



(51) International Patent Classification:

C08K 3/00 (2006.01) *C08K 3/22* (2006.01)
C08K 5/00 (2006.01) *C08K 3/26* (2006.01)
C08K 5/521 (2006.01) *C08K 5/092* (2006.01)
C08K 13/00 (2006.01) *C08K 5/11* (2006.01)
H01B 7/00 (2006.01) *C08K 5/12* (2006.01)

(21) International Application Number:

PCT/EP2014/079023

(22) International Filing Date:

22 December 2014 (22.12.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(71) Applicant: **PRYSMIAN S.P.A.** [IT/IT]; Viale Sarca, 222, I-20126 Milano (IT).

(72) Inventors: **SCRIMA, Vito**; c/o PRYSMIAN S.p.A., Viale Sarca, 222, I-20126 Milano (IT). **TOSI, Fabio**; c/o PRYSMIAN S.p.A., Viale Sarca, 222, I-20126 Milano (IT).

(74) Agents: **VIGANO', Elena** et al.; Via Trebbia, 20, I-20135 Milano (IT).

(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 HEAVY METAL-FREE COATING FOR AN ELECTRICAL CABLE

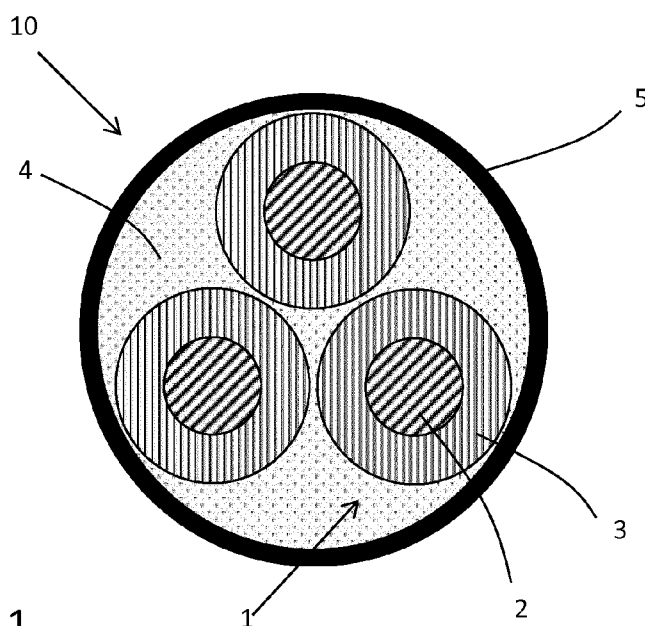


Figure 1

(57) Abstract: The present invention relates to an electrical cable comprising at least one conductor and at least one coating made from a flame-retardant heavy metal-free composition comprising (a) polyvinyl chloride (PVC) as polymer base material; (b) a calcium aluminum hydrate carbonate; (c) an aryl phosphate; (d) an inorganic flame-retardant filler; (e) a plasticizer.

FLAME-RETARDANT HEAVY METAL-FREE COATING FOR AN ELECTRICAL CABLE

DESCRIPTION

Background of the invention

5 The present invention relates to flame-retardant heavy metal-free electrical cables, in particular for low voltage power transmission. Also, the invention relates to flame-retardant heavy metal-free compositions suitable for producing said cables.

Flame-retardant cables are generally produced by extruding a flame-retardant coating made of a polymer composition having flame-retardant properties *per se* or imparted by the addition of a suitable flame-retardant additive over the core of the cable.

10 Polyvinyl chloride (PVC) is a polymeric material widely used in cable construction. Pure PVC is rather rigid and to make it suitably flexible for cable manufacturing it is added with plasticizers, the very commonly used being phthalates as from, for example, WO 2013/048775.

15 Although PVC by itself has valuable flame resistance, the majority of plasticizers used to impart flexibility to the PVC polymer can compromise this important technical characteristic as from, for example, WO 2014/013284.

Therefore, when PVC polymer is added with plasticizers in order to become flexible and suitable for being used in many different applications where its flexibility is an issue, it should be also added with suitable flame-retardant fillers, such as magnesium or
20 aluminium hydroxides, so that the resulting PVC polymer can impart the cable with suitable flame retardancy according to the standard, for example IEC 60332-1-2 (07-2004).

