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(54) **Title:** POLYETHYLENE-BASED GRANULATED MATERIAL, PRODUCTION PROCESS THEREOF AND USE THEREFOR FOR MANUFACTURING CABLES

(57) **Abstract:** Granulated material and production process thereof, the granulated material comprising: (a) from 70% to 95% by weight of at least one ethylene homopolymer or copolymer of ethylene with at least one alpha-olefin C₃-C₁₂, having a density from 0.910 g/cm³ to 0.926 g/cm³; (b) from 2% to 25% by weight of at least one polymer selected from: (b1) copolymers of ethylene with at least one alpha-olefin C₃-C₁₂, having a density from 0.860 to 0.905 g/cm³, and a molecular weight distribution index (MWDI) not greater than 4; (b2) copolymers of ethylene with at least one ester having one ethylenic unsaturation; (c) from 0.1% to 7% by weight of at least one organic peroxide. The above granulated material allows to considerably reduce exudation of the peroxide and of possible other additives, in particular following prolonged exposure to extreme ambient temperatures. Moreover, the impregnation times of the granulated material with the peroxide are substantially shortened, so as to increase the productivity and reduce processing costs. Such a granulated material has advantageous use in the production of at least one coating layer of an electrical cable.

POLYETHYLENE-BASED GRANULATED MATERIAL, PRODUCTION
PROCESS THEREOF AND USE THEREOF FOR MANUFACTURING
CABLES

5 The present invention concerns a polyethylene-based
granulated material, the production process thereof and
the use thereof for manufacturing cables. More
specifically, the present invention concerns a
polyethylene-based granulated material containing at
10 least one organic peroxide, the production process
thereof and the use thereof for manufacturing cables
having at least one cross-linked insulating layer.

As known, suitable substances are often
incorporated in plastic materials, like for example
15 crosslinking agents, antioxidants and other additives,
in order to provide the end product with specific
chemical-physical, mechanical and electrical
properties. In particular, in the manufacture of
electrical cables to be used for transporting or
20 distributing medium, high or very high voltage
electrical energy, at least one layer of polyolefin-
based electrically insulating material is deposited on
the conductor through extrusion from a granulated
material of the polymeric base in which at least one
25 crosslinking agent has been incorporated, in particular
an organic peroxide (for example dicumyl peroxide).
After the extrusion, the cable is suitably heated so as
to carry out the cross-linking process of the polymeric
material thanks to the action of the radicals deriving
30 from the decomposition of the cross-linking agent. The
polyolefin base generally consists of a low density
polyethylene (LDPE), which, after crosslinking, is

endowed with the necessary mechanical and electrical properties suitable for ensuring effective electrical insulation for the lifetime foreseen for the electrical cable itself (in general 40 years). In these cases,
5 they are generally known as XLPE insulated cables.

In order to manufacture cables with XLPE insulation, the polymeric base in granular form and containing the organic peroxide is fed to the extruder that makes the coating of the conductor. In order to
10 produce the polyethylene-based granulated material containing the organic peroxide in general two different techniques are followed.

According to a first technique, in a first step the polymeric base and all the other additives excluding
15 the organic peroxide are mixed through a compounding machine (for example a ko-kneader). The product thus obtained is reduced into granules and then fed to a second compounding machine (for example another ko-kneader) where the organic peroxide is added and
20 incorporated in conditions such as to avoid the premature decomposition thereof. The product thus obtained is then reduced into granules.

Conversely, a second technique, in general preferred since it is less cumbersome and expensive
25 than the first one and characterised by a greater productivity, includes making the granulated material of the polymeric material containing all of the additives except the organic peroxide according to the first technique, followed by a soaking process of said
30 granules with the organic peroxide in liquid state. In general, for LDPE granules, the maximum temperature for the impregnation step is about 60°C. During such

impregnation step, to increase speed and homogeneity of the impregnation, the granules, placed in contact with the organic peroxide in liquid form, for example through nebulisation, are continuously mixed in a suitable mixer (for example a rotating drum), which must avoid as much as possible the rubbing of the granules themselves with formation of fines. Indeed, fines, having a high exchange surface, would absorb a greater amount of peroxide with respect to the granules, with an inevitable influence on the extrusion process of the insulating layer on the conductor, decreasing the homogeneity of the latter at the microscopic level and thus its electrical performance. After the first step of impregnation in dynamic conditions, the impregnated granules are in general subjected to a step of static maturation, during which the organic peroxide distributes, by diffusion, as homogeneously as possible inside the granules.

