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Cable-making Compositions		

NJP-9304823

5 This invention relates to compositions for making electric cables (including power and communications cables) and optical cables, and more particularly to compositions for incorporation into cable sheaths for the purpose of reducing the susceptibility of the cables to attack by termites. It includes cables made by use of the compositions and cable installations in which the cables are used.

10 In GB1538222, one of the present applicants has proposed the use of a synthetic pyrethroid insecticide that has since become known as permethrin as additive to a cable sheath for this purpose, but there are difficulties in handling such substances in the plant normally available in cable-making factories and custom
15 compounders have been unwilling to incorporate them in to polymer-based sheathing materials because the relatively small quantities of material required for this specialised market were not considered sufficient to justify the special decontamination régime that would
20 have to be imposed on a large mixing plant. This problem is aggravated because cable purchasers wish to have available sheaths based on a range of base polymers, including polyethylene (PE or polythene), polyvinyl chloride (PVC) and certain ethylene/vinyl
25 acetate copolymers (EVA's); polyethylene and PVC, in particular, are very different in their melt characteristics and require different designs of plant



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to formulate them. Lindane has remained in use on a small scale.

Subsequently, a number of other effective synthetic pyrethroid insecticides have become available and widely used for agricultural and public health applications. Notable among these are cypermethrin, alphacypermethrin and betacypermethrin, all of which are different isomer mixtures corresponding to the same structural formula, being a derivative of permethrin having a -CN group in the *alpha* position (the derivative has *cis-trans* forms in addition to two independent optically active centres, giving rise to eight stereoisomers of differing insecticidal potency).

We have now discovered that these synthetic pyrethroid insecticides can be dispersed in relatively high concentrations in ethylene-vinyl acetate copolymers to form a "masterbatch" that is compatible with both PE-based and PVC-based cable sheathing compositions, as well as EVA-based ones. This facilitates use of the materials considerably, not only because a single masterbatch composition can be used to meet all cable sheath composition requirements, but also because the volume of material to be produced in the insecticide-handling plant is much reduced, allowing the use of smaller machinery that can be more readily decontaminated.

The invention thus provides a polymer masterbatch for making cable sheaths in conjunction with a base

polymer selected from a class including at least polyethylene, ethylene/vinyl acetate copolymers and polyvinyl chloride, the masterbatch comprising a thermoplastic copolymer of ethylene and vinyl acetate and dispersed in it from about 1 to 15% (preferably 2-10%) of a synthetic pyrethroid insecticide.

Preferred copolymers are the non-elastomeric ones with vinyl acetate contents up to about 28%, but preferably not exceeding 20%, and more especially about 10-15%.

Preferred insecticides are permethrin, alphacypermethrin, betacypermethrin, sigmacypermethrin, deltamethrin and most especially cypermethrin.

Masterbatches in accordance with the invention can be made in any suitable and conventional way. For example, the insecticide (in most cases marketed as an oily liquid) may be tumble-mixed with granular copolymer until sufficiently imbibed to give a stable mixture; the insecticide may be diluted with a volatile swelling agent for the copolymer and granular copolymer exposed to the mixture until absorbed, after which the swelling agent may be distilled off under vacuum; or the liquid or melted insecticide may be injected into already plastified copolymer in a cavity-transfer mixer fitted to an extruder or in a twin-screw or other mixing extruder.

In the cable factory, the master-batch may be added to the base polymer (PE, PVC or EVA, and possibly





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some others) and other conventional additives by metering into the extruder hopper or by prior tumble-mixing, using a dilution ratio (dependent on the insecticide concentration in the masterbatch) to achieve an effective insecticidal concentration in the cable sheath, say in the range from 0.01 to 0.8%. Since the insecticide is already dispersed in the polymer, handling precautions need not be onerous.

Example

A masterbatch of 5% cypermethrin in an ethylene/vinyl acetate copolymer of 12.5% vinyl acetate content was used as masterbatch to make cable sheaths and plaques of cable-sheathing compositions.

For the sake of verifiability, the polyethylene-based compositions were based on a commercially-available cable-sheath material, namely a composition sold by Neste Oy under the designation "3420" the base for the PVC-based composition was a cable-sheathing composition in regular use by one of the applicants. These base compositions were blended with the masterbatch in appropriate proportions to give 0.06%, 0.12%, 0.25% and 0.5% of cypermethrin; two of the polyethylene-based compositions were also extruded as outer sheaths on cables with corrugated aluminium inner sheaths, the maximum outer diameter of the outer sheaths being about 110mm. In accordance with Test B of BS 6239 (EN117), test pieces measuring 50 by 25mm were cut from the plaques and from the outer sheaths; those cut from



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plaques were 3mm thick and those cut from the outer sheaths about 7mm thick. Each of the test pieces was individually exposed to 200 workers and 30 soldiers of the termite species *Coptotermes formosanus* for a period of 8 weeks, using three samples of each composition. Controls of the same dimensions were made from the commercially available sheathing compositions without any masterbatch.

