



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification⁶ : C08K 5/37, C08L 67/02, C08G 81/02, H01B 3/42</p>	<p>A1</p>	<p>(11) International Publication Number: WO 95/12636 (43) International Publication Date: 11 May 1995 (11.05.95)</p>
<p>(21) International Application Number: PCT/US94/12034 (22) International Filing Date: 21 October 1994 (21.10.94) (30) Priority Data: 08/147,247 4 November 1993 (04.11.93) US (71) Applicant: RAYCHEM CORPORATION [US/US]; 300 Constitution Drive, Menlo Park, CA 94025-1164 (US). (72) Inventors: TONDRE, Stephen, L.; 33455 Caliban Drive, Fremont, CA 94555 (US). YEUNG, Alan; 724 Portwalk Place, Redwood City, CA 94065 (US). (74) Agents: RICHARDSON, Timothy, H.,P. et al.; Raychem Corporation, Intellectual Property Law Dept., Mail Stop 120/6600, 300 Constitution Drive, Menlo Park, CA 94025-1164 (US).</p>		<p>(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i></p>
<p>(54) Title: STABILIZED THERMOPLASTIC POLYESTER ALLOY COMPOSITIONS</p>		
<p>(57) Abstract</p> <p>A PBT alloy blend including an effective amount of stabilizing compound contains at least one thioether linkage and at least one long chain alkyl group, particularly such a compound containing a carboxylic ester group. This composition is particularly useful as wire insulation.</p>		

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STABILIZED THERMOPLASTIC POLYESTER ALLOY COMPOSITIONS

This invention relates to a polymeric blend which exhibits improved thermal stability, and an electrical conductor coated with the polymeric blend.

Polyesters of many kinds are known. They include, for example, poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and the recently developed so-called polyester alloys, which comprise (1) a grafted polyester obtained by reacting a polyester with a polymeric grafting agent, and (2) a second polymer which has a chemical structure similar to the grafting agent. The presence of the polymeric side chains results in improved compatibility between the polyester and the second polymer, so that they can form an intimate mixture having remarkably good physical properties. There may be a chemical reaction between the grafting agent and the second polymer so that part or all of the second polymer becomes part of the grafted polyester. Particular polyester alloys are disclosed in PCT (International) Application No. WO 93/08234 (E.I. du Pont de Nemours) which was published on April 29, 1993, and claims priority from U.S. Serial No. 07/781,459 (Hausmann et al., assigned to E. I. du Pont de Nemours), available on April 29, 1993, as the priority document for that PCT application. The disclosures of that PCT application and that U.S. application are incorporated herein by reference for all purposes.

A problem which arises with compositions comprising polyesters (including both conventional polyesters and polyester alloys), especially such compositions in the form of coatings on wires, is that they suffer from a lack of stability, in particular a loss of elongation on aging, particularly at elevated temperatures. This loss of elongation is particularly apparent when the composition includes a flame retardant, particularly a bromine-containing flame retardant.

We have now discovered that the properties of compositions comprising polyester alloys can be greatly improved by the incorporation therein of an effective amount of a stabilizing compound which contains at least one thioether linkage and at least one long chain alkyl group, particularly such a compound containing a carboxylic ester group. This improvement is particularly apparent when the composition is in the form of insulation around a wire or cable, since the presence of the stabilizing compound reduces the rate at which the insulation loses elongation at elevated temperatures. This result is most surprising, since the presence of such a stabilizing compound has little or no beneficial effect on the retention of elongation of conventional polyesters such as PBT.

In a first preferred aspect, this invention provides a thermoplastic composition which comprises

- 20 (A) a graft copolymer which comprises
 - 25 (a) a polyalkylene terephthalate backbone, and
 - (b) polymeric side chains which are grafted to the backbone and which comprise units derived from addition polymerization of a monomer containing ethylenic unsaturation;
- 30 (B) an addition polymer which comprises units derived from addition polymerization of a monomer containing ethylenic unsaturation; and
- 35 (C) an effective amount of a stabilizing compound containing a thioether linkage and a long chain alkyl group.