The Applicants have noticed that the impregnation process of the LDPE granules as described above is long and cumbersome since polyethylene, being a product with high crystallinity, absorbs the organic peroxide with a certain difficulty, so that it is necessary to keep the impregnation temperature as high as possible, up to values of around 60-70°C, values that in general do not cause sticking phenomena of the granules but that promote mechanical erosion of the granules by rubbing between themselves and the impregnation system in movement, with an increase in the amount of fines and therefore the drawbacks deriving therefrom.

Moreover, the high crystallinity of LDPE can, over time, during the storage phase, cause a substantial

exudation from the granules both of the organic peroxide and of other additives commonly present, like antioxidants. The exudation of such products, and therefore the increase in their concentration on the surface of the granules, inevitably reduces the homogeneity of the cross-linked material, with undesired consequences on reliability of the produced cables. In general, exudation of the peroxide is promoted by low temperatures (for example less than or equal to 5°C), whereas antioxidants tend to migrate onto the surface of the granules at relatively high temperatures (equal to or greater than 50°C). The quality of the granulated material thus tends to be reduced over time following storage at extreme ambient temperatures, typical in cold or hot climates.

The Applicants have thus aimed to solve the technical problem of exudation of peroxide and of possible other additives in polyethylene-based granulated materials, in particular following prolonged exposure to extreme ambient temperatures. Another aim is that of reducing impregnation times of the polyethylene granules with the organic peroxide, so as to increase productivity and reduce the process costs for producing the granulated material.

These and other aims of the present invention have been accomplished by the Applicants through a polyethylene-based granulated material and the production process thereof according to what is reported in the present description and in the attached claims.

According to a first aspect, the present invention therefore concerns a granulated material that

comprises:

(a) from 70% to 95% by weight, preferably from 80% to 92% by weight, of at least one ethylene homopolymer or copolymer of ethylene with at least one alpha-olefin
5 C₃-C₁₂, having a density from 0.910 g/cm³ to 0.926 g/cm³;

(b) from 2% to 25% by weight, preferably from 5% to 15% by weight, of at least one polymer selected from:

(b1) copolymers of ethylene with at least one
10 alpha-olefin C₃-C₁₂, having a density from 0.860 to 0.905 g/cm³, preferably from 0.865 to 0.900 g/cm³, and a molecular weight distribution index (MWDI) not greater than 4, preferably from 1.5 to 3.5;

(b2) copolymers of ethylene with at least one ester
15 having one ethylenic unsaturation;

(c) from 0.1% to 7% by weight, preferably from 0.5% to 5% by weight, of at least one organic peroxide.

In the present description and in the attached claims, except where indicated otherwise, the
20 percentages by weight of the various components of the granulated material are expressed with respect to the total weight of the granulated material.

In the present description and in the attached claims, by "alpha-olefin C₃-C₁₂" it is meant an olefin
25 of formula CH₂=CH-R, where R is a linear or branched alkyl having from 1 to 10 carbon atoms. Preferably, the alpha-olefin is an alpha-olefin C₄-C₈. The alpha-olefin is preferably selected from: 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-dodecene.

30 Melting temperature (T_m) and melting enthalpy (ΔH_m) are determined through differential scanning calorimetry (DSC) measurements, according to

conventional techniques. The melting temperature is determined at the maximum peak of the DSC curve.

The molecular weight distribution index (MWDI) can be determined, according to conventional methods,
5 through Gel Permeation Chromatography.

In a second aspect, the present invention concerns a process for producing a granulated material as defined above, which comprises:

(i) mixing in a molten state said at least one
10 homopolymer or copolymer (a) with said at least one polymer (b), in the absence of said at least one organic peroxide (c);

(ii) granulating the mixture thus obtained so as to obtain a first granulated material devoid of organic
15 peroxide;

(iii) letting said at least one organic peroxide in liquid form be absorbed by said first granulated material, so as to obtain the granulated material according to the present invention.