None of the samples containing cypermethrin showed any visible sign of attack at the end of the test, whereas two out of three of the polyethylene cable sheath samples without cypermethrin were already showing visible damage. Counts of termites surviving showed a wide statistical scatter (from zero to 58% of workers surviving in extreme cases) and there was no statistically significant difference between survival rates between the samples containing cypermethrin and those containing no insecticide. While inconclusive, this is consistent with the view that protection is due primarily to a deterrent effect and not primarily to the toxicity of the cypermethrin. This result may be contrasted with the old cable-sheathing formulations containing Aldrin and Dieldrin, which would have killed all the termites within the period of the test.

Tensile strength and elongation measurements were made on certain of the sheathing compositions as manufactured and after ageing for 14 days at 110°C, with the following results (mean of five plaque samples,

1.7mm thick, unless otherwise indicated):

<u>Base polymer</u>	<u>% cypermethrin</u>	<u>UTS(MPa)</u>	<u>Elongation(%)</u>	
Polyethylene 3420	none	19	800	unaged
		17	770	aged
	0.12	15	600	unaged
		9#	440#	aged
	0.25	14	470	unaged
		13	430	aged
PVC YV188	none	12.8	235	unaged
		12.8	260	aged
	0.12	12.8	260	unaged
		12.8	260	aged
	0.25	13	270	unaged
		12.5	240	aged
#	only two samples			

The polyethylene sample containing 0.25% cypermethrin was additionally tested for environmental stress cracking according to BS 6469 using as test liquid 10% and 100% Antarox CO-630; no failure was observed.

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CLAIMS

- 1 A polymer masterbatch for making cable sheaths in
conjunction with a base polymer selected from a class
including at least polyethylene, ethylene/vinyl acetate
copolymers and polyvinyl chloride, the masterbatch
5 comprising a thermoplastic copolymer of ethylene and
vinyl acetate and dispersed in it from about 1 to 15% of
a synthetic pyrethroid insecticide.
- 2 A masterbatch as claimed in Claim 1 containing
from 2 to 10% of the synthetic pyrethroid insecticide.
- 10 3 A masterbatch as claimed in Claim 1 or claim 2 in
which the copolymer is a non-elastomeric one with a
vinyl acetate contents up to about 28%.
- 4 A masterbatch as claimed in Claim 1 or claim 2 in
which the copolymer is a non-elastomeric one with a
15 vinyl acetate content not exceeding 20%.
- 5 A masterbatch as claimed in Claim 1 or claim 2 in
which the copolymer is a non-elastomeric one with a
vinyl acetate content about 10-15%.
- 6 A masterbatch as claimed in any one of Claims 1-5
20 in which the insecticide is permethrin,
alphacypermethrin or betacypermethrin.
- 7 A masterbatch as claimed in any one of Claims 1-5
in which the insecticide is sigmacypermethrin or
deltamethrin.
- 25 8 A masterbatch as claimed in any one of Claims 1-5
in which the insecticide is cypermethrin.
- 9 A masterbatch substantially as described in the



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Example.

10 A termite-resistant electric cable having a sheath incorporating an effective concentration of synthetic pyrethroid insecticide that was added in the form of the masterbatch claimed in any one of Claims 1-6 or Claim 8.

11 A termite-resistant electric cable having a sheath incorporating an effective concentration of synthetic pyrethroid insecticide that was added in the form of the masterbatch claimed in claim 7 or claim 9.

12 A cable as claimed in Claim 10 in which the sheath is based on polyethylene or polyvinyl chloride.

13 A termite-resistant cable substantially as described with reference to the Example.

14 A cable installation comprising at least one cable as claimed in any one of claims 10-13.

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ABSTRACT

Cable-making Compositions

A composition for use as a masterbatch in making cable sheaths with enhanced resistance to termites comprises about 1-15% of a pyrethroid insecticide in a base of an ethylene-vinyl acetate copolymer. The masterbatch is compatible with both main sheathing polymers for underground cables, namely polyethylene and polyvinyl chloride as well as with ethylene/vinyl acetate copolymer. Permethrin, alphacypermethrin, betacypermethrin, sigmacypermethrin, deltamethrin and most especially cypermethrin are preferred insecticides.

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DATE OF REPLACEMENT		19/6/97...