In a second preferred aspect, this invention provides an insulated wire or cable comprising at least one insulating layer of a composition according to the first preferred aspect of the invention. The layer is preferably
5 made by melt extruding the composition around the wire or cable. The layer can be the sole insulation around a single conductor, or one of two or more contiguous insulating layers around a single conductor, or can be all or part of a jacket around a plurality of insulated
10 conductors. The thickness of the layer can be for example 2-50 mils, preferably 4-30 mils, especially 6-20 mils.

In a third preferred aspect, this invention provides a method of making an insulated wire or cable which comprises
15 melt extruding a composition according to the first preferred aspect of the invention around a conductor.

The term "polyalkylene terephthalate" is used herein to denote a polymer in which at least 80%, preferably
20 substantially 100%, of the repeating units are alkylene terephthalate groups. (Percentages are by weight throughout this specification.) Preferably all the alkylene groups are the same. Preferably each of the alkylene groups contains 2 to 6 carbon atoms. The
25 invention is particularly useful when the polyalkylene terephthalate is polybutylene terephthalate (PBT), i.e. a polyester in which at least 80%, preferably 100%, of the repeating units are butylene terephthalate units, and the invention will be described chiefly by reference to PBT.
30 It is to be understood, however, that such description is also applicable, with modifications which will be apparent to those skilled in the art having regard to their own knowledge and the contents of this specification.

35 The polymeric side chains in the grafted polyester preferably contain

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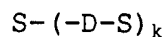
- (a) at least 50%, particularly at least 60%, of units derived from ethylene;
- (b) 1 to 15%, particularly 1 to 10%, especially 1 to 7%, of units derived from at least one ethylenically unsaturated compound containing an epoxide or isocyanate group, particularly such a compound containing up to 11 carbon atoms, for example glycidyl acrylate or methacrylate, allyl or vinyl glycidyl ether, glycidyl itaconate, vinyl isocyanate or isocyanato-ethyl methacrylate;
- and
- (c) 0 to 49%, particularly 10 to 35%, especially 20 to 30%, of units derivable from at least one alkyl acrylate or methacrylate wherein the alkyl group preferably contains 1 to 8 carbon atoms, for example methyl, n-butyl, or isobutyl acrylate.

The graft copolymer preferably contains a% of the polyalkylene terephthalate backbone and b% of the polymeric side chains, where a is 99.5 to 20, particularly 97 to 60, and b is 0.5 to 80, particularly 3 to 40, and a + b is 100.

In one embodiment, the addition polymer (B) preferably comprises a polymer containing at least 50%, particularly at least 60%, of units derived from ethylene, and 0.5 to 50%, particularly 5 to 50%, of units which are derived from an ethylenically unsaturated monomer and which contain a carboxyl group, a metal carboxylate group (e.g. a sodium, zinc, magnesium or calcium salt), or a carboxylic ester group (e.g. an alkyl ester in which the alkyl group contains 1 to 8 carbon atoms), for example acrylic and methacrylic acids, and methyl, isobutyl, and n-butyl acrylates and methacrylates.

In another embodiment, the addition polymer (B) preferably comprises a styrene/diene block copolymer, preferably one having the formula

5



where S is a polystyrene block,
D is a hydrogenated polyisoprene block or a
10 hydrogenated polybutadiene block,
and
k is an integer,

particular such a copolymer in which the polystyrene
15 content is less than 50%. Such copolymers can be grafted with maleic acid to form graft copolymers containing 0.1 - 10, e.g. 0.2 - 5, % of units derived from maleic anhydride.

The addition polymer (B) can be a single polymer or a
20 mixture of polymers. The composition preferably contains x% of the graft copolymer (A) and y% of the addition polymer (B), where x is 55 to 95, y is 45 to 5, and x + y is 100.

25 The composition can also contain other polymeric ingredients, for example up to 25% of a thermoplastic elastomer, particularly a copolyester ester or a copolyether ester, for example the polymers sold under the trade names Hytrel (du Pont) and Arnitel (Akzo).

30

The polymeric ingredients of the compositions of the invention are preferably made by melt blending (i) polyalkylene terephthalate, (ii) a polymeric grafting agent which contains reactive groups which can graft to the
35 polyalkylene terephthalate and which comprises repeating units derived from addition polymerization of a monomer containing ethylenic unsaturation, and (iii) an addition polymer which comprises units derived from addition

polymerization of a monomer containing ethylenic unsaturation. When the grafting agent and the addition polymer contain groups which will react with each other, and especially when a melt blending process as described above is used, part or even all of the addition polymer may be present as a reaction product with the grafting agent and/or the grafted polyester.