20 According to a further aspect, the present invention concerns the use of a granulated material as defined above to manufacture at least one coating layer of an electrical cable. Preferably, said at least one coating layer is an electrically insulating layer or a
25 semiconductive layer.

In a preferred embodiment, the aforementioned component (b) consists of a mixture of at least one copolymer (b1) with at least one copolymer (b2). Preferably, the weight ratio between said at least one
30 copolymer (b1) and said at least one copolymer (b2) is from 10:90 to 90:10, more preferably from 30:70 to 70:30.

As far as the homopolymer or copolymer of ethylene (a) is concerned, it preferably has a melting temperature (T_m) higher than 100°C and/or a melting enthalpy (ΔH_m) higher than 110 J/g, more preferably a melting temperature (T_m) higher than 110°C and/or a melting enthalpy (ΔH_m) higher than 115 J/g.

The homopolymer or copolymer of ethylene (a) in general has a molecular weight distribution index (MWDI) greater than 4, preferably greater than 5.

Preferably, in the case of copolymers (a), said at least one alpha-olefin is present in an amount from 1 to 15% in moles, more preferably from 2 to 10% in moles.

Preferably, the homopolymer or copolymer of ethylene (a) is preferably a low density polyethylene (LDPE). LDPE is generally produced through a high pressure process in which ethylene is homopolymerised in the presence of oxygen or of a peroxide as initiator, with formation of polyethylene chains having long branching.

As far as the copolymer of ethylene with at least one alpha-olefin (b1) is concerned, this preferably has the following monomeric composition: 75-97% in moles, preferably 90-95% in moles, of ethylene; 3-25% in moles, preferably 5-10% in moles, of at least one alpha-olefin C_3-C_{12} ; 0-5% in moles, preferably 0-2% in moles, of at least one diene.

Preferably, said at least one diene is selected from: linear diolefins C_4-C_{20} , conjugated or not conjugated (for example 1,3-butadiene, 1,4-hexadiene, 1,6-octadiene); monocyclic or polycyclic dienes (for example 1,4-cyclohexadiene, 5-ethylidene-2-norbornene,

5-methylene-2-norbornene).

Said copolymer of ethylene with at least one alpha-olefin (b1) can be produced through copolymerization of ethylene with at least one alpha-olefin, and optionally
5 with a diene, in the presence of a single-site catalyst, in particular a metallocene catalyst, as described, for example, in patents US-5,246,783 and US-5,272,236. The metallocenes used as olefin catalysts are in general coordination complexes between a
10 transition metal, usually from group IV, in particular titanium, zirconium or hafnium, and two cyclopentadienyl binders, which are optionally substituted, used in combination with a co-catalyst, for example an aluminoxane, preferably a
15 methylaluminoxane, or a boron compound. Other single-site catalysts commonly used are so-called Constrained Geometry Catalysts, described, for example, in patents EP-416,815, EP-418,044, US-5,703,187.

Examples of copolymers of ethylene (b1) are
20 commercial products Engage™ by Dow Chemical, Queo™ by Borealis, Tafmer™ by Mitsui Chemicals and Lucene™ by LG Chem.

As far as the copolymers of ethylene with at least one ester having one ethylenic unsaturation (b2) are
25 concerned, in general these are copolymers of ethylene with at least one ester selected from: C₁-C₈ (preferably C₁-C₄) alkyl acrylates, C₁-C₈ (preferably C₁-C₄) alkyl methacrylates, and vinyl C₂-C₈ (preferably C₂-C₅) carboxylates. The amount of ester present in the
30 copolymer may in general vary from 5% to 50% by weight, preferably from 15% to 40% by weight. Examples of C₁-C₈ acrylates and methacrylates are: ethylacrylate,

methylacrylate, methacrylate, tert-butylacrylate, n-butylacrylate, n-butylmethacrylate, 2-ethylhexylacrylate, and similar. Examples of vinyl C₂-C₈ carboxylates are: vinylacetate, vinylpropionate, 5 vinylbutanoate, and similar.

