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(71) Applicant : **PIRELLI CABOS S/A**
Al. Barao de Piracicaba, 740
Sao Paulo - SP (BR)

(72) Inventor : **Goncalves, Jose Francisco**
Rua Caspio 71, Sao Bernardo do Campo
Sao Paulo (BR)
Inventor : **Picoli, Valter Marques**
Rua Angelo Picoli, 194, Sao Bernardo do
Campo
Sao Paulo (BR)

(74) Representative : **Smith, Philip Antony**
REDDIE & GROSE 16 Theobalds Road
London WC1X 8PL (GB)

(54) **Insulation compositions of moisture cross-linked polyethylene (XPLE) for use in low tension power cables.**

(57) To reduce contraction of the insulation which may occur at an operating temperature of 130°C, the polyethylene that is usually employed for the application of the "Sioplas" cross-linking process is modified with polypropylene (PP).

The polypropylene presents a softening point between 155 and 165°C, which guarantees, up to 130°C, the dimensional stability of the extruded material.

The mixture of the PP with low density polyethylene (LDPE) or low density linear polyethylene (LLDPE) or co-polymeric polyethylene of ethylene vinyl acetate (EVA) in an adequate concentration is the solution for the contraction problem.

The present invention relates to an electric cable, insulated with compositions of low density polyethylene, which are crosslinked by moisture. More precisely, it refers to the application of compositions with a low density polyethylene base, and which are cross-linked by moisture for insulating and covering cables. The process is known as "SIOPLAS".

The commercial processes for obtaining cross-linked polyethylene in the cable industry are basically the following:-

The oldest one consists in applying to the polyethylene as additives organic peroxides, with an activating temperature above the softening temperature for the polyethylene used. These composites are applied in the case of cables manufactured through an extrusion process followed by a thermo-chemical cross-linking process instantaneous simultaneous with the heating of the insulated cable above the peroxide activating temperature, for instance, through saturated vapor heating or through radiant heat produced by electric resistances, followed by a process corresponding to water cooling. In both cases, the process is done under pressure, since the decomposition gases generated by the chemical reactions cause the existence of bubbles in the extruded insulation. This process is still widely used for the production of medium/high tension cables, because it is the only way to obtain large extruded and crosslinked insulation sections without empty spots. This process requires high cost industrial installations.

Another process for obtaining cross-linked polyethylene insulation is irradiation by means of electron beams or sources of gamma radiation. According to this process, the cable is insulated by means of a normal extrusion process that may be applied to thermoplastic polyethylene, followed by a crosslinking process, in a subsequent phase, by means of high energy electron beam radiation or gamma radiation sources. In this case the process is mainly used for cables with a small extruded section, since the penetration capacity of the electrons is limited. Both processes, the electron beam radiation and gamma sources, require high cost installations, mainly because of special protection needed for the operator and for the environment. The production speed of cables is limited by the amount of energy that these sources can liberate and by the amount of material (insulation) to be cross-linked. These processes are usually indicated and applied to special cables.

Another process is the chemical cross-linking done by means of moisture. In this process, an organo-silane that can be hydrolysed is introduced to the polyethylene molecule which still maintains its thermoplastic characteristics, being applied on the cable by means of a usual extrusion process that can be applied to the thermoplastic polyethylene, where the extrusion speed is only limited by the extrusion and the material characteristics. The polyethylene cross-linking in the cable occurs in the reel, either in the environmental temperature and humidity conditions or by exposing the reel to a "sauna" type environment, depending on the material.

This is a low cost process for the production of low tension cables, since it only requires usual process equipment for thermoplastic materials. And, above all, it is advantageous for the insulation of conductors which have a non-round section, as, for instance, sector conductors (shape of a shell), which are previously twisted. This process is not advantageous for the production of medium/high tension cables, since the diffusion of moisture through large extruded sections is slow and moisture is one of the factors for the formation of arborescence in polyethylene that are under electric "stress" of high gradient.

This last process for obtaining cross-linked polyethylene as described above is, nowadays, widely used by the manufacturers of cables, mainly for insulation of power cables for low tension. The process is widely mastered by the manufacturers of cables, with at least two ways of obtaining the composite for extrusion:

a) Composites with organo-silane that is previously inserted into the polyethylene are commercially available or can be prepared locally by the manufacturer of cables. Here, two families of composites are identified; a.1) Polyethylene with inserted organo-silane applied to commercial polyethylene (this process may be done by any thermoplastic processor that has adequate equipment); a.2) Polyethylene with organo-silane that is copolymerized during the ethylene polymerization process (obviously, this process is only known to the petrochemical industry which is involved in the production of polyethylene).

