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(54) Titre : TUYAUX MULTICOUCHES A POLYAMIDES RESISTANT A L'HYDROLYSE
(54) Title: MULTILAYERED PIPES COMPRISING HYDROLYSIS RESISTANT POLYAMIDES

(57) **Abrégé/Abstract:**

Multilayered pipes are provided wherein at least one layer comprises polyamide compositions having good hydrolysis resistance and that may optionally contain plasticizer. Such pipes are suited for applications transporting hydrocarbons. The pipes of the present invention may be in the form of flexible pipes.



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(54) Title: MULTILAYERED PIPES COMPRISING HYDROLYSIS RESISTANT POLYAMIDES

(57) Abstract: Multilayered pipes are provided wherein at least one layer comprises polyamide compositions having good hydrolysis resistance and that may optionally contain plasticizer. Such pipes are suited for applications transporting hydrocarbons. The pipes of the present invention may be in the form of flexible pipes.

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MULTILAYERED PIPES COMPRISING HYDROLYSIS RESISTANT POLYAMIDES

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Field of the Invention

The present invention relates multilayered pipes comprising hydrolysis resistant polyamide compositions that may optionally comprise plasticizer.

10 The pipes may be in the form of flexible pipes.

Background of the Invention

Pipes are used to convey a wide variety of liquids, gases, and fine
15 solids under a wide variety of conditions. Pipes are typically made from
metals, polymers, and metal-polymer composite structures, depending on the
materials to be conveyed and the conditions the pipes will be subjected to
during use. Because they have good chemical resistance, good physical
properties, and can be conveniently formed into pipes with a variety of
20 diameters and incorporated into multilayered pipes, polyamides are often a
desirable material to use for pipes. Multilayered pipes have many
applications, particularly in the oil and gas industry, where they are used to
transport oil and gas from undersea and under-land wells to the surface,
across the surface both above and below ground to refineries, to and from
25 storage tanks, etc. However, many applications using multi-layered pipes
require elevated temperatures. Examples include an undersea oil pipe that
comes into contact with hot oil from the earth's interior. Under such
conditions, the amide bonds of many polyamides may be susceptible to
hydrolysis in the presence of water and the rate of hydrolysis increases with
30 temperature. Hydrolysis of the amide bonds can cause a reduction in
molecular weight and concomitant loss in physical properties that can result in
failure of the pipe during use. Such a failure can be catastrophic, with the loss
of fluid causing undesirable consequences ranging from the impairment of the
performance of the device within which the piping is incorporated, to contact
35 of the fluid with the surrounding environment.

Aliphatic polyamides such as polyamide 6,12 or polyamide 11 are frequently used to make multilayered pipes, but many applications require greater hydrolysis resistance than can be obtained from currently available polyamides.

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It would be desirable to obtain a pipe comprising polyamide that has both improved hydrolysis resistance and can be conveniently plasticized to give it the flexibility needed to be useful in many applications. A further object of the present invention is to provide piping, tubing and the like which is readily prepared by conventional means well accepted in the field. A feature of the present invention is that the instant compositions are formable into any of a wide variety of structural designs and configurations. An advantage of the present invention is that these structural components can be further optimized for specialized functions with the addition of an assortment of additives including stabilizers, colorants, molding agents, and the like. These and other objects, features and advantages of the invention will become better understood upon having reference to the following description of the invention.

20

Summary of the Invention

There is disclosed and claimed herein multi-layered pipes comprising at least two concentric layers, wherein at least one layer comprises a polyamide composition comprising a polyamide comprising:

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- (a) about 2 to about 35 mole percent of repeat units derived from at least one aromatic dicarboxylic acid having 4 to 16 carbon atoms and/or at least one alicyclic dicarboxylic acid having 8 to 20 carbon atoms and at least one aliphatic diamine having 4 to 20 carbon atoms and/or at least one alicyclic diamine having 6 to 20 carbon atoms; and
- (b) about 65 to about 98 mole percent of repeat units derived from at least one aliphatic dicarboxylic acid having 6 to 36 carbon atoms and at least one aliphatic diamine having 4 to 20 carbon atoms and/or at least one alicyclic diamine having

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6 to 20 carbon atoms, and/or repeat units derived from at least one lactam having 4 to 20 carbon atoms and/or aminocarboxylic acid having 4 to 20 carbon atoms.