Particularly preferred are ethylene-n-butylacrylate (EBA) copolymers, preferably having a n-butylacrylate content from 7 to 20%, which, with respect to other copolymers such as EVA (ethylene-vinylacetate) having 10 an equivalent comonomer content, have a decomposition temperature higher of about 30-50°C, so that they allow higher process temperatures to be used.

The copolymers of ethylene (b2) can be produced, for example, by high pressure copolymerization 15 analogous to that used for LDPE. Examples of copolymers of ethylene of type (b2) as described above are for example commercial products Lotryl™ by Arkema, EBA Alcludia™ PA by Repsol, Lucofin® by Lucobit.

As far as the organic peroxide (c) is concerned, 20 this is preferably a peroxide of formula R₁-O-O-R₂, where R₁ and R₂, equal to or different from each other, are alkyls C₁-C₁₈, aryls C₆-C₁₂, alkylaryls or arylalkyls C₇-C₂₄, linear or, preferably, branched. Particularly preferred are: dicumyl peroxide, t-butyl cumyl 25 peroxide, 2,5-dimethyl-2,5-di(t-butyl peroxy)hexane, di-t-butyl peroxide, or mixtures thereof.

The granulated material in accordance with the present invention can possibly comprise an effective amount of one or more additives, like, for example:

30 (1) processing aids, with the purpose of reducing friction coefficient between the insulating material and metallic parts with which it comes into contact

during processing both in the compounding step and in the cable extrusion step; such additives may for example be selected from: fatty acid amides (e.g. stearamides, erucamides, stearylerucamides), fatty acids (e.g. stearic, oleic), fatty acid salts (e.g. zinc stearate), polyethoxy derivatives (e.g. polyethylenglycol, alkylethoxy derivatives, polypropylenglycol), pentaerythritol, ethoxy-propylenoxy derivative copolymers including derivatives of diamines, fluoroderivates (e.g. thermoplastic fluorinated polymers);

(2) cross-linking coagents, i.e. chemical substances capable of improving cross-linking efficiency; such additives may for example be selected from: triallylcyanurate, triallylisocyanurate, possibly functionalised polybutadiene having a high vinyl degree, N,N'-m-phenylene dimaleimide (HVA-2), mono and di-functional acrylates including mono and diethoxylated acrylates, organic silanes or titanates, mono and oligomeric with different functionalisations.

Other additives that may be used in the granulated material in accordance with the present invention may be: heat stabilizers, pigments, water-tree retardant additives, voltage stabilizer additives, antiscorching agents, inorganic fillers (for example calcium carbonate, talc, kaolin and similar), and others.

When the granulated material is intended for manufacturing a semiconductive layer of an electrical cable, preferably the granulated material also comprises at least one semiconductive filler, in particular carbon black, in amounts such as to obtain the desired semi-conductive properties, preferably a

resistivity value of the semiconductive layer, measured at room temperature, less than $500 \Omega \cdot m$, preferably less than $20 \Omega \cdot m$. Typically, the amount of carbon black in the granulated material, when present, can vary from 1
5 to 40% by weight, preferably from 10 to 35% by weight.

Preferably, the granulated material according to the present invention comprises from 0.1% to 5% by weight, more preferably from 0.2% to 3% by weight, of at least one antioxidant. As anti-oxidants it is
10 possible to use those known for polyolefins, for example: 4,4'-thio-bis(6-t-butyl-n-cresol) (Santonox™ TBMC), tetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyl-oxymethyl]methane (Irganox™ 1010), 2,2'-thio-bis(4-metyl-6-t-butylphenol) (Irganox™
15 1081), 2,2'-thiodiethylene bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] (Irganox™ 1035), 4,6-bis(octylthiomethyl)-o-cresol (Irgastab™ Cable KV 10), or mixtures thereof, possibly in combination with a synergic thermal stabilizer such as dioctadecyl-3,3'-
20 thiodipropionate (Irganox™ PS 802) or didodecyl 3,3'-thiodipropionate (Irganox™ PS 800).

It should be noted that the granulated material according to the present invention shows a low exudation over time, also for prolonged exposure to low
25 or high temperatures, not only of the organic peroxide, but also of the other additives possibly present, like for example anti-oxidants and process adjuvants. This makes it possible to maintain characteristics of homogeneity and flowability of the granulated material
30 over time even after storage in extreme environmental conditions, in particular at temperatures less than or equal to $0^{\circ}C$ or greater than or equal to $50^{\circ}C$.