High levels of inorganic flame retardant filler lead to a reduction in processability and in mechanical and elastic properties of the resulting mixture, in particular as regards
25 impact resistance, elongation and stress at break. WO 2014/013284, for example, shows that substantial loading (i.e. about 40-100 phr or even more) with metal hydrates like aluminum or magnesium hydroxide is necessary to realize the flame retardant effects of these additives, so that their effect on the mechanical properties as well as on certain other properties of the PVC can be considerable.

30 Therefore, a flame-retardant synergistic agent, typically antimony trioxide (Sb_2O_3), is needed to keep the amount of inorganic filler within a limit not impairing the mechanical properties of the final product, as reported, for example, by Posner, S.

(2009), "Guidance on alternative flame retardants to the use of commercial pentabromodiphenylether (c-PentaBDE)", Norwegian Pollution control Authority (SFT) on behalf of UNEP, United Nations. The same paper refers that antimony trioxide is ranked as possible carcinogen by International Agency for Research on Cancer and by European Union.

Proposed substitutes for antimony trioxide as flame-retardant synergistic agent in PVC are triaryl phosphate, as reported, for example, by Paul Y. Moy, Proceedings of the 61st IWCS Conference, 2012, page 373.

PVC must also be stabilized, in order to be processed, against the action of heat required at processing temperatures, as reported, for example, by WO 2014/013284. The necessary protection is provided by the addition of heat stabilizers. PVC molecule is unstable to heat and light. Heating PVC causes breakage of the polymer chains, liberating hydrochloric acid in the gaseous state. HCl catalyzes additional degradation, releasing large quantities of corrosive HCl. The main classes of PVC stabilizers are complex mixtures of metal, for example calcium/zinc (Ca/Zn) stabilizers.

However, as reported, for example, by US 8,506,854, stabilizers containing heavy metals, like Ca/Zn, have an impaired environmental compatibility.

In 2010, Nabaltec launched a product based on calcium aluminum hydrate carbonate (CAHC). In particular, the presentation "ATO replacement" of Nabaltec (Feb 2013) relates to formulations comprising PVC (Vinnolit S4170), diisononyl phthalate (DINP) and Ca/Zn stabilizer (Naftosafe P KX 163 G) and optionally comprising aluminium hydroxide (ATH = Apyral 40CD), antimony oxide (ATO), calcium aluminum hydrate carbonate (CAHC Actilox) and/or zinc borate. It is stated and shown that a LOI (limiting oxygen index) of 31% O₂ can only be achieved with formulations containing 30 phr of aluminium hydroxide in the presence of antimony oxide.

Summary of the invention

The Applicant faced the problem of providing flame-retardant cables having a significant limiting oxygen index (LOI) (preferably greater than 30%) by using a flame-retardant heavy metal-free composition (free from antimony trioxide and Ca/Zn stabilizers) having good processability and suitable mechanical properties, particularly in terms of tensile strength and elongation at break, even after thermal ageing.

Within the present description and claims, the limiting oxygen index (LOI) is the minimum concentration of oxygen, expressed as a percentage, that will support combustion of a polymer. Higher values of LOI indicate greater fire retardancy. LOI

values are determined by standardized tests, such as CEI 20-22/2 (2006).

The Applicant observed that Ca/Zn stabilizers can be replaced by calcium aluminum hydrate carbonate (CAHC), while Sb_2O_3 can be replaced by aryl phosphates that, in addition, can play a role as co-plasticizer. But when a cable with a substantial LOI is sought (greater than 30%), the use of CAHC requires the presence of Sb_2O_3 anyway. Therefore, a heavy-metal free PVC composition with improved LOI value is sought.

The Applicant found that a cable with at least one flame-retardant heavy metal-free coating based on polyvinyl chloride (PVC) comprising a calcium aluminum hydrate carbonate, an aryl phosphate, a inorganic flame-retardant filler and a plasticizer have a LOI greater than 30% when an amount of inorganic flame-retardant filler of at least 50 phr and up to 100 phr or even more is used. Surprisingly, the Applicant found that with the above combination of components, such a “heavy” amount of inorganic filler does not decrease processability and mechanical properties, even after thermal ageing, of the resulting composition.