The polyamide composition may optionally further comprise plasticizer.

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Detailed Description of the Invention

There are a number of terms used throughout the specification for which the following will be of assistance in understanding their scope and meaning. As used herein and as will be understood by those skilled in the art, the terms "terephthalic acid", "isophthalic acid", and "dicarboxylic acid/dioic acid" refer also to the corresponding carboxylic acid derivatives of these materials, which can include carboxylic acid esters, diesters, and acid chlorides. Moreover and as used herein, and as will be understood by one skilled in the art, the term "hydrolysis resistant" in conjunction with a polyamide refers to the ability of the polyamide to retain its molecular weight upon exposure to water.

As used herein, the term "multilayered pipes" refers to structures defining a cavity therethrough for conducting a fluid, including without limitation any liquid, gas, or finely divided solid. They may have a circular or roughly circular (e.g. oval) cross-section. However more generally the pipes may be shaped into seemingly limitless geometries so long as they define a passageway therethrough. For example suitable shapes may include polygonal shapes and may even incorporate more than one shape along the length thereof. The pipes may further be joined together by suitable means to form T-sections, branches, and the like. The multilayered pipes may be flexible or stiff and have a variety of wall thicknesses and (in the event that the pipes are circular in cross section) diameters. The pipes comprise at least two layers, wherein at least one layer comprises a polyamide composition. The layers are concentric and at least two of the layers are made from different materials. Other layers may comprise other polymeric materials or metals. Polymeric materials include thermoplastic polymers and thermoset polymers such as an epoxy resin. Other layers may be formed from a tape or

other wrapping material, which made comprise a polyamide composition, other polymer material, metal, or other material. Other layers may also comprise a polymeric and/or metal mesh or sleeve.

5 The multilayered pipes of the present invention are particularly suitable for use in transporting hydrocarbons, including crude oil, natural gas, and petrochemicals. The hydrocarbons may contain water and/or alcohols.

10 The multilayered pipes of the present invention comprise at least one layer comprising a polyamide composition. The polyamide composition comprises a polyamide comprising about 2 to about 35 mole percent, or preferably about 4 to about 20 mole percent, or more preferably about 5 to about 11 mole percent of repeat units (a) derived from at least one aromatic dicarboxylic acid having 4 to 16 carbon atoms and/or at least one alicyclic
15 dicarboxylic acid having 8 to 20 carbon atoms and at least one aliphatic diamine having 4 to 20 carbon atoms and/or at least one alicyclic diamine having 6 to 20 carbon atoms. The polyamide comprises about 65 to about 98 mole percent, or preferably about 80 to about 96 mole percent, or more preferably about 89 to about 95 mole percent of repeat units (b) derived from
20 at least one aliphatic diamine having 4 to 20 carbon atoms and/or at least one alicyclic diamine having 6 to 20 carbon atoms and at least one aliphatic dicarboxylic acid having 6 to 36 carbon atoms and/or repeat units derived from at least one lactam and/or aminocarboxylic acid having 4 to 20 carbon atoms.

25

By "aromatic dicarboxylic acid" is meant dicarboxylic acids in which each carboxyl group is directly bonded to an aromatic ring. Examples of suitable aromatic dicarboxylic acids include terephthalic acid; isophthalic acid; 1,5-naphthalenedicarboxylic acid; 2,6-naphthalenedicarboxylic acid; and 2,7-naphthalenedicarboxylic acid. Terephthalic acid and isophthalic acid are
30 preferred. By "alicyclic dicarboxylic acid" is meant dicarboxylic acids in which each carboxyl group is directly bonded to a saturated hydrocarbon ring. An example of a suitable alicyclic dicarboxylic acids includes 1,4-cyclohexanedicarboxylic acid. By "alicyclic diamine" is meant diamines

possessing two primary or secondary amine groups and containing at least one saturated hydrocarbon ring. Alicyclic diamines preferably contain at least one cyclohexane moiety. Examples of suitable alicyclic diamines include 1-amino-3-aminomethyl-3,5,5-trimethylcyclohexane; 1,4-bis(aminomethyl)cyclohexane; and bis(*p*-aminocyclohexyl)methane. Any stereoisomers of the alicyclic diamines may be used.