The granulated material in accordance with the present invention is in the form of granules or beads of very variable shapes (spherical, cylindrical, oval, flakes, etc.), and with average dimensions from 0.2 mm
5 to 50 mm, preferably from 0.3 to 5 mm.

As far as the process for producing the granulated material in accordance with the present invention is concerned, the initial mixing step in molten state of said at least one homopolymer or copolymer (a) with
10 said at least one polymer (b), is carried out in the absence of said at least one organic peroxide (c), and possibly in the presence of the other additives intended for the final formulation, so as to allow complete and homogeneous mixing between the polymeric
15 components and the other additives without running the risk of prematurely decomposing the organic peroxide, triggering undesired pre-crosslinking phenomena of the polymeric material. Such mixing is preferably carried out with a continuous mixing apparatus, for example a
20 ko-kneader type mixer (X-Compound) or a single screw or two-screw extruder (co-rotating or counter-rotating). At the outlet from the mixing apparatus, the product is filtered and granulated according to conventional techniques, for example through pelletization having
25 head cutting systems and subsequent cooling of the granules in water.

In a preferred embodiment, in the case in which the component (b) consists of a mixture of at least one copolymer (b1) with at least one copolymer (b2), said
30 copolymers are pre-mixed and granulated so as to obtain a product in subdivided form that is then used for the production of the final granulated material.

The granulated material devoid of peroxide is then dried and impregnated with the organic peroxide at a temperature such as to have the peroxide in liquid state, by promoting penetration kinetics of the
5 peroxide inside the granules without however causing either a premature decomposition of the peroxide itself or sticking phenomena of the granules. In general, the impregnation step is carried out at a temperature from 40°C to 80°C, more preferably from 50°C to 70°C.

10 During the impregnation step the granules are kept in movement by means of, for example, a rotating drum. The movement of the granules is carried out so as to reduce as much as possible the formation of polymeric material fines, which would promote appearance of
15 microstructural defects in the material after cross-linking. The impregnation step may last very variable amounts of time as a function of impregnation temperature, type of apparatus used and specific organic peroxide added. In general, the impregnation
20 step is carried out for a time from 2 to 60 minutes, more preferably from 10 to 30 minutes. At the end of the movement step of the granules, the organic peroxide has been absorbed by the granules in a substantially complete manner. However, in order to complete the
25 absorption of the organic peroxide and its homogeneous distribution inside the granules, after the dynamic impregnation step, the granules are preferably subjected to a step of static maturation. The maturation is generally carried out in static
30 conditions, for example in a silo that is insulated or in any case kept hot, so as to prolong exposure time of the granules to heat, for times of from 1 to 6 hours,

so as to obtain granules that are completely dry and with maximum homogenisation of the peroxide absorbed. The granules according to the present invention may be used to manufacture at least one coating layer of an electrical cable, in particular an electrically insulating layer and/or a semiconductive layer. Such production can be carried out according to conventional techniques, in particular by extrusion of the coating layers around at least one metallic conductor, which is carried out preferably with a triple extrusion head, so as to obtain, in the case of electrical cables for the distribution or transportation of medium, high or very high voltage energy, the simultaneous deposition of the inner semiconductive layer, of the insulating layer and of the outer semiconductive layer. The granulated material according to the present invention is directly fed to the extruder through a hopper, according to techniques well known in the art. The cable is then inserted into a tubular-shaped device, well known in the art (the so-called "catenary line"), in which a heating of the cable is carried out as homogeneously as possible in order to cause decomposition of the peroxide and therefore crosslinking of the polymeric material.

The following working examples are provided merely to illustrate the present invention and should not be intended to limit the scope of protection defined by the attached claims.

EXAMPLES 1-5

By means of a single-screw ko-kneader mixer the components shown in Table 1 were mixed, in the amounts given there (% by weight with respect to the total

weight of the granules), except the organic peroxide. At the outlet from the continuous mixer, the material was filtered, reduced into granules of average size equal to about 2 mm, by head cutting with cooling in
5 water.