The above flame-retardant cable coating according to the invention, being totally free of heavy metals, allows to overcoming the above mentioned drawbacks, in particular in terms of toxicity.

Therefore, according to a first aspect, the present invention relates to an electrical cable comprising at least one conductor and at least one coating made from a flame-retardant heavy metal-free composition, composition comprising:

(a) polyvinyl chloride (PVC) as polymer base material;

(b) a calcium aluminum hydrate carbonate;

(c) an aryl phosphate;

(d) an inorganic flame-retardant filler;

(e) a plasticizer;

wherein the inorganic flame-retardant filler (d) is present in an amount of at least 50 phr.

For the purpose of the present description and of the appended claims, except where otherwise indicated, all numbers expressing amounts, quantities, percentages, and so forth, are to be understood as being modified in all instances by the term “about”. Also, all ranges include any combination of the maximum and minimum points disclosed and

include any intermediate ranges therein, which may or may not be specifically enumerated herein.

According to the present description and claims, as "flame-retardant" is meant a cable provided with a material having the capacity of delaying the flame propagation
5 according to IEC 60332-1-2 (07-2004).

In the present description and in the subsequent claims, as "heavy metal" it is meant an element provided with atomic number greater than 20, such as: zinc, arsenic, lead, copper, iron, manganese and antimony.

In the present description and in the subsequent claims, as "conductor" is meant a
10 element of elongate shape made of an electrically conductive metallic material, e.g. aluminium or copper or composite thereof.

Polyvinyl chloride (PVC) is produced by polymerization of the monomer vinyl chloride (VCM). The PVC is a synthetic polymer material or resin, product by repetitive addition of VMC, whose formula $\text{CH}_2=\text{CHCl}$.

15 The electrical cable according to the invention is preferably a low voltage cable. In the present description and claims as "low voltage" is meant a voltage of 1.5 kV at most.

The electrical cable of the invention can have one or more conductors.

Each conductor of the electrical cable of the invention can be surrounded by insulating layer, preferably in contact therewith, and by a sheath. In the case of more conductors,
20 the sheath preferably collectively surrounds all of the cable conductors. Advantageously at least the sheath is made from a flame-retardant heavy metal-free composition according to the present invention.

The electrical cable of the invention has a limiting oxygen index (LOI) greater than 30%.

25 According to another aspect, the present invention relates to a flame-retardant heavy metal-free composition comprising:

(a) polyvinyl chloride (PVC) as polymer base material;

(b) a calcium aluminum hydrate carbonate;

(c) an aryl phosphate;

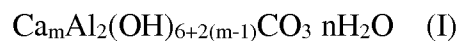
30 (d) an inorganic flame-retardant filler;

(e) a plasticizer;

wherein the inorganic flame-retardant filler (d) is present in an amount of at least 50 phr.

Detailed description of the invention

- 5 The calcium aluminium hydrate carbonate (b) can be selected from those which can be identified, for example, by the following general formula (I):



wherein $m = 3.5$ to 4.5 and $n = 0$ to 6 as described, for example, in patent US 7,919,066.

Preferably, m and n are equal to 4 .

- 10 Examples of calcium aluminium hydrate carbonates which are currently commercially available include the product Actilox® CAHC from Nabaltec.

The calcium aluminium hydrate carbonate is advantageously used in the present invention as PVC stabilizer in order to replace Ca/Zn stabilizer.

- 15 The aryl phosphate (c) is preferably selected from triaryl phosphates, alkyl diaryl phosphates and mixtures thereof.

- More preferably, the aryl phosphate (c) of the invention is selected from: triphenyl phosphate, trixylenyl phosphate, tricresyl phosphate, cresyl diphenyl phosphate, tris(isopropylphenyl) phosphate, isopropylphenyl diphenyl phosphate, tertbutylphenyl diphenyl phosphate, 2-ethylhexyl diphenyl phosphate, isodecyl diphenyl phosphate and
20 tetraphenyl resorcinol diphosphate.

Even more preferably, the triaryl phosphate (c) is triaryl phosphate isopropylated.

The aryl phosphates (c) are advantageously used in the present invention in order to replace antimony trioxide.