b) Composites with the organo-silane inserted during the cable extrusion process. Usually, this process is used by the cable manufacturers. The variations for this process are: b.1) Humectation of the granules with organo-silane and peroxide immediately before the extrusion; b.2) Dosage and direct injection of the organo-silane and peroxide in the extruding material (Monosil Process); b.3) Dosage and direct injection of the organo-silane and peroxide through "CTN" (Cavity Transfer Mixer), connected to the head of the extruding material, known as Silanox Process. The process of cross-linking the polyethylene through moisture, as described above, has been widely accepted for the manufacture of power cables for low tension in preference to the other processes, due, mainly, to the cost saving aspect of the process, that is, the larger productivity, less consumption of energy, less investment. On the other hand, the moisture cross-linking process presents technical advantages for the application process. The most important ones are the possibility of extrusion for any conductor profile and the possibility of embossing during the extrusion. The extrusion processes commonly used for insulating conductors differ according to the type of tools used

for the formation of insulation on the conductor. The keywords used to differentiate the processes are "Extrusion under Pressure", "Extrusion under Semi-tubes" and "Extrusion under Tubes". For the "Extrusion under Pressure", the tools used have, approximately, the final insulation dimensions (the polyethylene is placed over the conductor without stretching); for the "Extrusion under Semi-tubes", the tools are slightly bigger than the dimensions of the insulation and they are generally used when the composite tends to flow backwards along the male die; and for the "Extrusion under Tubes", the male and female dies are, generally, much bigger than the insulation dimension of the conductor, and they are used when the profile of the conductor is not round, which makes it impossible to use tight tools, or in the case of composites applied on very thin materials (typical example: FEP "Teflon"). In this case, the final shape of the insulation is obtained by stretching the tube up to the final dimension.

A problem that is always present in the extrusion of thermoplastic materials is the residual tensions left by the conformation process, since the thermoplastic materials are polymeric (macromolecules) which, in the extrusion process, are squeezed and stretched. Usually, the polymeric materials require a relatively long time for relaxing the tensions stored during the passage through the tools. Since the insulation is rapidly cooled, to obtain productivity and to avoid deformities in the reel, a large part of the tensions is stored.

The power cables for low tension are covered by international specifications, such as IEC 502(83), NBR ABNT Project 3.20.3-026(90). Under the service conditions, these cables are classified for continuous service at a 90°C temperature (in the conductor), and at an overload process, during a short period of time, up to 130°C, and under a short circuit condition up to 250°C.

The cross-linked polyethylene obtained by the "Sioplas" process, when heated above its softening temperature (95 to 115°C), tends to relax the tensions left by the extrusion process, creating a contraction, especially in the ends of the cable exposing the conductor.

To prevent accidents created by the contraction against the installations, the rules described above include a qualification test. Such a test consists in cutting 200mm from the central part of a sample that has at least 1200mm of the isolated cable, then exposing this sample to heat for 1 hour at 130°C in an air stove, and measuring the isolation contraction at both ends. The value found must not exceed 4%.

In practice, what was noticed was that for the polyethylene that were cross-linked through the "Tube Extruded Sioplas", the contraction can reach 20% causing serious inconveniences for the use of the cable.

The current invention has the purpose of solving the current technical problems, through the modification of the polyethylenes that are usually employed in the "Sioplas" process, with the addition of polypropylene (PP). The polypropylene has a softening temperature between 155 and 165°C, which guarantees, up to 130°C, the dimensional stability of the extruded material.

The mixture of the PP with the low density polyethylene (LDPE) or linear low density polyethylene (LLDPE) or co-polymeric polyethylene of vinyl ethylene acetate (EVA) in an adequate concentration is the solution for the contraction problem.

The low density polyethylene (LDPE) is a homopolymeric or copolymeric vinyl acetate (VA) or methacrylate (MA) up to 10%. The linear low density polyethylene (LLDPE) is a butene or hexane copolymer. The polypropylene is a propylene-ethylene copolymer with a co-monomer level (ethylene) over 6%, being used in a preferred proportion between 15 and 25%.

Below is the description of experimental results obtained with compositions of the known technique and of the current invention.

Examples 1,2,3 (with contraction):

Usual compositions with polyethylene base which can be crosslinked through the "Sioplas" process.

Ingredient	Example 1	Ex. 2	Ex. 3
LDPE (MFI 1,3)	100	-	-
LDPE (Co-polymeric 9% Vinyl			

	Acetate) MFI 4	-	-	100
	LLDPE (MFI 4)			
5	Anti-oxidant	0.2	0.2	0.2
	VIMO	1.5	1.5	1.5
	Cumila			
	Peroxide (96-100%)	0.12	0.12	0.12
10	DBTL	0.05	0.05	0.05

NOTES: VIMO (Vinyl Trimethoxy Silane): Organo Silane with three methoxy radicals to one vinyl radical.

DBTL (Di-Butyl Tin Laurate): Organic salt of tin used as a catalyzer for hydrolysis.

These compositions can be easily reproduced in a laboratory using the technique of humectation for the granulated polyethylene with the silane, peroxide and DBTL. The above compositions were extruded with tube extrusion tools over a flat profile conductor with a rate of section reduction of 2 (DDR - draw down ration).