TABLE 1

Example	1 (*)	2	3	4	5
Alcudia™ PE 004	97.00	87.00	87.00	87.00	82.00
Engage™ 8200	--	--	10.00	4.00	--
Alcudia™ PA 1770	--	10.00	--	6.00	--
Pre-mix	--	--	--	--	10.00
Irganox™ 1035	0.30	0.30	0.30	0.30	0.30
Irganox™ PS 802	0.20	0.20	0.20	0.20	0.20
Crodamide™ SR 212	0.20	0.20	0.20	0.20	0.20
Perkadox™ BC-FF	2.30	2.30	2.30	2.30	2.30
Total	100.00	100.00	100.00	100.00	100.00

(*) comparative

10

Alcudia™ PE 004 : low density ethylene homopolymer obtained with high pressure radical initiator, density: 0.920 g/cm³, MFI (190°C/2.16 kg): 2 g/10 min, ΔH_m : 92 J/g, T_m : 111°C;

15

Engage™ 8200 : ethylene/1-octene copolymer obtained by metallocene catalysis, ethylene/1-octene weight ratio: 76/24, density: 0.870 g/cm³, MFI (190°C/2.16 kg): 0.5 g/10 min, MWDI < 4, ΔH_m : 24 J/g, T_m : 60°C;

20

Alcudia™ PA 1770: ethylene/butylacrylate copolymer, weight ratio ethylene/butylacrylate 83/17, density = 0.924 g/cm³, MFI (190°C/2.16 kg) = 7 g/10 min, T_m :

93°C;

Pre-mix: granules consisting of a mixture of Alcludia™ PA 1770 and Engage™ 8200 in weight ratio 60:40;

Irganox™ 1035 : phenolic antioxidant (2,2'-
5 thiodiethylene bis[3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate]);

Irganox™ PS 802 : thermal stabilizer (dioctadecyl-3,3'-thiodipropionate);

Crodamide™ SR 212: stearyl erucamide, melting
10 temperature : 70-75°C;

Perkadox™ BC-FF : dicumyl peroxide, melting temperature : 39.5°C.

The granulated material thus obtained was impregnated with dicumyl peroxide in the amounts
15 indicated in Table 1, using the following method.

100 g of granules are introduced into a conical flask and preheated in an air oven to 60°C for 1 hour. The dicumyl peroxide in the form of crystals is added in the predetermined amount to the pre-heated granules,
20 and the conical flask is inserted into a thermostatic bath at 60°C. The granules are kept under agitation through rotation at constant speed of the conical flask with a rotavapor device for 15 minutes. Every 3 minutes the granules are agitated manually for 30 sec, still at
25 60°C. The conical flask containing the granules impregnated with peroxide is inserted into an air oven and kept in static conditions (without agitation) at 60°C. At predetermined time intervals, corresponding to 1 hour, 2 hours, 4 hours, 6 hours and 24 hours from the
30 start of the static maturation step, a sample of granules weighing 10 g is taken.

Each sample was analysed so as to determine the

amount of peroxide present on the surface according to the following method, based on the "Methanol Wash - Analysis of Surface Content of XLPE" method, ART 235 21.05.09 Ed. 2 by Borealis.

5 The peroxide on the surface is dissolved by keeping the 10 g granule sample in a conical flask under agitation with a magnetic agitator for 5 min in 50 ml of methanol. The liquid phase is filtered and analysed with HPLC to determine the amount of peroxide present
10 (HPLC UPLC-DAD apparatus, column: Acquity UPLC BEH C18 17 μm , 2.1 x 100 mm, mobile phase: acetonitrile/water (0.1% H_3PO_4), flow: 0.3 ml/min).

The results are given in Table 2, as the percentage of peroxide absorbed inside the granules (and therefore
15 not dissolved by the methanol) with respect to the amount of peroxide actually added to the granules.