- 25 As to the flame-retardant filler (d), it may be selected from hydroxides, carbonates, hydrated oxides, hydrated salts of metals, such as: magnesium hydroxide (either synthetic or natural, e.g. brucite), aluminium hydroxide, hydrated magnesium carbonate, magnesium carbonate, calcium carbonate or mixtures thereof. Magnesium carbonate, aluminium hydroxide and magnesium hydroxide are particularly preferred.

The plasticizer (e) is selected from phthalate and non-phthalate plasticizers.

Phthalate plasticizers suitable for the present invention can be selected from the group comprising di(2-ethylhexyl) phthalate (DEHP), diisononyl phthalate (DINP), diisodecyl phthalate (DIDP) and diisotridecyl phthalate (DITP).

- 5 Non-phthalate plasticizers suitable for the present invention can be selected from the group comprising dioctyl terephthalate (DOTP), trioctyl trimellitate (TOTM), 1,2-cyclohexane dicarboxylic acid diisononyl ester (DINCH) and citrate-based plasticizers. DOTP and TOTM are particularly preferred.

Non-phthalate plasticizers are advantageous also due to some favorable toxicological profile compared to phthalates.

- 10 According to a preferred embodiment, the calcium aluminum hydrate carbonate (b) is present in an amount of from 2.5 to 10 phr.

The term “phr” (acronym of “parts per hundred of rubbers”), is used to indicate parts by weight per 100 parts by weight of the polymer base material.

- 15 Preferably, the aryl phosphate (c) is present in an amount of from 15 to 50 phr. More preferably, the aryl phosphate (c) is present in an amount from 25 to 30 phr.

- Preferably, the inorganic flame-retardant filler (d) is present in an amount of from 50 to 100 phr. More preferably, the inorganic flame-retardant filler (d) is present in an amount from 50 to 90 phr. Amounts of inorganic flame-retardant filler (d) greater than 100 phr could provide a flame-retardant composition according to the invention with suitable mechanical features for the use in a cable coating, though limited LOI value increases are expected.
- 20

Preferably, the plasticizer (e) is present in an amount of from 15 to 50 phr. More preferably, the plasticizer (e) is present in an amount from 15 to 30 phr.

- 25 Other conventional components such as processing co-adjuvants, lubricants, pigments, other fillers and the like can be added to the flame-retardant heavy metal-free composition according to the present invention. Antioxidants are not usually necessary because of the presence of calcium aluminium hydrate carbonate (b) as stabilizer.

Preferably, said at least one processing co-adjuvant is added in an amount of from 1 to 2 phr.

- 30 The flame-retardant heavy metal-free compositions according to the present invention can be prepared by mixing the PVC resin and the additives according to methods known in the art, for example using an internal mixer (turbomixer), or continuous mixers of the

Ko-Kneader (Buss) type or of the co- rotating or counter-rotating twin-screw type.

The flame-retardant heavy metal-free composition according to the present invention may be used to make an outer sheath on a conductor previously coated with an insulating layer. The application of the flame-retardant heavy metal-free composition can be carried out, for example, by extrusion or by co-extrusion with the insulating layer.

Further details will be illustrated in the following detailed description, with reference to the appended Figure 1 which is a cross section view of a cable according to the present invention for power transmission at low voltage.

10 With reference to figure 1, the fire resistant power cable 10 is of the tripolar type comprising three conductors 2 each covered by an insulating layer 3 to form a core 1. The three cores 1 are encircled by a sheath 5. The three cores 1 are stranded together forming interstitial zones defined as the spaces between the cores 1 and the cylinder (the sheath 5) enveloping such cores. A bedding or interstitial filler 4 fills said interstitial zones.

The insulating constant k_i of the electrical insulating layer 3 is such that the required electric insulating properties are compatible with the standards (e.g. CEI 20-34_2001, IEC 60502-1, 2nded.-2004 or other equivalent thereto). For instance, the electrical insulating layer 3 has an insulating constant k_i equal to or greater than $3.67 \text{ MOhm}\cdot\text{km}$ at 90°C . The conductors 2 can be in form of a solid rod or of bundled wires made of electrically conductive metal such as copper or aluminum or composite thereof.

The sheath 5 is made of the flame-retardant heavy metal-free composition according to the present invention and, usually, is applied by extrusion.