Examples of aliphatic dicarboxylic acids having 6 to 36 carbon atoms include adipic acid, nonanedioic acid, decanedioic acid (also known as sebacic acid), undecanedioic acid, dodecanedioic acid, tridecanedioic acid, and tetradecanedioic acid. The aliphatic diamines having 4 to 20 carbon atoms may be linear or branched. Examples of preferred diamines include hexamethylenediamine, 2-methylpentamethylenediamine; 1,8-diaminooctane; methyl-1,8-diaminooctane; 1,9-diaminononane; 1,10-diaminodecane; and 1,12-diaminedodecane. Examples of lactams include caprolactam and laurolactam. An example of an aminocarboxylic acid includes aminodecanoic acid.

Preferred polyamides are semiaromatic polyamides. The polyamides preferably comprise repeat units (a) that are derived from terephthalic acid and/or isophthalic acid and hexamethylenediamine and repeats units (b) that are derived from at least one of nonanedioic acid and hexamethylenediamine; decanedioic acid and hexamethylenediamine; undecanedioic acid and hexamethylenediamine; dodecanedioic acid and hexamethylenediamine; tridecanedioic acid and hexamethylenediamine; tetradecanedioic acid and hexamethylenediamine; caprolactam; laurolactam; and 11-aminoundecanoic acid.

A preferred polyamide comprises from about 3 to about 40 mole percent of repeat units derived from terephthalic acid and hexamethylenediamine and complementally from about 60 to about 97 mole percent of repeat units derived from dodecanedioic acid and hexamethylenediamine. Another preferred polyamide comprises from about 3 to about 40 mole percent of repeat units derived terephthalic acid and

hexamethylenediamine and complementally from about 60 to about 97 mole percent of repeat units derived from decanedioic acid and hexamethylenediamine.

5 The polyamide used in the present invention may be prepared by any means known to those skilled in the art, such as in a batch process using, for example, an autoclave or using a continuous process. See, for example, Kohan, M.I. Ed. *Nylon Plastics Handbook*, Hanser: Munich, 1995; pp. 13-32. Additives such as lubricants, antifoaming agents, and end-capping agents
10 may be added to the polymerization mixture.

 The polyamide composition used in the present invention may optionally comprise additives. A preferred additive is at least one plasticizer. The plasticizer will preferably be miscible with the polyamide. Examples of
15 suitable plasticizers include sulfonamides, preferably aromatic sulfonamides such as benzenesulfonamides and toluenesulfonamides. Examples of suitable sulfonamides include *N*-alkyl benzenesulfonamides and toluenesulfonamides, such as *N*-butylbenzenesulfonamide, *N*-(2-hydroxypropyl)benzenesulfonamide, *N*-ethyl-*o*-toluenesulfonamide, *N*-ethyl-*p*-
20 toluenesulfonamide, *o*-toluenesulfonamide, *p*-toluenesulfonamide, and the like. Preferred are *N*-butylbenzenesulfonamide, *N*-ethyl-*o*-toluenesulfonamide, and *N*-ethyl-*p*-toluenesulfonamide.

 The plasticizer may be incorporated into the composition by melt-
25 blending the polymer with plasticizer and, optionally, other ingredients, or during polymerization. If the plasticizer is incorporated during polymerization, the polyamide monomers are blended with one or more plasticizers prior to starting the polymerization cycle and the blend is introduced to the polymerization reactor. Alternatively, the plasticizer can be added to the
30 reactor during the polymerization cycle.

When used, the plasticizer will be present in the composition in about 1 to about 20 weight percent, or more preferably in about 6 to about 18 weight percent, or yet more preferably in about 8 to about 15 weight percent, wherein
5 the weight percentages are based on the total weight of the composition.

The polyamide composition used in the present invention may optionally comprise additional additives such as impact modifiers; thermal, oxidative, and/or light stabilizers; colorants; lubricants; mold release agents;
10 and the like. Such additives can be added in conventional amounts according to the desired properties of the resulting material, and the control of these amounts versus the desired properties is within the knowledge of the skilled artisan.