TABLE 2

Example	1 (*)	2	3	4	5
t = 15 mins	57.7	77.8	76.5	78.2	80.1
t = 1 hour	79.0	89.6	82.7	90.1	90.4
t = 2 hours	85.3	96.0	94.4	97.2	98.1
t = 4 hours	95.4	97.5	96.7	98.0	98.5
t = 6 hours	97.1	98.0	98.1	98.5	99.0
t = 24 hours	97.2	99.0	99.2	99.4	99.3

20 (*) comparative

As can be seen from the data in Table 2, the absorption kinetics of the peroxide by the granules according to the invention is clearly faster and more

complete with respect to reference Example 1.

To determine the amount of peroxide and of antioxidant that tend to exude from the granules after storage in extreme temperature conditions, the same
 5 measurements are carried out on samples of granules after having kept them for 1, 2 and 4 weeks at -25°C and at +65°C. The results are given in Table 3 (T = -25°C) and Table 4 (T = +65°C).

TABLE 3 (storage carried out at T = -25°C)

Example		1	2	3	4	5
		(*)				
antioxidant (ppm)	1 week	80	50	60	80	50
	2 weeks	180	80	140	110	70
	4 weeks	210	120	170	130	110
Peroxide (ppm)	1 week	2500	150	270	140	120
	2 weeks	3500	300	350	250	190
	4 weeks	4800	400	420	310	270

10 (*) comparative

TABLE 4 (storage carried out at T = +65°C)

Example		1	2	3	4	5
		(*)				
antioxidant (ppm)	1 week	350	180	230	190	170
	2 weeks	570	220	320	240	190
	4 weeks	650	250	370	290	220
peroxide (ppm)	1 week	110	130	220	120	95
	2 weeks	150	110	410	150	120
	4 weeks	120	95	420	130	110

(*) comparative

From the data given in Tables 3 and 4, it is clear
 15 that the granules according to the invention have lower exudation of the additives (antioxidant and peroxide)

with respect to the reference granules of Example 1,
after conservation of the granules themselves both at
low and high temperatures. It is particularly clear
that there is low exudation of the peroxide after
5 conservation at -25°C and of the antioxidants at +65°C.

CLAIMS

1. Granulated material which comprises:

(a) from 70% to 95% by weight, preferably from 80% to 92% by weight, of at least one ethylene homopolymer or copolymer of ethylene with at least one alpha-olefin C₃-C₁₂, having a density from 0.910 g/cm³ to 0.926 g/cm³;

(b) from 2% to 25% by weight, preferably from 5% to 15% by weight, of at least one polymer selected from:

(b1) copolymers of ethylene with at least one alpha-olefin C₃-C₁₂, having a density from 0.860 to 0.905 g/cm³, preferably from 0.865 to 0.900 g/cm³, and a molecular weight distribution index (MWDI) not higher than 4, preferably from 1.5 to 3.5;

(b2) copolymers of ethylene with at least one ester having one ethylenic unsaturation;

(c) from 0.1% to 7% by weight, preferably from 0.5% to 5% by weight, of at least one organic peroxide.

2. Granulated material according to claim 1, wherein component (b) consists of a mixture of at least one copolymer (b1) with at least one copolymer (b2).

3. Granulated material according to claim 2, wherein said at least one copolymer (b1) and said at least one copolymer (b2) are present in a weight ratio from 10:90 to 90:10, preferably from 30:70 to 70:30.

4. Granulated material according to anyone of the preceding claims, wherein said at least one ethylene homopolymer or copolymer (a) has a melting temperature (T_m) higher than 100°C and/or a melting enthalpy (ΔH_m) higher than 110 J/g.

5. Granulated material according to anyone of the preceding claims, wherein said at least one ethylene

homopolymer or copolymer (a) has a molecular weight distribution index (MWDI) higher than 4, preferably higher than 5.

6. Granulated material according to anyone of the
5 preceding claims, wherein said at least one ethylene homopolymer or copolymer (a) is a low density polyethylene (LDPE).

7. Granulated material according to anyone of the preceding claims, wherein said at least one copolymer
10 of ethylene with at least one alpha-olefin C₃-C₁₂ (b1) has the following monomeric composition: 75-97% by mole, preferably 90-95% by mole, of ethylene; 3-25% by mole, preferably 5-10% by mole, of at least one alpha-olefin C₃-C₁₂; 0-5% by mole, preferably 0-2% by mole, of
15 at least one diene.

