



(43) International Publication Date
29 September 2016 (29.09.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/150698 A1

(51) International Patent Classification:

C08K 3/22 (2006.01) *H01B 3/28* (2006.01)
C08K 5/521 (2006.01)

(21) International Application Number:

PCT/EP2016/054929

(22) International Filing Date:

8 March 2016 (08.03.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

15160355.2 23 March 2015 (23.03.2015) EP

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(81) Designated States (*unless otherwise indicated, for every*

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every*

kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: FLAME RETARDANT COMPOSITION COMPRISING A THERMOPLASTIC POLYETHERESTER ELASTOMER

(57) Abstract: A polymer composition comprising: (A) a thermoplastic copolyetherester elastomer, (B) a metal hydrate and (C) a monophosphate ester. Also claimed are a jacket or an insulation of a cable or wire of the polymer composition.



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FLAME RETARDANT COMPOSITION COMPRISING A THERMOPLASTIC
POLYETHERESTER ELASTOMER.

The invention relates to a flame retardant composition comprising a
5 copolyester thermoplastic elastomer. Such a composition is for example known from
EP-2047482.

Also described therein are cables having an insulation produced of
that composition. In this way a cable is provided that can withstand heavy flame
retardancy tests, so that the cable is suitable for many applications where flame
10 retardancy is important. It is also of interest that the composition and therefore also the
insulation is free of halogens. This is contrary to cable insulations of plasticized PVC.
A problem of the known composition however is the high price of the flame retardants
used in the composition. This puts a limit to the application of the composition and for
example many possibilities to replace plasticized PVC by the halogen free composition
15 are not practiced, because of the high price.

From WO 2014/135377 a flame retardant composition comprising a
thermoplastic copolyetherester is known that is less costly, but that shows nevertheless
a good flame retardancy. The flame retardant composition comprises next to the
thermoplastic copolyether ester elastomer a metal hydrate and an oligomeric
20 phosphate ester as flame retardants.

A problem however with the known composition is that, depending on
the oligomeric phosphate ester used, the composition has a limited resistance against
hydrolysis and/or shows bleeding of the oligomeric phosphate ester. A good resistance
against hydrolysis is for instance important if the composition is used in consumer
25 electronics that are used in eras with high temperature and high humidity, for example
in eastern Asia or in the Caribbean. Bleeding causes decline in flame retardancy and
gives a bad appeal to for instance wires and cables comprising an insulation and or a
jacket of the composition comprising the oligomeric phosphate ester.

Aim of the invention is to provide a polymer composition that shows a
30 good flame retardancy, is less costly as the known composition, but that has an
improved resistance against hydrolysis and bleeding.

Surprisingly this aim is achieved if the composition contains (A) a
thermoplastic copolyether elastomer, (B) a metal hydrate and (C) a monophosphate
ester.

35 A further advantage of the flame retardant composition according to

the invention is that the amount of the monophosphate can be used in the composition is higher than the amount of oligomeric phosphate that can be used in the known composition, before bleeding out of the phosphate takes place.

Yet a further advantage is the good processability, even at high
5 loadings of the metal hydrate.

(A). Copolyester thermoplastic elastomer.

Suitably, the copolyester thermoplastic elastomer is a
10 copolyesterester thermoplastic elastomer, a polycarbonate-ester thermoplastic elastomer, and /or a copolyetherester thermoplastic elastomer; i.e. a copolyester block copolymer with soft blocks consisting of segments of polyester, polycarbonate or, respectively, polyether. Suitable copolyesterester thermoplastic elastomers are described, for example, in EP-0102115-B1. Suitable polycarbonate-ester
15 thermoplastic elastomers are described, for example, in EP-0846712-B1. Copolyetherester thermoplastic elastomers and the preparation and properties thereof are in the art and for example described in detail in Thermoplastic Elastomers, 2nd Ed., Chapter 8, Carl Hanser Verlag (1996) ISBN 1-56990-205-4, Handbook of Thermoplastics, Ed. O. Otabisi, Chapter 17, Marcel Dekker Inc., New York 1997, ISBN
20 0-8247-9797-3, and the Encyclopedia of Polymer Science and Engineering, Vol. 12, pp. 75-117 (1988), John Wiley and Sons, and the references mentioned therein.

Copolyester thermoplastic elastomers are available, for example, under the trade name Arnitel, from DSM Engineering Plastics B.V. The Netherlands.

The aromatic dicarboxylic acid in the hard blocks of the copolyester
25 thermoplastic elastomer suitably is selected from the group consisting of terephthalic acid, isophthalic acid, phthalic acid, 2,6-naphthalenedicarboxylic acid and 4,4-diphenyldicarboxylic acid, and mixtures thereof. Preferably, the aromatic dicarboxylic acid comprises terephthalic acid, more preferably consists for at least 50 mole %, still more preferably at least 90 mole %, or even fully consists of terephthalic acid, relative
30 to the total molar amount of dicarboxylic acid.