Processes for making Termite-resistant Cable Sheaths

This invention relates to processes for making sheaths for cables (including power and communications cables) and optical cables, and more particularly to processes for incorporation into cable sheaths of additives for the purpose of reducing the susceptibility of the cables to attack by termites. It includes cables made by use of the processes and cable installations in which the cables are used.

In GB1538222, one of the present applicants has proposed the use of a synthetic pyrethroid insecticide that has since become known as permethrin as additive to a cable sheath for this purpose, but there are difficulties in handling such substances in the plant normally available in cable-making factories and custom compounders have been unwilling to incorporate them in to polymer-based sheathing materials because the relatively small quantities of material required for this specialised market were not considered sufficient to justify the special decontamination régime that would have to be imposed on a large mixing plant. This problem is aggravated because cable purchasers wish to have available sheaths based on a range of base polymers, including polyethylene (PE or polythene), polyvinyl chloride (PVC) and certain ethylene/vinyl acetate copolymers (EVA's); polyethylene and PVC, in particular, are very different in their melt characteristics and require different designs of plant to formulate them. Lindane has remained in use on a small scale.

Subsequently, a number of other effective synthetic pyrethroid insecticides have become available and widely used for agricultural and public health applications. Notable among these are cypermethrin, alphacypermethrin and

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betacypermethrin, all of which are different isomer mixtures corresponding to the same structural formula, being a derivative of permethrin having a -CN group in the *alpha* position (the derivative has *cis-trans* forms in addition to
5 two independent optically active centres, giving rise to eight stereoisomers of differing insecticidal potency).

We have now discovered that these synthetic pyrethroid insecticides can be dispersed in relatively high concentrations in ethylene-vinyl acetate copolymers to form a
10 "masterbatch" that is compatible with both PE-based and PVC-based cable sheathing compositions, as well as EVA-based ones. This facilitates use of the materials considerably, not only because a single masterbatch composition can be used to meet all cable sheath composition requirements, but also
15 because the volume of material to be produced in the insecticide-handling plant is much reduced, allowing the use of smaller machinery that can be more readily decontaminated. The invention thus provides a process for making cable sheaths from a base polymer selected from a class including
20 at least polyethylene, ethylene/vinyl acetate copolymers and polyvinyl chloride, comprising blending with the selected base polymer a masterbatch comprising a thermoplastic copolymer of ethylene and vinyl acetate having dispersed in it from 1 to 15% (preferably 2-10%) of a synthetic pyrethroid
25 insecticide.

Preferred copolymers are the non-elastomeric ones with vinyl acetate contents up to 28%, but preferably not exceeding 20%, and more especially 10-15%.

Preferred insecticides are permethrin,
30 alphacypermethrin, betacypermethrin, sigmacypermethrin, deltamethrin and most especially cypermethrin.

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Masterbatches for use in the invention can be made in any suitable and conventional way. For example, the insecticide (in most cases marketed as an oily liquid) may be tumble-mixed with granular copolymer until sufficiently
5 imbibed to give a stable mixture; the insecticide may be diluted with a volatile swelling agent for the copolymer and granular copolymer exposed to the mixture until absorbed, after which the swelling agent may be distilled off under vacuum; or the liquid or melted insecticide may be injected
10 into already plastified copolymer in a cavity-transfer mixer fitted to an extruder or in a twin-screw or other mixing extruder.

In the cable factory, the masterbatch may be added to the base polymer (PE, PVC or EVA, and possibly some others)
15 and other conventional additives by metering into the extruder hopper or by prior tumble-mixing, using a dilution ratio (dependent on the insecticide concentration in the masterbatch) to achieve an effective insecticidal concentration in the cable sheath, say in the range from 0.01
20 to 0.8%. Since the insecticide is already dispersed in the polymer, handling precautions need not be onerous.

Example

A masterbatch of 5% cypermethrin in an ethylene/vinyl acetate copolymer of 12.5% vinyl acetate content was used as
25 masterbatch to make cable sheaths and plaques of cable-sheathing compositions.

For the sake of verifiability, the polyethylene-based compositions were based on a commercially-available cable-sheath material, namely a composition sold by Neste Oy
30 under the designation "3420" the base for the PVC-based composition was a cable-sheathing composition in regular use by one of the applicants. These base compositions were

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blended with the masterbatch in appropriate proportions to give 0.06%, 0.12%, 0.25% and 0.5% of cypermethrin; two of the polyethylene-based compositions were also extruded as outer sheaths on cables with corrugated aluminium inner sheaths, the maximum outer diameter of the outer sheaths being about 110mm. In accordance with Test B of BS 6239 (EN117), test pieces measuring 50 by 25mm were cut from the plaques and from the outer sheaths; those cut from plaques were 3mm thick and those cut from the outer sheaths about 7mm thick. Each of the test pieces was individually exposed to 200 workers and 30 soldiers of the termite species *Coptotermes formosanus* for a period of 8 weeks, using three samples of each composition. Controls of the same dimensions were made from the commercially available sheathing compositions without any masterbatch.