For further details of polymeric materials which can be used in this invention, reference may be made to PCT (International) Application WO 93/08234 and U.S. Serial No. 07/781,459 incorporated by reference herein. Thus the polymeric material may be a partially grafted, flexible thermoplastic composition formed by melt blending

15

(a) 40-65% by weight of a poly(1,4-butylene) terephthalate;

20

(b) 1-30% by weight of a polymeric grafting agent which is a copolymer of at least 50% by weight of ethylene, 0.5-15% by weight of at least one reactive moiety selected from the group consisting of (i) an unsaturated epoxide of 4-11 carbon atoms, (ii) an unsaturated isocyanate of 2-11 carbon atoms, (iii) an alkoxy or alkyl silane wherein the alkyl group is from 1-12 carbon atoms, (iv) an alkyl halide, (v) an alkyl alpha-halo ketone or aldehyde, and (vi) oxazoline, and 0-49% by weight of a moiety selected from at least one of an alkyl acrylate, alkyl methacrylate, vinyl ether, carbon monoxide, and sulfur dioxide, where the alkyl and ether groups above are of 1-12 carbon atoms;

25

30

35

(c) 0-20% by weight of an ethylene copolymer which comprises at least 50% by weight of ethylene, 1-35% by weight of an acid-containing unsaturated mono-carboxylic acid, and 0-49% by weight of a

moiety selected from at least one of alkyl acrylate, alkyl methacrylate, vinyl ether, carbon monoxide and sulfur dioxide, and further wherein the acid groups are neutralized from 0-100% by a metal ion; and

5

(d) at least one of:

10

(i) 0-25% by weight of a thermoplastic elastomer selected from the group consisting of a copolyester ester and a copolyether ester;

15

(ii) 0-45% by weight of a styrene/diene block copolymer, with 3 or more sequences, of the S-(D-S)_n structure where n is a whole number, S is a polystyrene block, D is a hydrogenated isoprenic block or hydrogenated butadienic block, with a content in styrene less than 50% by weight optionally grafted with maleic anhydride;

20

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(iii) 0-25% by weight of an adduct of maleic anhydride and a copolymer of ethylene, at least one C₃ to C₆ alphaolefin, and at least one nonconjugated diene; or

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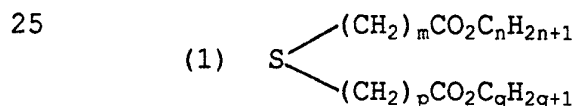
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(iv) 0-25% by weight of an acrylic-modified elastomer based polymer wherein the elastomeric portion is polymerized from a monomer mixture containing at least 50% by weight of at least one C₁ to C₁₅ alkyl acrylate, 0-5% by weight of at least one graftlinking monomer, 0-5% by weight of a crosslinking monomer, and the balance to 100% by weight of at least one other polymerizable ethylenically unsaturated monomer;

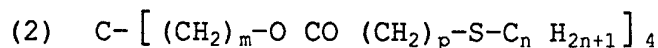
provided that:

- 5
- (1) the total of (a) - (d) is 100%;
- (2) the total polyester content of (a) and (d) (i) does not exceed 70%; and
- 10 (3) if (c) is 0%, then (d) cannot be (i), (iii), and (iv), and (ii) can be 10-45% by weight.

The stabilizing compounds used in this invention contain a thioether (-S-) linkage and a long chain alkyl group. Preferred stabilizing compounds contain at least 15 one carboxyl group in addition to the long chain alkyl group and the -S- group and preferably have the formula $\text{RCO}_2\text{R}'$, wherein each of R and R', which may be the same or different, comprises an alkyl group containing 8 to 22 carbon atoms and at least one of R and R' contains an -S- 20 group. Preferably, each of R and R' consists essentially of carbon, oxygen, hydrogen and sulfur. Particularly preferred stabilizing compounds have one of the two formulae set out below:



30 wherein each of m and p, which may be the same or different, is 1, 2 or 3; and each of n and q, which may be the same or different, is from 8 to 22 inclusive.



35 wherein each of m and p, which may be the same or different, is 1, 2 or 3, and n is from 8 to 22, inclusive.