8. Granulated material according to anyone of the preceding claims, wherein said at least one copolymer of ethylene with at least one alpha-olefin C₃-C₁₂ (b1) is produced by copolymerization of ethylene with at
20 least one alpha-olefin, and optionally with a diene, in the presence of a single-site catalyst, particularly a metallocene catalyst.

9. Granulated material according to anyone of the preceding claims, wherein said at least one copolymer
25 of ethylene with at least one ester having one ethylenic unsaturation (b2) is a copolymer of ethylene with at least one ester selected from: C₁-C₈ (preferably C₁-C₄) alkyl acrylates, C₁-C₈ (preferably C₁-C₄) alkyl methacrylates, and vinyl C₂-C₈ (preferably C₂-C₅)
30 carboxylates.

10. Granulated material according to claim 9, wherein said at least one copolymer of ethylene with at

least one ester having one ethylenic unsaturation (b2) is an ethylene-n-butylacrylate copolymer (EBA), preferably having a n-butylacrylate content from 7 to 20%.

5 11. Granulated material according to anyone of the preceding claims, wherein said at least one organic peroxide (c) is a peroxide of formula $R_1-O-O-R_2$, wherein R_1 and R_2 , equal or different from each other, are linear or, preferably, branched alkyls C_1-C_{18} , aryls C_6-
10 C_{12} , alkylaryls or arylalkyls C_7-C_{24} .

12. Granulated material according to claim 11, wherein said at least one organic peroxide (c) is selected from: dicumyl peroxide, t-butyl cumyl peroxide, 2,5-dimethyl-2,5-di(t-butyl peroxy)hexane,
15 di-t-butyl peroxide, or mixtures thereof.

13. Granulated material according to anyone of the preceding claims, further comprising an effective amount of one or more additives, selected from: antioxidants, heat stabilizers, processing aids,
20 lubricants, pigments, water-tree retardant additives, voltage stabilizer additives, antiscorching agents, inorganic fillers.

14. Granulated material according to claim 13, comprising from 0.1% to 5% by weight, preferably from
25 0.2% to 3% by weight, of at least one antioxidant.

15. Process for producing a granulated material according to anyone of claims from 1 to 14, which comprises:

(i) mixing in a molten state said at least one
30 homopolymer or copolymer (a) with said at least one polymer (b), in the absence of said at least one organic peroxide (c);

(ii) granulating the so obtained mixture so as to obtain a first granulated material devoid of organic peroxide;

5 (iii) letting said at least one organic peroxide in a liquid form to be absorbed by said first granulated material, so as to obtain the final granulated material.

16. Process according to claim 15, wherein, when component (b) consists of a mixture of at least one copolymer (b1) with at least one copolymer (b2), said
10 copolymers are premixed and granulated so as to obtain a product in a subdivided form which is then used to produce the final granulated material.

17. Process according to claim 15 or 16, wherein
15 the step of absorbing the organic peroxide is carried out at a temperature from 40°C to 80°C, preferably from 50°C to 70°C, while keeping the granulated material in movement.

18. Process according to claim 17, wherein the
20 step of absorbing the organic peroxide further comprises a step of static maturation.

19. Use of a granulated material according to anyone of claims from 1 to 15 to manufacture at least one coating layer of an electrical cable, preferably at
25 least one electrically insulating layer or at least one semiconductive layer.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2014/063387

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L23/08 C08K5/00 C08L23/16
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)
C08L C08K

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

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A	JP H02 283739 A (SUMITOMO ELECTRIC INDUSTRIES) 21 November 1990 (1990-11-21) abstract	1-19
A	EP 0 965 998 A1 (UNION CARBIDE CHEM PLASTIC [US]) 22 December 1999 (1999-12-22) the whole document paragraphs [0005], [0010]; examples	1-19
A	JP 2003 155387 A (MITSUI CHEMICALS INC) 27 May 2003 (2003-05-27) abstract	1-19
A	US 2008/304797 A1 (CASTELLANI LUCA [IT] ET AL) 11 December 2008 (2008-12-11) the whole document	1-19
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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 17 October 2014	Date of mailing of the international search report 27/10/2014
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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 Droghetti, Anna
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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2014/063387

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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