15 When present, additives may be incorporated into the polyamide composition used in the present invention by melt-blending using any known methods. The component materials may be mixed to homogeneity using a melt-mixer such as a single or twin-screw extruder, blender, kneader, Banbury mixer, etc. to give a polyamide composition. Or, part of the materials may be
20 mixed in a melt-mixer, and the rest of the materials may then be added and further melt-mixed until homogeneous.

The pipes of the present invention may be formed by any method known to those skilled in the art, such as extrusion. The polyamide
25 composition used in the present invention may be extruded over one or more additional layers, including polymeric and metal layers. Additional layers may be added to a pipe comprising at least one layer comprising the polyamide used in the present invention by wrapping one or more additional layers around a pipe comprising at least one layer comprising the polyamide used in
30 the present invention. A polymeric layer made from an additional polymeric material may be added to a pipe comprising at least one layer comprising the polyamide used in the present invention by extrusion. The pipes will preferably have sufficient flexibility to allow them to be conveniently stored and transported.

In one embodiment, the multilayered pipes of the present invention are flexible pipes used in crude oil production to transport oil from wells.

Particularly preferred are undersea flexible pipes used to transport crude oil from undersea wells to the surface. Flexible pipes are often subjected to internal pressure and external stressing. Such pipes are described in U.S. patent 6,053,213, which is hereby incorporated herein by reference. Such pipes are also described in API 17B and 17J, published by the American Petroleum Institute under the title "Recommended Practice for Flexible Pipe."

Flexible pipe is preferably assembled as a composite structure comprising metal and polymer layers where the structure allows large deflections without a significant increase in bending stresses. At least one layer of the flexible pipe comprises the polyamide composition used in the present invention.

The flexible pipe may be of an unbonded type where the layers may move to a certain degree relative to one another. The layers of a flexible pipe may include a carcass that prevents the pipe from being crushed under outside pressure, which may comprise a fabric tape; an internal sheath comprising a polymer; a pressure vault; one or more armor layers; an anti-collapse sheath; and/or an outer sheath comprising polymer. Not all of these layers need be present and additional layers, such a metal tube that may be corrugated, may also be present. Anti-wear strips may be present between metal layers and may be in the form of a tape wrapped around metal layer beneath it. The anti-wear strips will preferably comprise the polyamide composition used in the present invention. The pressure vault may comprise shaped interlocked metal wires. At least one of the sheath layers may comprise the polyamide composition used in the present invention.

Examples

Determination of hydrolysis resistance

5 It is well known in the art that when hydrolyzed, polyamides often lose physical properties. The loss of physical properties is often directly correlated with a decrease in inherent viscosity of the polyamide. The degree of degradation may be conveniently studied by observing the decrease of a polyamide's inherent viscosity over time. Such a method is described in API
10 (American Petroleum Institute) Technical Report 17TR2, June 2003, and is the method upon which the following procedure is based.

 Hydrolysis resistance testing was done on compositions molded into standard ISO tensile bars that were immersed in distilled water in a pressure
15 vessel. The water and samples were held under vacuum for 30 minutes and then high-purity argon was bubbled through the water for 30 minutes to remove dissolved oxygen. The vessel was then sealed and placed in a conventional electrical heating mantle. The temperature in the vessel was controlled by use of a thermocouple in a thermowell in the wall of the vessel
20 and was maintained at 105 ± 1 °C and samples were withdrawn at intervals and their inherent viscosities and plasticizer contents were measured. After each sample was withdrawn, the water was replaced, a new sample was added, and the procedure repeated.

Inherent viscosity (IV) was measured by dissolving a sample of the polymer in *m*-cresol and measuring the IV in a capillary viscometer following ASTM 2857. Because plasticizer present in the samples could leach out during the hydrolysis testing and hence affect the measured IV, it was necessary to correct for the amount of plasticizer present in each sample.

In order to correct for the amount of plasticizer in each sample, the weight percent plasticizer content was measured by heating samples under vacuum and measuring the weight loss that occurred during heating. The inherent viscosity corrected for plasticizer content (CIV) was calculated by formula (1) (where plasticizer % is the weight percentage plasticizer present in the sample):

$$CIV = \frac{IV}{(100\% - \text{plasticizer}\%)} * 100\% \quad (1)$$

The percent loss of CIV was calculated by formula (2):

$$\%CIV \text{ loss} = \frac{CIV(t=x)}{CIV(t=0)} * 100\% \quad (2)$$

where $CIV_{(t=x)}$ is the CIV for the sample taken at time x and $CIV_{(t=0)}$ is the CIV for a sample taken before hydrolysis testing.