The following working examples are given to better illustrate the invention, but without limiting it.

Preparation of the flame-retardant compositions

The flame-retardant compositions of the examples reported in Table 1 were prepared in a closed turbomixer (volume of the mixing chamber: 3000 cm^3). The amounts are reported as parts by weight with respect to 100 parts by weight of the PVC resin.

TABLE 1

Example	1*	2*	3*	4*	5*	6*	7*	8	9	10	11	12
PVC	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0
MgCO ₃	30,0	30,0	30,0	30,0	30,0	30,0	80,0	50,0	50,0	50,0	80,0	80,0
DINP	50,0	50,0	50,0	35,0	30,0	25,0	28,0	25,0	20,0	20,0	20,0	
DOTP												20,0
triArP i-Pro				15,0	20,0	25,0	20,0	25,0	30,0	30,0	30,0	30,0
Ca/Zn stabilizer	5,0	5,0					5,0					
CAHC	5,0		5,0	5,0	5,0	5,0		5,0	5,0	5,0	5,0	5,0
Sb ₂ O ₃							5,0					
SiO ₂	5,0	5,0	5,0	5,0	5,0	5,0		5,0	5,0			
Stearic acid	2,0	2,0	2,0	2,0	2,0	2,0	1,0	2,0	2,0	2,0	1,0	1,0

The examples marked by the asterisk (*) are the comparative ones.

DINP: diisononyl phthalate

DOTP: dioctyl terephthalate

triArP i-Pro : triaryl phosphate isopropylated

- 5 Ca/Zn stabilizer: Ca: Zn ratio of 16:1 (marketed by Baerlocher)

CAHC: calcium aluminum hydrate carbonate wherein m is 4 (marketed by Nabaltec as Actilox® CAHC)

SiO₂: spherical, submicron particles of amorphous silicon dioxide (BET 18-25 m²/g) marketed by Elkem AS, as Sidistar® T 120

- 10 The compositions of Examples 1-12 of Table 1 were evaluated for a number of properties and the results are set forth in Table 2.

TABLE 2

Example	Required values	1*	2*	3*	4*	5*	6*	7*	8	9	10	11	12
LOI (%)	>30	26	25	26	29	29	30	35,5	32	31	33	35	37,0
Thermal stability (min)	-	90	60	60	65	50	55	30	50	50	50	40	35
Tensile strength (Mpa)	≥12.5	17,6	15,6	18,1	20,4	20,0	20,3	16,3	18,6	18,7	20,5	17,5	17,4
Elongation at break (%)	≥150	284	232	281	268	264	253	217	247	230	235	246	232,9
Tensile strength after ageing (Mpa)	≥12.5	17,5	17,1	18,3	20,1	19,4	20,9	17,0	18,7	18,9	19,6	16,6	17,7
Elongation at break after ageing (%)	≥150	270	242	264	248	250	256	208	232	229	232	212	212,8

LOI (limiting oxygen index) was measured, according to CEI 20-22/2 (2006), on cable specimens obtained as described for the mechanical tests, but with a thickness of 3 mm.

The thermal stability was measured according to IEC 60811-3-2 (1985).

- 5 Tensile strength and elongation at break were measured according to IEC 60811-501 ED.1 (2012) on dumbbells. The same measurements of mechanical properties were also performed after thermal ageing, carried out on the same cable specimens after exposure in air oven for 168 hours at 100°C.

- 10 The Examples with the comparative compositions 1-6 does not have the sought LOI value greater than 30%. In particular, Examples 1-6 have a LOI of 30% or less showing that their concentration of aryl phosphate is not sufficient for boosting the action of the flame retardant filler at an amount lower than 50 phr. Moreover, the comparative compositions 1-2 comprise the potentially toxic Ca/Zn stabilizer.

- 15 The comparative composition of Example 7 has the sought LOI value greater than 30%, but comprises the potentially toxic heavy-metal additives (Ca/Zn and Sb_2O_3). The elongation at break – both at room temperature and after ageing - of this composition, though complying the standard requirement, is lower than that of the other examples.

Compositions 8-12 according to the invention have a LOI value greater than 30% and suitable mechanical properties even after ageing.