The alkylene diol in the hard blocks of the copolyester thermoplastic elastomer suitably is selected from the group consisting of ethylene glycol, propylene glycol, butylene glycol, 1,2-hexane diol, 1,6-hexamethylene diol, 1,4-butane diol, benzene dimethanol, cyclohexane diol, cyclohexane dimethanol, and mixtures thereof.
35 Preferably, the alkylene diol comprises ethylene glycol and/or 1,4 butane diol, more

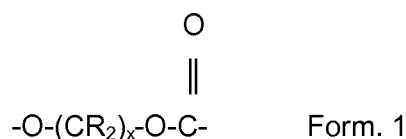
preferably consists for at least 50 mole %, still more preferably at least 90 mole %, or even fully consists of ethylene glycol and/or 1,4 butane diol, relative to the total molar amount of alkylene diol.

The hard blocks of the copolyester thermoplastic elastomer most preferably comprise or even consist of polybutylene terephthalate segments.

Copolyester thermoplastic elastomers have soft segments derived from at least one polyalkylene oxide glycol. Preferably, the polyalkylene oxide glycol is selected from the group consisting of polypropylene oxide glycol homopolymers (PPG), ethylene oxide / polypropylene oxide block-copolymers (EO/PO block copolymer) and poly(tetramethylene)glycol (PTMG), and mixtures thereof.

Copolycarbonate-ester thermoplastic elastomers have soft segments that comprise repeating units derived from an aliphatic carbonate. Suitable aliphatic carbonate units are represented by the formula

15



20 where

R = H, alkyl or aryl,

X=2 – 20.

Preferably R = H and x = 6, the aliphatic carbonate is therefore hexamethylene carbonate.

25 The soft segments may also comprise repeating units derived from an aliphatic diol and an aliphatic dicarboxylic acid and/or repeating units derived from a lactone.

The aliphatic diol contains preferably 2 – 20 carbon atoms, more preferably 3 – 15 carbon atoms. Most preferably the aliphatic diol is butylene glycol. The aliphatic

dicarboxylic acid preferably contains 2 – 10 carbon atoms, more preferably 4 – 15

30 carbon atoms. Most preferably the aliphatic dicarboxylic acid is adipic acid.

As lactone preferably caprolactone is used.

Preferably at least 40 wt. % of the soft segments consist of the aliphatic carbonate, more preferably at least 60 wt. %, even more preferably at least 80 wt. %, even more preferably at least 90 wt. %, even more preferably at least 95 wt. %, most preferably at least 99 wt. %.

35

The weight ratio of hard segments : soft segments may be between 20 : 80 and 90 : 10, preferably between 30 : 70 and 80 : 20, more preferably between 60 : 40 and 70 : 30.

One way of producing the copolycarbonate-ester thermoplastic elastomer is described in EP-A-1 964 871. According to this method polyester and aliphatic polycarbonate diols are reacted in the molten state by transesterification.

The hard segments and the soft segments of the copolycarbonate-ester thermoplastic elastomer are preferably connected by a bifunctional urethane group.

Preferably the soft segments of the copolyetherester are derived from poly(tetramethylene oxide)diol or poly(terahydrofuran)diol (pTHF) having a number average molecular weight (Mn) of between 1000 and 2500 kg/kmol. The value for Mn is normally provided by the supplier of the poly(terahydrofuran)diol and may be determined by GPC.

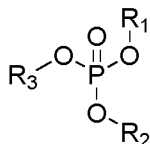
(B). Metal hydrate.

Examples of suitable metal hydrates include magnesium hydroxide, aluminum hydroxide, alumina monohydrate, hydromagnesite, zinc borate hydrate and any combination thereof. Preferably aluminum hydroxide is used.

The composition contains at least 15 wt.%, preferably at least 25 wt.%, more preferably at least 35 wt.%, most preferably at least 45 wt.% of the metal hydrate. The composition according to the invention preferably contains at most 70 wt.%, more preferably at most 65 wt.%, most preferably at most 55 wt.% of the metal hydrate.

(C). Monophosphate ester.

Suitable monophosphate esters are represented by formula 1.



Formula 1

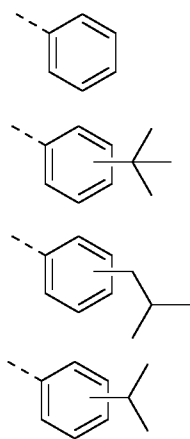
One group is formed by trialkyl phosphates where R1, R2 and R3 are

alkyl groups and are the same or different. Examples of such trialkylphosphates are trimethyl phosphate, triethyl phosphate, tributyl phosphate and trioctyl phosphate.