The % CIV loss was plotted as a function of $\log_{10}(\text{time})$, where time is the amount of time in hours each sample was exposed to water in the pressure vessel at 105 ± 1 °C. A linear least squares fit was made to the plot of % CIV loss as a function of $\log_{10}(\text{time})$ and a value for % CIV loss at 500 hours was calculated by interpolation from the least squares fit. The results are reported below.

Comparative Example 1

A polyamide 6,12 salt solution having a pH of about 8.0 and was prepared by dissolving hexamethylenediamine and 1,12-dodecanedioic acid in water. The concentration of salt in the solution was 45 percent by weight.

5 The salt solution (5,700 lbs) was charged to a vessel. A conventional antifoaming agent (250 g of a 10 percent by weight aqueous solution), phosphoric acid (about 0.18 lbs of a 78 percent weight aqueous solution), and *N*-butylbenzenesulfonamide (490 lbs) were added to the vessel. The resulting solution was then concentrated to 80 weight percent while heating under
10 pressure. The solution was then charged to an autoclave and heated. The pressure was allowed to rise to 265 psia. Heating was continued until the temperature of the reaction reached 255 °C, during which time steam was vented to maintain the pressure at 265 psia. The pressure was then reduced slowly to 14.7 psia while the reaction temperature was allowed to rise to 280
15 °C. The pressure was held at 14.7 psia and the temperature at 280 °C for 30 minutes. The resulting polymer melt was extruded into strands, cooled, and cut into pellets that were dried at 160 °C under nitrogen. The resulting polymer is referred to hereafter as "C1."

20 C1 (98.4 weight percent) was dry blended by tumbling in a drum with the stabilizers Tinuvin® 234 (0.5 weight percent), Irgafos® 168 (0.4 weight percent); Irganox® 1098 (0.4 weight percent); Chimassorb® 944F (0.3 weight percent). Each stabilizer is available from Ciba Specialty Chemicals, Tarrytown, NY. The resulting blend was then molded into standard ISO
25 tensile bars. The bars were subjected to hydrolysis testing as described above and the results are shown in Table 1. The % CIV loss at 500 hours was calculated to be 39.8% using the method described above.

Table 1

Sample	Exposure time (h)	Plasticizer content (wt. %)	Measured IV	CIV	CIV loss (%)
1	0	10.3	1.55	1.73	0
2	20	7.6	1.548	1.68	3.0
3	76	6.7	1.472	1.58	8.9
4	238	3.6	1.158	1.20	30.5
5	832	1.4	0.931	0.94	45.4
6	1153	0.8	0.878	0.89	48.8
7	1153	0.8	0.877	0.88	48.8

5

Example 1

A polyamide 6,12 salt solution having a pH of about 7.7 was prepared by dissolving hexamethylenediamine and 1,12-dodecanedioic acid in water. The solution had a concentration of about 44.6 weight percent. A polyamide
 10 6,T salt solution having a pH of about 8 was prepared by dissolving hexamethylenediamine and terephthalic acid in water. The 6,T salt solution had a concentration of about 40 weight percent. Both solutions were charged into an autoclave. A conventional antifoaming agent (10 g of a 10 percent by weight aqueous solution), sodium hypophosphite (0.014 g), and *N*-
 15 butylbenzenesulfonamide (51.1 g) were added to the autoclave. The resulting solution was then concentrated to 80 weight percent while heating under pressure. The concentrated solution was then heated and the pressure allowed to rise to 240 psia. Heating was continued until the temperature of the reaction reached 241 °C, during which time steam was vented to maintain
 20 the pressure at 240 psia. The pressure was then slowly reduced to 14.7 psia while the reaction temperature was allowed to rise to 270 °C. The pressure was held at 14.7 psia and the temperature at 280 °C for 60 minutes. The resulting polymer melt was extruded into a strand, cooled, and cut into pellets. The resulting polymer is referred to hereafter as "E1."