- 20 Clearly, a man skilled in the art may introduce modifications and variants to the invention described hereinbefore in order to meet specific and contingent application requirements, variants and modifications which anyway fall within the scope of protection as defined in the attached claims.

CLAIMS

1. An electrical cable comprising at least one conductor and at least one coating made from a flame-retardant heavy metal-free composition comprising:

(a) polyvinyl chloride (PVC) as polymer base material;

5 (b) a calcium aluminum hydrate carbonate;

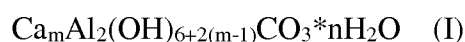
(c) an aryl phosphate;

(d) an inorganic flame-retardant filler;

(e) a plasticizer;

10 wherein the inorganic flame-retardant filler (d) is present in an amount of at least 50 phr.

2. The electrical cable according to claim 1, wherein the calcium aluminum hydrate carbonate (b) is selected from those having the following general formula (I):



wherein $m = 3.5$ to 4.5 and $n = 0$ to 6 , preferably n and m are equal to 4 .

15 3. The electrical cable according to claim 1, wherein the aryl phosphate (c) is selected from triaryl phosphates, alkyl diaryl phosphates and mixtures thereof.

4. The electrical cable according to claim 3, wherein the aryl phosphate (c) is selected from the group comprising triphenyl phosphate, trixylenyl phosphate, tricresyl phosphate, cresyl diphenyl phosphate, tris(isopropylphenyl) phosphate, isopropylphenyl
20 diphenyl phosphate, tertbutylphenyl diphenyl phosphate, 2-ethylhexyl diphenyl phosphate, isodecyl diphenyl phosphate and tetraphenyl resorcinol diphosphate.

5. The electrical cable according to claim 1, wherein the inorganic flame-retardant filler (d) is selected from hydroxides, carbonates, hydrated oxides, hydrated salts of metals.

6. The electrical cable according to claim 5, wherein the inorganic flame-retardant filler
25 (d) is selected from the group comprising magnesium hydroxide, aluminium hydroxide, magnesium carbonate, calcium carbonate and mixtures thereof.

7. The electrical cable according to claim 1, wherein the plasticizer (e) is selected from phthalate and non-phthalate plasticizers.

8. The electrical cable according to claim 7, wherein the phthalate plasticizer is selected from the group comprising di(2-ethylhexyl) phthalate (DEHP), diisononyl phthalate (DINP), diisodecyl phthalate (DIDP) and diisotridecyl phthalate (DITP).
9. The electrical cable according to claim 7, wherein the non-phthalate plasticizer is selected from the group comprising dioctyl terephthalate (DOTP), trioctyl trimellitate (TOTM), 1,2-cyclohexane dicarboxylic acid diisononyl ester (DINCH) and citrate-based plasticizers.
10. The electrical cable according to claim 1, wherein the calcium aluminum hydrate carbonate (b) is present in an amount of from 2.5 to 10 phr.
11. The electrical cable according to claim 1, wherein the aryl phosphate (c) is present in an amount of from 15 to 50 phr, preferably from 25 to 30 phr.
12. The electrical cable according to claim 1, wherein the at least one inorganic flame-retardant filler (d) is present in an amount of from 50 to 100 phr, preferably from 50 to 90 phr.
13. The electrical cable according to claim 1, wherein the plasticizer (e) is present in an amount of from 15 to 50 phr, preferably from 15 to 30 phr.
14. The electrical cable according to claim 1 wherein the conductor/s is/are surrounded by a sheath made from a flame-retardant heavy metal-free composition.
15. A flame-retardant heavy metal-free composition comprising:
- (a) polyvinyl chloride (PVC) as polymer base material;
 - (b) a calcium aluminum hydrate carbonate;
 - (c) an aryl phosphate;
 - (d) an inorganic flame-retardant filler;
 - (e) a plasticizer;
- wherein the inorganic flame-retardant filler (d) is present in an amount of at least 50 phr.
16. The flame-retardant heavy metal-free composition according to claim 15, defined according to anyone of claims from 2 to 13.