Another group is formed by alkylaryl phosphates, where R1 is an alkyl group, R2 is an aryl group and R3 is an alkyl or aryl group and can be the same or different as R1 or R2. An example of a suitable alkylaryl phosphate is octyldiphenyl phosphate.

Another group is formed by triaryl phosphates where R1, R2 and R3 are aryl groups and are the same or different. Examples of suitable aryl phosphates are triphenyl phosphate, tricresyl phosphate, trixylenyl phosphate, xylenyldiphenyl phosphate, and cresyldiphenyl phosphate.

Preferably the aryl groups R1, R2 and R3 are phenyl, tert-butylphenyl, isobutylphenyl or isopropylphenyl according to formula 2. Such aryl phosphate display high thermal stability.



The monophosphate ester may also be a mixture of one or more different monophosphate esters.

More preferably, the monophosphate ester is a mixture of triaryl phosphates where the aryl groups are chosen from phenyl, tert-butylphenyl, isobutylphenyl or isopropylphenyl where the component with R1 and R2 as well as R3 are a phenyl group is present in less than 5wt.% relative to the total weight of the monophosphate ester. Such monophosphate esters combine high thermal stability with high phosphorous content and thus good flame retardancy performance and low toxicity.

Preferably the monophosphate ester is a liquid at room temperature. Such monophosphate esters allow for easy possessing an good mechanical properties of the flame retardant composition comprising a thermoplastic polyetherester

elastomer.

Most preferably the monophosphate ester is a mixture of triaryl phosphates where the aryl groups are chosen from phenyl and tert-butylphenyl, and wherein the phenyl group is present in less than 5wt.% relative to the total weight of the monophosphate ester.

The composition according to the invention contains preferably between 4 and 30 wt.%, more preferably 8 – 25 wt.% of the monophosphate ester relative to the total weight of the thermoplastic composition. With this amount of monophosphate ester very good results are obtained with compounding of the composition and the metal hydrate keeps its function.

The composition according to the invention may suitably contain an anti-dripping agent. Suitable anti-dripping agents are fluorinated polymers such as polytetrafluoroethylene (PTFE). The thermoplastic composition according to the invention may comprise the anti-dripping agent in an amount of less than 2 wt.%, more preferably less than 1 wt.%, still more preferably 0.5 wt.%, even less than 0.2 wt.% relative to the total weight of the composition according to the invention.

The composition according to the invention may suitably comprise one or more additives.

Suitable additives include stabilizers, such as antioxidants, UV-absorbers and heat stabilizers, tougheners, impact modifiers, plasticizers, lubricants, emulsifiers, nucleating agents, fillers, pigments, optical brighteners, further flame retardants, and antistatic agents. Suitable fillers are, for example, calcium carbonate, silicates, talcum, and carbon black.

In a preferred embodiment of the invention the flame retardant thermoplastic composition comprises one or more additives in a total amount of 0.01 - 20 wt.%, more preferably 1-10 wt.%, still more preferably 2 - 4 wt.%.

Preferably the composition according to the invention comprises:

- (A) one or more thermoplastic copolyetherester elastomers
- (B) 15 - 70 wt. % metal hydrate,
- (C) 12.5 – 30 wt.% monophosphate ester,
- (D) 0.01 – 5 wt.% of one or more additives.

The invention also relates to jackets and insulations of electrical wires and cables of the composition according to the invention. The invention also relates to strain relieves of electrical cables of the composition according to the invention.

Examples:*Polyetherester:*

Polyetherester having 55 wt. % of soft blocks of pTHF having a number average molecular weight of 1000 kg/kmol and hard segments of polybutyleneterephthalate.

5

Flame retardants:

ATH: Apyral[™] 60 CD, aluminium hydroxide, delivered by Nabaltec from Germany.

Flame retardant.

10 RDP: Fyrolflex[™] RDP, resorcinol diphenyl phosphate, ICL Industrial Products from Israel.

TtBP: Phosphlex[™] 71B-HP, t-butylated triphenyl phosphate mixture, ICL Industrial Products from Israel.

Tests:

15 -VW-1: Vertical flame test, UL1581 VW-1.

-Hydrolysis resistance: Cable samples are exposed to 85 °C and 85% relative humidity conditions in a suitable climate chamber for 500 hrs. Samples are visually inspected for formation of solid or liquid residue formed on the cable surface.

20 -Bleeding: Cable samples are exposed to 25 °C and 50% relative humidity conditions in a suitable climate chamber for 500 hrs. Samples are visually inspected for formation of solid or liquid residue formed on the cable surface.

- Shore A: Shore A Hardness (3s), ISO 868.