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E1 (98.4 weight percent) was dry blended by tumbling in a drum with the stabilizers Tinuvin® 234 (0.5 weight percent), Irgafos® 168 (0.4 weight

percent); Irganox® 1098 (0.4 weight percent); Chimassorb ® 944F (0.3 weight percent). Each stabilizer is available from Ciba Specialty Chemicals, Tarrytown, NY. The resulting blend was then molded into standard ISO tensile bars. The bars were subjected to hydrolysis testing as described
 5 above and the results are shown in Table 2. The % CIV loss at 500 hours was calculated to be 29.8% using the method described above.

Table 2

Sample	Exposure time (h)	Plasticizer content (wt. %)	Measured IV	CIV	CIV loss (%)
1	0	5.9	1.056	1.12	0
2	18	3.1	0.973	1.00	10.5
3	127	1.6	0.822	0.84	25.6
4	361.5	1.3	0.787	0.80	28.9
5	839	0.3	0.781	0.78	30.2

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A comparison of the results of Example 1, wherein the composition comprises a polyamide comprising repeat units derived from hexamethylenediamine and terephthalic acid and hexamethylenediamine and
 15 1,12-dodecanedioic acid, with those of Comparative Example 1, wherein the composition comprises a polyamide comprising only repeat units derived from hexamethylenediamine and 1,12-dodecanedioic acid, demonstrates that incorporation of repeat units derived from hexamethylenediamine and terephthalic acid leads to a substantial decrease in % CIV loss, and hence
 20 improvement in hydrolysis resistance.

What is Claimed is:

- 5 1. A multi-layered pipe comprising at least two concentric layers, wherein at least one layer comprises a polyamide composition comprising a polyamide comprising:
- 10 (a) about 2 to about 35 mole percent of repeat units derived from at least one aromatic dicarboxylic acid having 4 to 16 carbon atoms and/or at least one alicyclic dicarboxylic acid having 8 to 20 carbon atoms and at least one aliphatic diamine having 4 to 20 carbon atoms and/or at least one alicyclic diamine having 6 to 20 carbon atoms; and
- 15 (b) about 65 to about 98 mole percent of repeat units derived from at least one aliphatic dicarboxylic acid having 6 to 36 carbon atoms and at least one aliphatic diamine having 4 to 20 carbon atoms and/or at least one alicyclic diamine having 6 to 20 carbon atoms, and/or repeat units derived from at least one lactam having 4 to 20 carbon atoms and/or
- 20 aminocarboxylic acid having 4 to 20 carbon atoms.
2. The pipe of claim 1, wherein repeat units (a) are derived from terephthalic acid and hexamethylenediamine.
- 25 3. The pipe of claim 1, wherein repeat units (a) are derived from isophthalic acid and hexamethylenediamine.
4. The pipe of claim 1, wherein repeat units (b) are derived from decanedioic acid and hexamethylenediamine.
- 30 5. The pipe of claim 1, wherein repeat units (b) are derived from dodecanedioic acid and hexamethylenediamine.

6. The pipe of claim 2, wherein repeat units (b) are derived from decanedioic acid and hexamethylenediamine.

5 7. The pipe of claim 2, wherein repeat units (b) are derived from dodecanedioic acid and hexamethylenediamine

8. The pipe of claim 1, wherein the polyamide composition further comprises about 1 to about 20 weight percent, based on the total weight of the composition, of a plasticizer.

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9. The pipe of claim 8, wherein the plasticizer is a sulfonamide.

10. The pipe of claim 8, wherein the plasticizer is one or more of *N*-butylbenzenesulfonamide, *N*-(2-hydroxypropyl)benzenesulfonamide, *N*-ethyl-*o*-toluenesulfonamide, *N*-ethyl-*p*-toluenesulfonamide, *o*-toluenesulfonamide, and *p*-toluenesulfonamide.

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11. The pipe of claim 1, wherein the polyamide composition further comprises one or more of thermal oxidative, and/or light stabilizers; mold release agents; colorants; and lubricants.

20

12. The pipe of Claim 1 in the form of a flexible pipe.

13. The pipe of claim 12, wherein the pipe is an undersea oil pipe.

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