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(54) Title: PIPE PRODUCED WITH A POLYMER COMPOSITION COMPRISING A POLYETHYLEN

(57) Abstract: The invention relates a pipe for the transport of water with improved resistance to chlorinated disinfectants. The pipe is produced with a polymer composition comprising polyethylene and zinc sulfide.

PIPE PRODUCED WITH A POLYMER COMPOSITION
COMPRISING A POLYETHYLEN

The present invention relates to a pipe for the transport of water produced with a polymer composition comprising a polyolefin. The pipe has an improved resistance to chlorinated disinfectants.

Pipes for the transport of gas, for sanitation and for water supply may be produced with for example bimodal polyethylene compositions. Pipes have a very good resistance to water however their lifetime is shortened when the pipes come into contact with disinfectants which are often added to water for hygienic reasons. The chlorine dioxide used as disinfectant in water degrades most materials including polyethylene (Colin, Aging of polyethylene pipes transporting drinking water disinfected by chlorine dioxide, part I, Chemical aspects; Polymer engineering and Science 49(7); 1429-1437; July 2009). Other chlorinated solvents are for example chloramine and chlorine. It is known in the art to apply additives for example antioxidants and stabilizers to prevent said degradation. Several types of additives are proposed to protect polymers during processing and to achieve the desired end-use properties. However, appropriate combinations of stabilizers have to be carefully selected, depending on the desired final properties the polymeric article should have.

It is the object of the present invention to provide pipe applications with improved service lifetime for the transportation of water containing chlorinated disinfectants, for example chlorine dioxide, chloramine and chlorine.

The pipe according to the invention is produced with a polymer composition comprising polyethylene and zinc sulfide.

The drinking water pipe, preferably a pressure pipe, based on this polymer composition has an improved protection against for example chlorine dioxide containing cold or hot water and consequently a longer life time. It is also possible to transport waste water or water for cooling.

According to a further preferred embodiment of the invention the pipe is produced with a composition comprising

- (a) polyethylene
- (b) zinc sulfide
- (c) polyphenolic compound and/or
- (d) organic phosphite and/or phosphonite.

wherein the weight ratio (b): (c+d) ranges between 7:1 and 1:7.

Polyethylene may be selected from multimodal polyethylene for example bimodal or trimodal polyethylene.

Preferably, the polyolefin is bimodal polyethylene.

Suitable polyphenolic compounds include for example tetrakis[methylene-3-(3',5'-di-t-butyl-4-hydroxyphenyl)propionate] methane; 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane; 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene,
 5 bis(3,3-bis(4'-hydroxy-3'-t-butylphenyl)butanoic acid]-glycol ester; tris(3,5-di-t-butyl-4-hydroxy benzyl)isocyanurate; 1,3,5-tris(4-t-butyl-2,6-dimethyl-3-hydroxy-benzyl)isocyanurate; 5-di-t-butyl-4-hydroxy-hydrocinnamic acid triester with 1,3,5-tris(2-hydroxyethyl)-s-triazine-2,4,6(1H, 3H, 5H)-trione; p-cresol/ dicyclopentadiene butylated reaction product; 2,6-bis(2'-bis-hydroxy-3'-t-butyl-5'-methyl-phenyl-4-methyl-phenol).

10 A preferred polyphenolic compound is 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene (Irganox 1330 supplied by BASF).

Suitable organic phosphites and phosphonites include for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol
 15 diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphate, bis(2,6-di-tert-butyl-4-methylphenyl) pentaerythritol diphosphate, bisisodecyloxy-pentaerythritol diphosphite, bis(2,4-di-tert-butyl- 6-methylphenyl) pentaerythritol diphosphite, bis(2,4,6-tri-tert-butylphenyl) pentaerythritol diphosphite, tristearyl sorbitol triphosphite,
 20 tetrakis(2,4-di-tert-butylphenyl) 4,4'- biphenylenediphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenzo[d,g]-1,3,2-dioxaphosphocin, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyldibenzo[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl) methyl phosphite, bis(2,4-di-tert-butyl- 6-methylphenyl) ethyl phosphite.