Examples of stabilizing compounds as defined above are distearyl thiodipropionate (often referred to herein as

DSTDP), which is the most preferred compound and has the formula



dilauryl thiodipropionate, and dimyristyl thiodipropionate, which are also preferred, ditridecyl thiodipropionate, mixed esters (lauryl and stearyl) of thiodipropionic acid, and pentaerythritol tetrakis(3-(dodecylthio)propionate).

The compositions of the invention can also include one or more flame retardants. The flame retardants can be free of halogen atoms or can contain halogen atoms. Suitable flame retardants are for example the known brominated and chlorinated flame retardants, including brominated aromatic and aliphatic compounds, such as decabromodiphenyl ether, ethylene bis tetrabromophthalimide, and the brominated flame retardant available from Great Lakes Chemical under the trade name Saytex BT8010. The amount of halogen-containing flame retardant present will generally be at least 3%, preferably at least 5%, e.g., 5-30% or 5-25%, by weight of the composition. The halogen-containing flame retardant can be used in conjunction with an inorganic flame retardant, for example antimony trioxide. Polyester compositions with bromine-containing flame retardants have been described, for example in copending, commonly assigned U.S. Patent Application Serial No. 07/537,558, filed on June 13, 1990 by Lunk et al and commonly assigned, U.S. Patent No. 4,332,855 (Zingheim et al), the disclosures of which are incorporated herein by reference for all purposes.

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The invention is illustrated by the following Examples, in which the following abbreviations are employed

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- ETP is a polyester alloy available from du Pont under the trade name ETP-1383 and which is described in a trade brochure for that alloy as "an intimately alloyed, permanent blend of poly(butylene terephthalate) PBT and polyacrylic elastomers" and "intimately mixed alloys of PBT and polyacrylic elastomers"
- 5
- PBT is polybutylene terephthalate available from Celanese under the trade name Celanex 1600A
- 10
- EEA is an ethylene/ethyl acrylate copolymer available from du Pont under the trade name Alathon A710
- 15
- DSTDP is distearyl thiodipropionate
- BT93 is ethylene bis tetrabromophthalimide available from Great Lakes Chemical under the trade name Saytex BT-93
- 20
- Sb₂O₃ is antimony trioxide.

Compositions were prepared by mixing the ingredients and amounts thereof in Table I in a twin screw extruder, and the compositions were then extruded over tin-coated copper 20 AWG wire, using a 1 inch (2.54 cm) extruder, to give insulating layers about 8 mil thick. In Examples 6 and 8, the ingredients were mixed at about 180 - 220°C, and extruded over the wire at about 250°C. Samples of the insulation, about 3 inch long, were stripped from the wire, and the elongation measured initially and after aging in a circulating air oven at 180°C for 168 hours, or at 200°C for 30 hours, or at 220°C for 5 hours. The percentage of the original elongation which was retained after such aging was then calculated. The results are also shown in Table I, in which Examples 6 and 8 are Examples of the invention and the other Examples are comparative Examples.

25

30

35

TABLE I

Ingredients	Example No.							
	1*	2*	3*	4*	5*	6	7*	8
ETP	-	-	-	-	100	98	82	80
PBT	100	98	65	63.7	-	-	-	-
EEA	-	-	35	34.3	-	-	-	-
DSTDP	-	2	-	2	-	2	-	2
BT93	-	-	-	-	-	-	12	12
Sb ₂ O ₃	-	-	-	-	-	-	6	6
% elongation retained after aging at								
180°C/168 hr	0	0	0	0	29	51	0	34
200°C/30 hr	-	-	-	-	11	56	-	-
220°C/5 hr	-	-	-	-	5	36	-	-

*Comparative Example

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It is apparent from these results that the presence of DSTDP had no useful effect, under the test conditions, on the retention of elongation of the compositions in which the polymer was PBT or a mixture of PBT and EEA, but substantially improved the retention of elongation of the compositions in which the polymer was the polyester alloy ETP.

