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(71) Applicant(s)
Cryovac, Inc.

(72) Inventor(s)
Bernhard Thele

(74) Agent/Attorney
Davies Collison Cave, Level 15, 1 Nicholson Street, MELBOURNE VIC 3000

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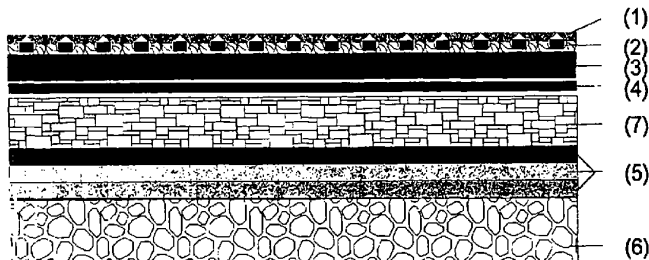
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OVAC, INC. [US/US]; 100 Rogers Bridge Road, Duncan,
SC 29334 (US).Published:
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(75) Inventor/Applicant (*for US only*): THELE, Bernhard
[DE/DE]; Grebertstrasse 1, D-65307 Bad Schwalch (DE).(74) Agent: DE CARLI, Elda; Sealed Air S.p.A., Via Trento,
7, I-20017 Passirana Di Rho (IT).

(54) Title: PROTECTING LAMINATE FOR AUTOMOTIVE CARPETING



(57) Abstract: A thermoplastic laminate comprising i) a first outer layer comprising an ethylene homo- or co-polymer; ii) a core layer comprising a polyamide; iii) a second outer layer comprising a thermoplastic polyurethane. The thermoplastic laminate is used as an intermediate protective laminate in the manufacture of a polyurethane padded carpet wherein a polyurethane foam layer is formed on the surface of the protective laminate in its turn hot bonded to an upper fibrous layer.

PROTECTING LAMINATE FOR AUTOMOTIVE CARPETTING

The present invention relates to carpeting, in particular to automotive carpeting, to a process for the production thereof and to a thermoplastic multilayer film particularly suitable for use as a protective laminate for molded carpets with polyurethane foam-padded backing.

5 The interior (floor, inside roof, door and side paneling, rear window shelf, columns, etc.) and the luggage compartment (rear partitions, rear load floor, side paneling, tailgate, etc.) in a vehicle are covered with carpets of various classes and qualities, which by means of molding (pressing the carpet pattern) can be exactly adjusted to fit the shell body of the respective vehicle model.

10 Carpets are usually fitted into vehicles, particularly cars, to improve comfort by reducing noise levels, increasing thermal insulation and resilience underfoot and adding to the decor.

The floor covering of small and middle-class vehicles is usually of pile. In upper classes as well as in the comfort and luxury classes high-grade velvet-pile carpeting is used with few exceptions.

15 Vehicles from the upper class to the luxury class are fitted with high-grade velvet-pile molded carpet, which is padded with a polyurethane soft foam backing.

Besides an upper fibrous layer and a flexible polyurethane foam layer, all the carpets also comprise a thermoplastic resin interlayer.

There are at least two general processes for the manufacture of automotive carpets.

20 In one of them the upper fibrous layer is sprinkled on the reverse side with polyethylene powder (about 200-400 g/m²). The powder is melted into a film by means of radiant heat treatment. A thermoplastic protective laminate is bonded under pressure to the polyethylene film and then a heavy layer (fleece, non-woven fabric or felt) is laminated onto the surface of the protective laminate. Sometimes the heavy layer is fixed without using the polyethylene
25 powder.

Rolled goods are then divided into carpet pieces. The individual pieces are placed in the feeder of the molding machine where they undergo radiant heat treatment in particular areas and strengthened with additional, fitted heavy material.

Finally the carpet pieces are conveyed to a forming station, heated to approximately 140 °C and shaped with the appropriate plug.

The shaped sections are hung on a conveyor belt and transported one by one into the foam-padding chamber. In these closed chambers, whose inside shape on the reverse side of the carpet corresponds exactly to the shape of the vehicle floor it will be applied to, the hollow on the back of the molded carpet is filled under pressure with polyurethane soft foam.

When the element has cooled, a robot cuts it exactly to fit using a water jet.

The function of the protective laminate in molded carpet manufacturing is to tightly protect the shaped carpet from the high-pressure injected polyurethane foam. The foam must be prevented from penetrating the underside of the carpet and soiling the surface.

Typically protective laminates 40 to 60 µm thick, comprising a core polyamide layer and outer polyethylene layers are employed in this process.

In the other process, the upper fibrous layer is sprinkled on the reverse side with polyethylene powder (about 400 to 600 g/m²) in a laminating machine. Then a heavy layer is fixed upon it and a protective thermoplastic laminate is put onto the heavy layer.

The outer layer of the protective laminate bonded to the heavy layer will typically be of polyethylene while the other outer layer will be of polyamide. Since polyurethane soft foam adheres directly to polyamide, this outer layer is foam coated on the back.