Sample preparation:

25 Compositions were compounded by making a dry blend of the copolyetherester, other additives, the flame retardants and 0.1 wt% (with respect to the total composition) of anti-dripping agent in a tumbler in amounts indicated in Table 1. The dry blends were fed to and molten in a co-rotating twin screw extruder. After melting and mixing the sample was granulated at the die head of the twin screw
30 extruder. The melt temperature in the extruder was below 200 °C. Thereafter a cable with jacket thickness of approximately 0.40 mm was extruded on a metal conductor.

Testing.

35 The Vertical flame test, UL1581 VW-1, the hydrolysis resistance and the bleeding were determined according to the tests as described above. The results

are given in Table 1.

Discussion of the results of Examples I, II and comparative experiments A, B and C.

The amounts of phosphate ester were chosen that all samples pass
 5 the VW-1 test for flame retardancy. The monophosphate ester is good on both bleeding
 and hydrolysis resistance. The diphosphate ester RDP is insufficient w.r.t. hydrolysis
 resistance (comp. exp. A) or even insufficient w.r.t. both hydrolysis resistance and
 bleeding. The diphosphate ester BDP is insufficient w.r.t. bleeding. In addition, the high
 10 amount of phosphate ester that can be added in the case of the composition according
 to the invention results in low shore A hardness values that are desirable for application
 in flexible cables (see example II verses comparative experiment C).

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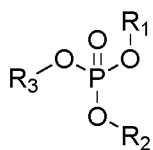
Table 1.

Data		Example				
		I	II	A	B	C
<i>Composition details</i>						
Polyetherester + additives	wt%	31.5	25.5	38.5	36.5	25.5
ATH	wt%	48.5	48.5	48.5	48.5	48.5
Phosphate	type	TtBP	TtBP	RDP	BDP	RDP
	wt%	20.0	26.0	13.0	15.0	26.0
<i>Test results</i>						
RT Bleeding		OK	OK	OK	NOK	NOK
VW-1		pass	pass	pass	pass	pass
Hydrolysis		OK	OK	NOK	OK	NOK
Shore A		87	83	93	92	84

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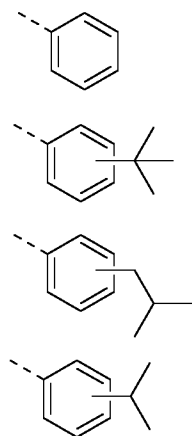
CLAIMS

1. A polymer composition comprising:
 - 5 (A) a thermoplastic copolyetherester elastomer,
 - (B) a metal hydrate and
 - (C) a monophosphate ester.
2. A polymer composition according to claim 1, wherein the copolyether ester contains soft segments derived from poly(tetrahydrofuran)diol.
- 10 3. A polymer composition according to any one of claims 1 or 2, wherein the composition comprises at least 15 wt. % of the metal hydrate.
4. A polymer composition according to any one of claims 1 – 3, wherein the monophosphate ester is represented by formula 1.



Formula 1.

- 15 5. A polymer composition according to claim 4, wherein phosphates where R1, R2 and R3 are alkyl groups and are the same or different.
- 6 A polymer composition according to claim 4, wherein where R1 is an alkyl group, R2 is an aryl group and R3 is an alkyl or aryl group and can be the same or different as R1 or R2.
- 20 7. A polymer composition according to claim 6, wherein R1, R2 and R3 are aryl groups and are the same or different.
8. A composition according to claim 4, wherein the aryl groups R1, R2 and R3 are phenyl, tert-butylphenyl, isobutylphenyl or isopropylphenyl according to



Formula 2.

9. Composition according to claim 8, wherein the aryl groups are chosen from phenyl and tert-butylphenyl, and wherein the phenyl group is present in less than 5wt.% relative to the total weight of the monophosphate ester.
10. Composition according to any one of the preceding claims, wherein the composition comprises:
 - (A) one or more thermoplastic copolyetherester elastomers
 - (B) 15 - 70 wt. % metal hydrate,
 - (C) 12.5 – 30 wt.% monophosphate ester,
 - (D) 0.01 – 5 wt.% of one or more additives
11. A jacket or an insulation of a cable or wire of the polymer composition according to any one of the preceding claims.
12. Strain relieve for an electrical cable of the polymer composition according to any one of the preceding claims.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/054929

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08K3/22 C08K5/521 H01B3/28
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 H01B

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/011939 A1 (DSM IP ASSETS BV [NL]; SCHMIDT ANGELIKA [NL]; SCHROEDER CHRISTIAAN [NL]) 31 January 2008 (2008-01-31)	1,3,4, 10-12
A	page 11, line 6 page 11, line 9 - line 24 page 7, line 5 claim 1 -----	2,5-9



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

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"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

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Date of the actual completion of the international search

31 March 2016

Date of mailing of the international search report

07/04/2016

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/054929

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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