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CLAIMS

1. A thermoplastic composition which comprises
 - (A) a graft copolymer which comprises
 - (a) a polyalkylene terephthalate backbone, and
 - (b) polymeric side chains which are grafted to the backbone and which comprise units derived from addition polymerization of a monomer containing ethylenic unsaturation;
 - (B) an addition polymer which comprises units derived from addition polymerization of a monomer containing ethylenic unsaturation; and
 - (C) an effective amount of a stabilizing compound containing a thioether linkage and a long chain alkyl group.
2. A composition according to Claim 1 wherein the polyalkylene terephthalate is polybutylene terephthalate.
3. A composition according to Claim 1 or 2 wherein the graft copolymer contains a% by weight of the polyalkylene terephthalate backbone and b% by weight of the polymeric side chains, where a is 99.5 to 20, preferably 97 to 60, b is 0.5 to 80, preferably 3 to 40, and a + b is 100.
4. A composition according to Claim 1, 2 or 3 wherein the polymeric side chains contain at least 50% by weight of units derived from ethylene, 1 to 15% by weight of units derived from at least one ethylenically unsaturated compound containing an epoxide or isocyanate group, and 0 to 49% by weight of units derivable from at least one alkyl

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acrylate or methacrylate wherein the alkyl group contains 1 to 8 carbon atoms.

5. A composition according to any one of the preceding claims which contains x% by weight of the graft copolymer (A) and y% by weight of the addition polymer (B), where x is 55 to 95, y is 45 to 5 and x + y is 100.

6. A composition according to any one of the preceding claims wherein the addition polymer (B) is (1) a polymer which contains at least 50% by weight of units derived from ethylene, and 0.5 to 50% by weight of units which are derived from an ethylenically unsaturated monomer and which contain a carboxyl group, a metal carboxylate group, or a carboxylic ester group, or (2) a block copolymer containing blocks derived from styrene and blocks derived from a diene.

7. A composition according to any one of the preceding claims which also contains

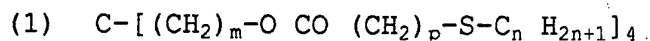
(D) up to 25% by weight of a thermoplastic elastomer which is a copolyester ester or a copolyether ester.

8. A composition according to Claim 1 wherein the stabilizing compound has the formula



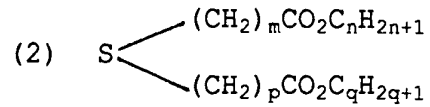
wherein each of R and R', which may be the same or different, comprises an alkyl group containing 8 to 22 carbon atoms; and at least one of R and R' contains an -S- group;

preferably a compound of the formula



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wherein each of m and p, which may be the same or different, is 1, 2 or 3, and n is from 8 to 22, inclusive, or



wherein each of m and p, which may be the same or different, is 1, 2 or 3; and each of n and q, which may be the same or different, is from 8 to 22, inclusive.

9. A composition according to any one of the preceding claims which contains 1 to 10% by weight of the stabilizing compound.

10. A composition according to any one of the preceding claims which also contains at least 5% by weight of a brominated flame retardant.

11. An insulated wire or cable which comprises a metal conductor, and an insulating coating around the conductor, wherein the insulating coating comprises a composition as claimed in any one of the preceding claims.

12. An insulated wire as defined in Claim 11 wherein said composition is in the form of a layer which (a) surrounds a single conductor and is 4 to 30 mils thick, or (b) surrounds a plurality of individually insulated conductors and is 4 to 30 mils thick.

INTERNATIONAL SEARCH REPORT

Internat. Application No
PCT/US 94/12034

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C08K5/37 C08L67/02 C08G81/02 H01B3/42		
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) IPC 6 C08K C08L C08G 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 practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DATABASE WPI Derwent Publications Ltd., London, GB; AN 85-293378 & JP,A,60 202 147 (TORAY IND INC) 12 October 1985 see abstract	1-12
Y	--- WO,A,93 08234 (E.I. DU PONT DE NEMOURS AND COMPANY) 29 April 1993 cited in the application see claims see examples 17,18 ---	1-12
	-/--	
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Date of the actual completion of the international search <p align="center">10 February 1995</p>		Date of mailing of the international search report <p align="center">24.02.95</p>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer <p align="center">Persson, E</p>

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 928 279 (TEIJIN LIMITED) 23 December 1975 see claims see column 1, line 50 - line 56 see column 2, line 4 - line 5 see column 2, line 14 - line 18 -----	1
A	US,A,3 758 549 (CIBA-GEIGY CORPORATION) 11 September 1973 see claim 3 see column 1, line 62 -----	8

INTERNATIONAL SEARCH REPORT

information on patent family members

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