This latter process appears to be the most advanced one but still presents some disadvantages:

- i) since the protective laminate lies on the outside of the molded carpet to be padded with foam polyurethane, the essential polyamide layer will be more readily damaged and a thicker laminate, with respect to that required by the former process, is needed;
- ii) if all free surfaces are not covered during the radiant heat treatment, the laminate will burn through on the unprotected areas.

Protective laminates with a different structure have been proposed to overcome these drawbacks.

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Japanese Kokai 201940/85 (Derwent Accession Number 85-293325) describes for instance the use of a thermoplastic elastomer layer, typically formed from partially cross-linked ethylene- α -olefin copolymer rubber, laminated to a polyurethane foam layer by means of an adhesive based on a high vinyl acetate EVA copolymer.

- 5 Japanese Kokai 147172/93 (Derwent Accession Number 93-223931) teaches the use of an elastomer composition of ethylene-propylene diene copolymer and EVA.

Still however the mechanical properties provided by the polyamide are missing and the adhesion of the polyurethane foam to said intermediate laminate is insufficient.

- 10 Hence, there is a need in the art for a thermoplastic laminate, particularly suitable for use as protective laminate in the manufacture of a polyurethane padded carpet for the automotive industry, that is characterized by good mechanical properties at low thickness and by a suitable adhesive strength to the polyurethane foam without the need of an additional adhesive in-between.

- 15 The protective thermoplastic laminate according to the present invention comprises at least three layers and is characterized by the presence of a first outer layer comprising an ethylene homo- or copolymer, a core layer comprising a polyamide and a second outer layer comprising a thermoplastic polyurethane.

If necessary or advisable to improve the bond between the outer layer and the core layer, suitable tie layers may also be present in the laminate.

- 20 DEFINITIONS

As used herein, the phrases "inner layer" and "internal layer" refer to any film layer having both of its principal surfaces directly adhered to another layer of the film.

As used herein, the phrase "outer layer" refers to any film layer having only one of its principal surfaces directly adhered to another layer of the film.

- 25 As used herein, the term "core", and the phrase "core layer" refer to any internal film layer that has a primary function other than serving as an adhesive or compatibilizer for adhering two layers to one another.

As used herein, the phrase "bulk layer" refers to any layer that is present for the purpose of improving the abuse-resistance, toughness, modulus, etc., of the film. Bulk layers generally comprise polymers which are inexpensive relative to other polymers in the film which provide some specific purpose unrelated to abuse-resistance, modulus, etc.

5 As used herein, the phrase "tie layer" refers to any internal layer having the primary purpose of adhering two layers to one another.

As used herein the terms "polyethylene" and "ethylene homopolymer" identify polymers consisting essentially of an ethylene repeating unit. Depending on the polymerization process employed, polymers with a different degree of branching and a different density can be obtained. Those characterized by a low degree of branching and showing a density higher than 0.940 g/cm³ are called HDPE while those with a higher level of branching and a density up to 0.940 g/cm³ are called LDPE.

As used herein the term "ethylene copolymer" refers to the copolymers of ethylene with one or more other olefins and/or with a non-olefinic comonomer copolymerizable with ethylene, such as vinyl monomers, modified polymers thereof, and the like. Specific examples include ethylene- α -olefin copolymers, ethylene/vinyl acetate copolymers, ethylene/ethyl acrylate copolymers, ethylene/butyl acrylate copolymers, ethylene/methyl acrylate copolymers, ethylene/acrylic acid copolymers, ethylene/methacrylic acid copolymers, ionomer resins, ethylene/alkyl acrylate/maleic anhydride ter-polymers, etc..

20 As used herein, the phrase "heterogeneous polymer" refers to polymerization reaction products of relatively wide variation in molecular weight and relatively wide variation in composition distribution, i.e., polymers made, for example, using conventional Ziegler-Natta catalysts. Such polymers typically contain a relatively wide variety of chain lengths and comonomer percentages.

25 As used herein, the phrase "homogeneous polymer" refers to polymerization reaction products of relatively narrow molecular weight distribution and relatively narrow composition distribution. Homogeneous polymers exhibit a relatively even sequencing of comonomers

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within a chain, the mirroring of sequence distribution in all chains, and the similarity of length of all chains, and are typically prepared using metallocene. or other single-site type catalysis.

More particularly, homogeneous ethylene/ α -olefin copolymers may be characterized by one or more methods known to those of skill in the art, such as molecular weight distribution (M_w/M_n), composition distribution breadth index (CDBI), and narrow melting point range and single melt point behavior.

As used herein, the term "ethylene/ α -olefin copolymer" refers to such heterogeneous materials as linear low density polyethylene (LLDPE), linear medium density polyethylene (LMDPE) and very low and ultra low density polyethylene (VLDPE and ULDPE); and homogeneous polymers such as metallocene catalyzed polymers such as EXACTTM materials supplied by Exxon, AFFINITYTM and ENGAGETM materials supplied by Dow, LUFLEXENTM materials supplied by BASF and TAFMERTM materials supplied by Mitsui Petrochemical Corporation. These materials generally include copolymers of ethylene with one or more comonomers selected from C₄ to C₁₀ α -olefins such as butene-1, hexene-1, octene-1, etc..