25 A preferred phosphite is tris(2,4-di-tert-butylphenyl) phosphite (Irgafos 168 supplied by BASF).

According to another preferred embodiment of the invention the pipe is produced with a composition comprising

- (a) multimodal polyethylene
- (b) zinc sulfide
- 30 (c) polyphenolic compound
- (d) organic phosphite and/or phosphonite

wherein the weight ratio (b): (c+d) ranges between 7:1 and 1:7.

Preferably (b), (c) and (d) are added during the granulation step of the multimodal, for example bimodal, high density polyethylene powder.

According to a preferred embodiment of the invention the components are added to the polyethylene resin while the polyethylene is in a molten state during extrusion.

The components may be added together and may be added separately.

5 Preferably the components are added in one step.

Preferably the amount of the olefin polymer in the composition is higher than 95.0 wt%.

Preferably the amount of zinc sulphide, in the composition is lower than 2.0 wt%.

10 More preferably this amount is lower than 1.0 wt%.

Most preferably this amount ranges between 0.05 and 0.9 wt%.

These amounts protect the pipe against chlorine dioxide during a long period.

The multimodal ethylene polymer may be an ethylene homo- or copolymer.

The multimodal ethylene grades to be applied in pipe applications may
15 comprise additives such as for example carbon black, pigments, stearates, a UV stabilizer for example a sterically hindered amine, fillers, minerals, lubricants and/or other stabilisers.

The production processes for bimodal high density polyethylene (HDPE) are summarised at pages 16-20 of "PE 100 Pipe systems" (edited by Bromstrup; second
20 edition, ISBN 3-8027-2728-2).

The production of bimodal high density polyethylene (HDPE) via a low pressure slurry process is described by Alt et al. in "Bimodal polyethylene-Interplay of catalyst and process" (Macromol.Symp. 2001, 163, 135-143). Bimodal high density polyethylene may be produced via a low pressure slurry process for the production of
25 comprising a polymerisation stage, a powder drying stage, an extrusion and pellet handling stage, a recycling stage and a wax removal unit. In a two stage cascade process the reactors may be fed continuously with a mixture of monomers, hydrogen, catalyst/co-catalyst and diluent recycled from the process. In the reactors, polymerisation of ethylene occurs as an exothermic reaction at pressures in the range
30 between for example 0.5 MPa (5 bar) and 1MPa (10 bar) and at temperatures in the range between for example 75 °C and 88 °C. The heat from the polymerisation reaction is removed by means of cooling water. The characteristics of the polyethylene are determined amongst others by the catalyst system and by the concentrations of catalyst, co monomer and hydrogen. The production of bimodal high density
35 polyethylene (HDPE) via a low pressure slurry process may also be performed via a three stage process.

The concept of the two stage cascade process is elucidated at pages 137-138 by Alt et al. "Bimodal polyethylene-Interplay of catalyst and process" (Macromol. Symp. 2001, 163). The reactors are set up in cascade with different conditions in each reactor including low hydrogen content in the second reactor. This allows for the production of HDPE with a bimodal molecular mass distribution and defined co monomer content in the polyethylene chains.

Suitable catalysts for the production of multimodal polyethylene include Ziegler Natta catalysts, chromium based catalysts and single site metallocene catalysts. In all potential possible technologies the process and the catalyst have to form a well-balanced system. The catalyst is crucial for the polymerisation reaction of multimodal polyethylene. By cooperation of process and catalyst a definite polymer structure is produced.

The invention will be elucidated by means of the following non-limiting examples.

Examples

SABIC Vestolen A5924 (Resin A) used as base polymer in all examples was a bimodal high density polyethylene with MFR₅ of 0.24 g/10min and density 958 kg/m³.

Examples I and Comparative Examples A-C

The Example I and Comparative Examples A-B use different additive packages in combination with Resin A to protect the polyethylene from attack by chlorine dioxide (see Table 1). The components as indicated in Table 1 were mixed at 245 degrees Celcius using a twin screw extruder.