1/1

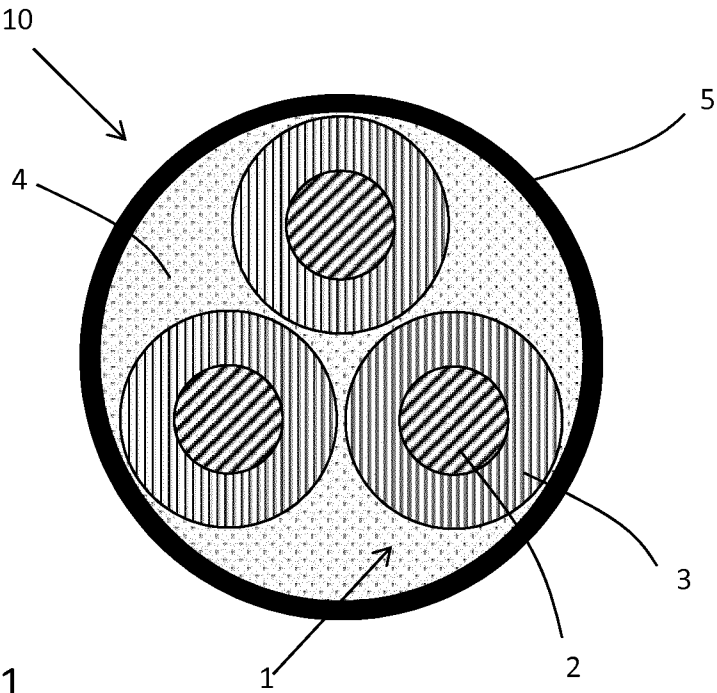


Figure 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/079023

A. CLASSIFICATION OF SUBJECT MATTER		
INV. C08K3/00	C08K5/00	C08K5/521
ADD. C08K3/22	C08K3/26	C08K5/092
		C08K13/00
		C08K5/11
		H01B7/00
		C08K5/12
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, 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	WO 2014/013284 A1 (ITALMATCH CHEMICALS SPA [IT]; ZUCCHELLI UGO [IT]) 23 January 2014 (2014-01-23) cited in the application	15,16
Y	abstract; claims 1-14 page 3, last paragraph pages 6-7 page 10, paragraph 3	1-16
Y	US 7 919 066 B2 (SAUERWEIN REINER [DE] ET AL) 5 April 2011 (2011-04-05) cited in the application abstract; examples 6,7; table 3 column 4, lines 3-19 column 5, lines 5-8,48-67 column 6, lines 1-5 column 7, lines 22,43 ----- -/-	1-16
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 12 August 2015		Date of mailing of the international search report 20/08/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Schütte, Maya

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/079023

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2011/275747 A1 (HACKER PETER [DE] ET AL) 10 November 2011 (2011-11-10) abstract; claims 1-12; table 1.1 paragraphs [0012], [0021], [0055] - [0057], [0062] - [0079] paragraphs [0157], [0161] - [0163], [0180] -----	1-16
Y	US 2012/208941 A1 (REITH WALTER [DE]) 16 August 2012 (2012-08-16) abstract; claim 1 paragraphs [0002], [0019], [0023], [0061], [0062], [0172], [0175] - [0191] -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/079023

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014013284	A1	23-01-2014	EP 2875069 A1 27-05-2015
			KR 20150042159 A 20-04-2015
			WO 2014013284 A1 23-01-2014

US 7919066	B2	05-04-2011	CN 101541680 A 23-09-2009
			DE 102006055214 A1 29-05-2008
			EP 2099714 A1 16-09-2009
			ES 2394860 T3 06-02-2013
			JP 5345064 B2 20-11-2013
			JP 2010510149 A 02-04-2010
			KR 20090092814 A 01-09-2009
			MY 148795 A 31-05-2013
			PT 2099714 E 28-11-2012
			RU 2009123484 A 27-12-2010
			US 2009292052 A1 26-11-2009
			US 2011152430 A1 23-06-2011
			WO 2008061664 A1 29-05-2008
			ZA 200903434 A 28-04-2010

US 2011275747	A1	10-11-2011	NONE

US 2012208941	A1	16-08-2012	DE 102009045701 A1 21-04-2011
			EP 2488578 A1 22-08-2012
			RU 2012119162 A 20-11-2013
			US 2012208941 A1 16-08-2012
			WO 2011045168 A1 21-04-2011
