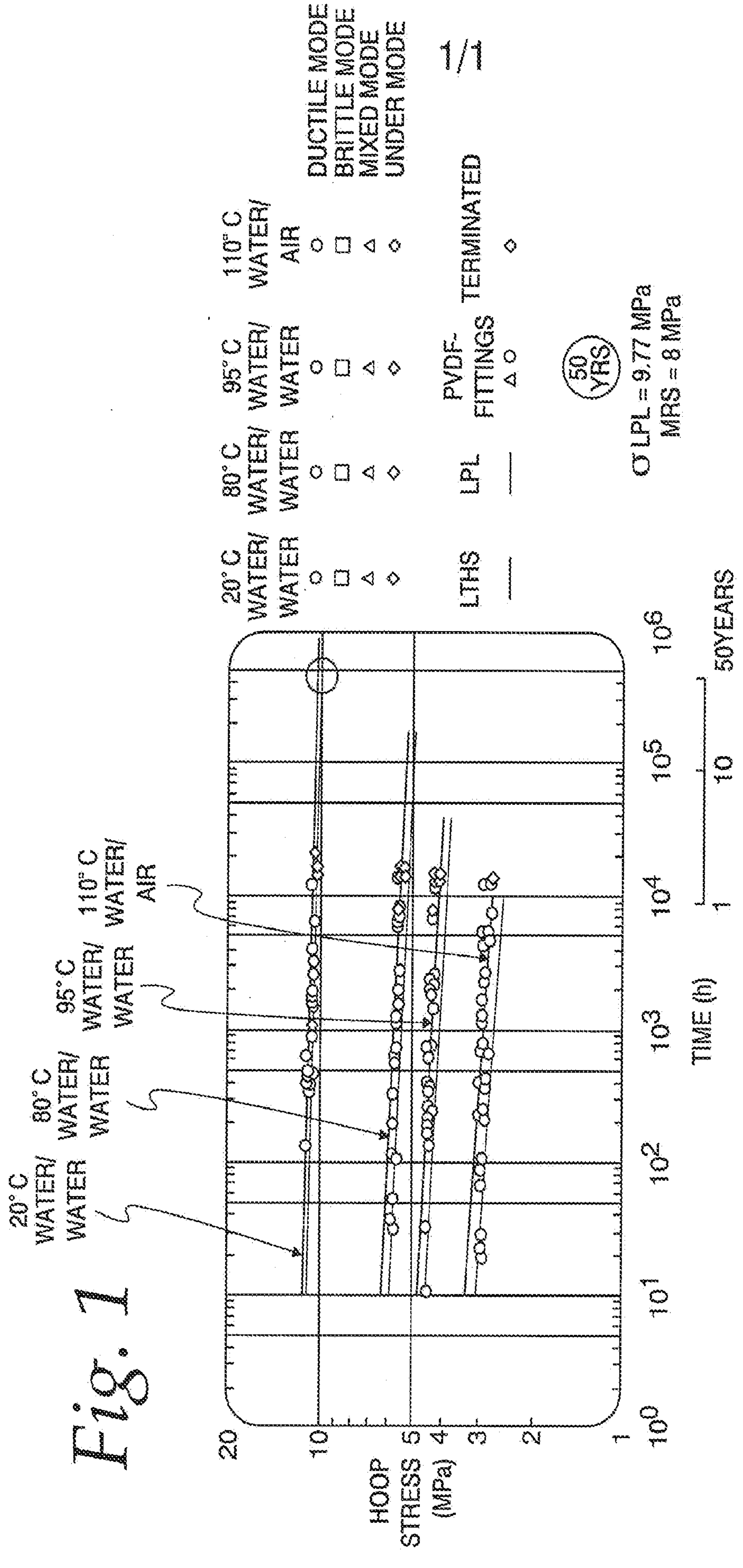
f) about 0.1 to about 0.5 wt% of an acid neutralizer; and

g) about 20 to about 30 wt% of a carbon black, wherein said carbon black is a furnac carbon black, and wherein the percentages by weight add up to 100% and are based on the total weight of the master batch composition.

10. A geomembrane liner prepared by letting down the master batch composition of claim 9 in a base resin (PERT).

11. The geomembrane liner of claim 10, wherein said geomembrane liner comprises about 1100 to about 1400 ppm of said primary antioxidant; about 400 to about 500 ppm of said secondary antioxidant; about 0 to about 100ppm of tris (2,4-di-tert-butylphenyl) phosphite; about 1200 to about 1500 ppm of said UV stabilizer; about 300 to about 400 ppm of said acid neutralizer; and about 20,000 to about 25,000 ppm of said carbon black.

Fig. 1


HOOP STRESS (MPa)
20
10
5
4
3
2
1
10^0
10^1
10^2
10^3
10^4
10^5
10^6
TIME (h)
1
10
50YEARS
20° C WATER/ WATER
80° C WATER/ WATER
95° C WATER/ WATER
110° C WATER/ AIR
DUCTILE MODE
BRITTLE MODE
MIXED MODE
UNDER MODE
LTHS
LPL
PVDF- FITTINGS
TERMINATED
50 YRS
σ LPL = 9.77 MPa
MRS = 8 MPa

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 14/38714

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B09B 1/00 (2014.01)
USPC - 405/129.75,129.45,129.6
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)
IPC(8)-B09B 1/00 (2014.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC- 405/129.75,129.45,129.6
CPC- B09B 1/00; E02D 31/004

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase, Google Patents, Google Scholar (without Patents) Keywords: Geomembrane liners hazardous waste containment system PERT HDPE LLDPE MDPE primary secondary tertiary antioxidant master batch compositions UV stabilizer acid neutralizer carbon black filler base resin carrier aging oven creep resistance

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2004/0024095 A1 (Vaillant) 5 February 2004 (05.02.2004) Abstract, para [0038], para [0032], para [0036	1-11
A	US 2012/0245260 A1 (Lunghi et al.) 27 September 2012 (27.09.2012) abstract, para[0016]-[0019], para [0067]-[0069]	1-11
A	US 2011/0034635 A1 (Kapur et al.) 10 February 2011 (10.02.2011) Abstract, para [0302], para [0293]	1-11
A	US 2013/0137828 A1 (Michie et al.) 30 May 2013 (30.05.2013) para [0002], para [0006], para [0161]	1-11
A	US 5,221,570 A (Gokcen et al.) 22 June 1993 (22.06.1993) col 3 ln 25-35	1-11
A	US 5,920,005 A (Moss) 6 July 1999 (06.07.1999) entire document	1-11
A	Muller; 'HDPE materials and Geomembrane manufacture in HDPE Geomembranes in geotechnics: Springer' [978-3-540-37288-2 (Online ISBN)]; pp 11-33 (2007)	1-11
A	Rowe et al.; 'Aging of HDPE geomembranes; J. Geotech. Geoeng. Engg. Vol 134, no. 7 pp 906-916 (July 2008) entire document'	1-11

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

* 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 19 August 2014 (19.08.2014)	Date of mailing of the international search report 15 SEP 2014
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774