Table 1

Composition	Resin A wt%	Calcium stearate ppm	Carbon black wt%	Irganox 1010 ppm	Irgafos 168 ppm	Zinc sulfide ppm	Irganox 1330 ppm	DHT4A ppm
A	97	2000	2.5	2000	1000	0	0	0
B	96.15	2000	2.5	2000	2500	0	5000	2000
I	96.00	2000	2.5	2000	2500	2000	5000	2000

wherein:

- Irganox 1010 :Tetrakis [methylen- 3-(3 ',5 ')di-t-butyl-4 '-hydroxyphenyl) propionate] methane commercially available from Ciba Speciality Chemicals,
- Zinc sulfide: Sachtolith HS obtained from Sachtleben;
- 5 • Irganox 1330 : 1,3,5-Trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene;
- Irgafos 168: Tris(2,4-di-tert-butylphenyl) phosphite ;
- DHT-4A[®], commercially available hydrotalcite from Kisuma Chemicals.
- Resin A: SABIC Vestolen A5924; bimodal high density polyethylene with
- 10 MFR₅ 0.24 g/10min and density 958 kg/m³.

Compounds were compression molded using ISO1872-2 resulting in plaques, which were cut to ISO527-1A tensile bars (4 mm thick).

Ageing test

15 The tensile bars were aged in a continuous water flow at a temperature of 40 °C with a chlorine dioxide concentration maintained at 1 mg/L and a pH maintained at 7.2. Flow rate was regulated at 200 L/h. Water hardness was regulated to 20 °F. A constant fresh water flow was added during testing allowing full renewal of the testing water each 4 hrs.

20 The compression molded samples were aged for 1000 hrs.

Tensile tests according to Plastics- Determination of tensile properties ISO527-1 at room temperature at a strain rate of 50 mm/min on aged and non-aged tensile bars were performed to determine the residual elongation at break for the aged samples and reported in Table 2.

25

Table 2

Composition	Elongation @ break before ageing in %	Elongation @ break after ageing in %
A	466	33
B	301	259
I	347	321

Table 2 shows that Example I demonstrates significantly higher elongation at break after being exposed to water containing chlorine dioxide than Comparative Example A.

30 Comparing Comparative Example B to Example I shows that the effect of adding zinc sulfide had an additional effect on the elongation at break as obtained after

exposure to water containing chlorine dioxide.

CLAIMS

1. Pipe for the transport of water produced with a polymer composition comprising polyethylene and zinc sulphide.
2. Pipe according to Claim 1 characterised in that the composition comprises a
5 polyphenolic compound and/or an organic phosphite and/or phosphonite.
3. Pipe according to any one of Claims 1-2 characterised in that the polyolefin is multimodal polyethylene.
4. Pipe according to Claim 3 characterised in that the polyolefin is bimodal polyethylene.
- 10 5. Pipe according to any one of Claims 2-4 characterised in that the polyphenolic compound is 1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene
6. Pipe according to any one of Claims 2-5 characterised in that the phosphite is tris(2,4-di-*tert*-butylphenyl) phosphite.
7. Pipe according to any one of Claims 1-6 characterised in that the amount of zinc
15 salt in the composition is lower than 2.0 wt%.
8. Pipe according to any one of Claims 1-7 characterised in that the composition comprises
 - (a) polyethylene
 - (b) zinc sulfide
 - 20 (c) polyphenolic compound
 - (d) organic phosphite and/or phosphonitewherein the weight ratio (b): (c+d) ranges between 7:1 and 1:7.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08K3/30 C08L23/00 C08K5/13 C08K5/526 C08L23/06
 ADD.

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

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C08K C08L

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 361 951 A1 (BOREALIS AG [AT]) 31 August 2011 (2011-08-31)	1,2,5-8
Y	paragraphs [0080], [0085], [0086], [0070]; claim 19; examples IE1, IE2; tables	3,4
Y	----- US 2013/122226 A1 (LANIER ELIZABETH M [US] ET AL) 16 May 2013 (2013-05-16) claims 6,10; examples	3,4
Y	----- US 2015/090671 A1 (HJERTBERG THOMAS [SE] ET AL) 2 April 2015 (2015-04-02) paragraphs [0152] - [0155]	3,4

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	"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
"E" earlier application or patent but published on or after the international filing date	"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
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"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/051356

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