To enable the reaction of the insertion of the silane to occur, a fusion temperature (Melt) of 220°C was used. After treating them in waterbath at 70°C for 16 hours, in a contraction controlled way, they became faded and a fracture in the flecion occurred.

Results obtained:

Property	Ex. 1:	Ex. 2:	Ex- 3:
Contraction	13%	5.5%	19%
Fading	none	none	none
Fracture	none	none	none

Examples 4 and 5 (with fracture): Polyethylene compositions modified with homo-polymeric polypropylene.

Ingredient	Example 4:	Example 5:
LDPE (MFI 1,3)	80	-
LLDPE (MFI 1,0)	-	80
Homopolymeric PP (MFI 4.0-KMT 6100		
from Polibrasil)	20	20
Antioxidant	0.2	0.2
VTMO	1.5	1.5
Cumila Peroxide (96-100%)	0.12	0.12
DBTL	0.05	0.05

Examples 4 and 5 were processed the same was as Examples 1, 2 and 3.

Results obtained:

	Property	Ex. 4:	Ex. 5:
5	Contraction	1.5%	1.0)%
	Fading	occurred	occurred
	Fracture occurred	occurred	

10 Examples 6 and 7 (without contraction or fracture) : Compositions of polyethylene modified with copoly-
meric polypropylene.

	Ingredient	Example 6:	Example 7:
15	LDPE (MFI 1,3)	80	-
	LLDPE (MFI 1,0)	-	80
20	Copolymeric PP (8% ethylene) MFI 4; EPT30RSF Spheripol from HI-MONT	20	20
	Antioxidant	0.2	0.2
	VTMO	1.5	1.5
25	Cumila Peroxide (96-100%)	0.12	0.12
	DBTL	0.05	0.05

Examples 6 and 7 were processed the same way as examples 1, 2, 3, 4 and 5.

30 Results obtained:

	Property	Ex. 6:	Ex. 7:
35	Contraction	3.0%	3.0%
	Fading	none	none
	Fracture	none	none

40 Examples 8, 9, and 10 aimed at estimating the best PP/LDPE relation; the smaller PP level, the greater
cost reduction.

	Ingredient	Ex. 8:	Ex. 9:	Ex. 10
45	LDPE (MFI 1,3)	85	82.5	80
	(Copolymeric PP (8% ethylene) MFI4; EPT30RSF from HIMONT	15.0	17.5	20
	Antioxidant	0.2	0.2	0.2
50	VTMO	1.5	1.5	1.5
	Cumila Peroxide (96-100%)	0.12	0.12	0.12
	DBTL	0.05	0.05	0.05

55 Examples 8, 9 and 10 were processed the same way as examples 1, 2, 3, 4, 5, 6 and 7.

Results obtained:

Property	Ex. 8:	Ex. 9:	Ex. 10:
Contraction	7.0%	4.5%	4.0%
Fading	none	none	none
Fracture	none	none	none

COMPARATIVE TABLE BETWEEN EXAMPLES 7 AND 9 AND SPECIFICATIONS IEC 502/83 (3rd ISSUE 1991) AND ABNT 3.20.3-026/90 (REVISION NBR-6251/86: Both specifications have the same requirements.

Properties	Unit	Requirement	Ex. 7	Ex. 9
I) Initial Tension				
and rupture	MPa	12.5	21.9	16.6
Stretching and				
rupture	%	200	480	480
II) After aging in air stove at 135oC for 168 hours				
Variation of tension				
and rupture	%	MAX 25	+4	+5
Variation of stretching				
at rupture	%	MAX 25	-2	-3
Stretching at heat (200oC) with				
load of 0.2MPa	%	MAX 175	60	60
Permanent deformity after				
stretching test at				
heat	%	MAX 15	15	15

Claims

1. Insulation compositions in moisture cross-linked polyethylene (XLPE) for use in low tension power cables". Characterized by the fact that they are compositions with polyethylene base modified by the addition of polypropylene.
2. Compositions according to claim 1, characterized by the fact that the polypropylene is a co-polymeric of propyleneethylene with a proportion of ethylene above 6%.
3. Compositions according to claim 2, characterized by the fact that the proportion of the added polypropylene is between 15 and 25%.
4. Compositions according to claim 1, characterized by the fact that the polyethylene has low density, medium density or high density.
5. Compositions according to claim 4, characterized by the fact that the polyethylene is linear and has low density.
6. Compositions according to claim 4, characterized by the fact that the low density polyethylene is a co-polymeric of vinyl acetate or methyl acrylate up to 10%.

7. Compositions according to claim 5, characterized by the fact that the low density linear polyethylene is a co-polymeric of butene or hexene.
8. Compositions according to claims 1 through 7, characterized by the fact that the insulation has its contraction below 4%, in compliance with rules IEC 502 FROM 1983 (3rd issue 1991), and ABNT Project 3.20.3-026/90 (revision NBR-6251/1986).

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