None of the samples containing cypermethrin showed any visible sign of attack at the end of the test, whereas two out of three of the polyethylene cable sheath samples without cypermethrin were already showing visible damage. Counts of termites surviving showed a wide statistical scatter (from zero to 58% of workers surviving in extreme cases) and there was no statistically significant difference between survival rates between the samples containing cypermethrin and those containing no insecticide. While inconclusive, this is consistent with the view that protection is due primarily to a deterrent effect and not primarily to the toxicity of the cypermethrin. This result may be contrasted with the old cable-sheathing formulations containing Aldrin and Dieldrin, which would have killed all the termites within the period of the test.

Tensile strength and elongation measurements were made on certain of the sheathing compositions as manufactured

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and after ageing for 14 days at 110°C, with the following results (mean of five plaque samples, 1.7mm thick, unless otherwise indicated):

	Base polymer	% cypermethrin	UTS(MPa)	Elongation(%)	
5	Polyethylene	none	19	800	unaged
	3420		17	770	aged
		0.12	15	600	unaged
			9#	440#	aged
10		0.25	14	470	unaged
			13	430	aged
	PVC YV188	none	12.8	235	unaged
15			12.8	260	aged
		0.12	12.8	260	unaged
			12.8	260	aged
20		0.25	13	270	unaged
			12.5	240	aged
	#	only two samples			

The polyethylene sample containing 0.25% cypermethrin was additionally tested for environmental stress cracking according to BS 6469 using as test liquid 10% and 100% Antarox[†] CO-630; no failure was observed.

[†]Registered Trade Mark

CLAIMS

- 1 A process for making cable sheaths from a base polymer
selected from a class including at least polyethylene,
ethylene/vinyl acetate copolymers and polyvinyl chloride,
5 comprising blending with the selected base polymer a
masterbatch comprising a thermoplastic copolymer of ethylene
and vinyl acetate having dispersed in it from 1 to 15% of a
synthetic pyrethroid insecticide.
- 2 A process as claimed in Claim 1 comprising using a
10 masterbatch containing from 2 to 10% of the synthetic
pyrethroid insecticide.
- 3 A process as claimed in Claim 1 or claim 2 comprising
using a masterbatch in which the copolymer is a
non-elastomeric one with a vinyl acetate content up to 28%.
- 15 4 A process as claimed in Claim 1 or claim 2 comprising
using a masterbatch in which the copolymer is a
non-elastomeric one with a vinyl acetate content not
exceeding 20%.
- 5 A process as claimed in Claim 1 or claim 2 comprising
20 using a masterbatch in which the copolymer is a
non-elastomeric one with a vinyl acetate content 10-15%.
- 6 A process as claimed in any one of Claims 1-5
comprising using a masterbatch in which the insecticide is
permethrin, alphacypermethrin or betacypermethrin.
- 25 7 A process as claimed in any one of Claims 1-5
comprising using a masterbatch in which the insecticide is
sigmacypermethrin or deltamethrin.
- 8 A process as claimed in any one of Claims 1-5
comprising using a masterbatch in which the insecticide is
30 cypermethrin.



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9 A process for making cable sheaths containing
cypermethrin substantially as described in the Example.

10 A termite-resistant electric cable having a sheath
incorporating an effective concentration of synthetic
5 pyrethroid insecticide that was made by the process claimed
in any one of Claims 1-6 or Claim 8.

11 A termite-resistant electric cable having a sheath
incorporating an effective concentration of synthetic
pyrethroid insecticide that was made by the process claimed
10 in claim 7 or claim 9.

12 A cable as claimed in Claim 10 in which the sheath is
based on polyethylene or polyvinyl chloride.

13 A termite-resistant cable having a sheath containing
cypermethrin substantially as described with reference to the
15 Example.

14 A cable installation comprising at least one cable as
claimed in any one of claims 10-13.



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REPLACEMENT SHEET

18 MAY 1998

ABSTRACT

Cable-making Compositions

A composition for use as a masterbatch in making cable sheaths with enhanced resistance to termites comprises about 1-15% of a pyrethroid insecticide in a base of an ethylene-vinyl acetate copolymer. The masterbatch is compatible with both main sheathing polymers for underground cables, namely polyethylene and polyvinyl chloride as well as with ethylene/vinyl acetate copolymer. Permethrin, alphacypermethrin, betacypermethrin, sigmacypermethrin, deltamethrin and most especially cypermethrin are preferred insecticides.

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Date: 18 MAY 1998