As used herein the term "ethylene-acrylic acid and ethylene-methacrylic acid copolymers" refers to copolymers of ethylene with a copolymerisable ethylenically unsaturated carboxylic acidic monomer selected from acrylic acid and methacrylic acid. The copolymer typically contains from about 4 to about 18% by weight of acrylic or methacrylic acid units. Said copolymer can also contain, copolymerised therein an alkyl (meth)acrylate, such as n-butyl acrylate or methacrylate or isobutyl acrylate or methacrylate. Said copolymer can be in the free acid form as well as in the ionized or partially ionized form wherein the neutralizing cation can be any suitable metal ion, e.g. an alkali metal ion, a zinc ion or other multivalent metal ions: in this latter case the copolymer is also termed "ionomer".

As used herein the term "ethylene-vinyl acetate copolymer" or "EVA" is intended to refer to a copolymer formed from ethylene and vinyl acetate monomers wherein the ethylene derived units in the copolymer are present in major amounts, preferably between about 60%

and 98% by weight and the vinyl acetate derived units in the copolymer are present in minor amounts, preferably between about 2% and about 40% by weight.

As used herein the term "ethylene-alkyl (meth)acrylate copolymers" refers to copolymers of ethylene with alkyl (meth)acrylates, e.g. methyl (meth)acrylate, butyl (meth)acrylate, and iso-butyl (meth)acrylate wherein the ethylene derived units in the copolymer are present in major amounts and the alkyl (meth)acrylate derived units in the copolymer are present in minor amounts, preferably between about 2% and about 28% by weight.

As used herein, the term polyamide is intended to refer to both polyamides and copolyamides. This term specifically includes those aliphatic polyamides or copolyamides commonly referred to as e.g. polyamide 6 (homopolymer based on ϵ -caprolactam), polyamide 66 (homopolycondensate based on hexamethylenediamine and adipic acid), polyamide 69 (homopolycondensate based on hexamethylenediamine and azelaic acid), polyamide 610 (homopolycondensate based on hexamethylenediamine and sebacic acid), polyamide 612 (homopolycondensate based on hexamethylenediamine and dodecandioic acid), polyamide 11 (homopolymer based on 11-aminoundecanoic acid), polyamide 12 (homopolymer based on ω -aminododecanoic acid or on laurilactam), polyamide 6/12 (polyamide copolymer based on ϵ -caprolactam and laurilactam), polyamide 6/66 (polyamide copolymer based on hexamethylenediamine and adipic acid and ϵ -caprolactam), polyamide 66/610 (polyamide copolymers based on hexamethylenediamine, adipic acid and sebacic acid), terpolyamides, modifications thereof and blends thereof. Said term also includes crystalline or partially crystalline, aromatic or partially aromatic, polyamides.

As used herein the term "modified polyolefin" is inclusive of modified polymer prepared by copolymerizing the homopolymer of the olefin or copolymer thereof with an unsaturated carboxylic acid, e.g., maleic acid, fumaric acid or the like, or a derivative thereof such as the anhydride, ester or metal salt or the like; as well as of modified polymer obtained by incorporating, into the olefin homopolymer or copolymer, an unsaturated carboxylic acid.

e.g. maleic acid, fumaric acid, or the like, or a derivative thereof such as the anhydride, ester or metal salt or the like. Examples of said modified polyolefins are graft copolymers of maleic acid or anhydride onto ethylene/ α -olefin copolymers, graft copolymers of fused ring carboxylic anhydrides onto polyethylene, resin mixtures of these and mixtures with
5 polyethylene or ethylene/ α -olefin copolymers.

DETAILED DESCRIPTION OF THE INVENTION

The protective laminate according to the present invention comprises at least three layers :
a first outer layer, a core layer and a second outer layer.

The first outer layer comprises an ethylene homo- or co-polymer as defined above. In a
10 preferred embodiment of the present invention said first outer layer comprises an ethylene homo- or copolymer selected from the group consisting of ethylene homo-polymers and ethylene- α -olefin copolymers. In a more preferred embodiment said first outer layer comprises an ethylene homo- or co-polymer selected from the group consisting of polyethylene of low, medium or high density, and homogeneous or heterogeneous ethylene- α -
15 olefin copolymers of low or medium density (LLDPE or LMDPE).

Said first outer layer may also comprise in addition to the ethylene homo- or co-polymer a modified polyolefin, preferably a modified ethylene homo- or co-polymer, to possibly avoid the use of a separate tie layer to improve the bond between said first outer layer and the core polyamide layer. In such a case the amount of modified polyolefin may be as low as 5-10 %
20 by weight of the overall weight of the first outer layer and still provide for the desired improved adhesion.

The core layer comprises a polyamide as defined above.

In a preferred embodiment of the present invention the polyamides suitable for use in said core layer have a melting temperature below 220 °C. In a more preferred embodiment said
25 core layer comprises a polyamide with a melting temperature below 210 °C. Certain copolyamides 6/12 (such as PA6/12 CR-8 and CR-9 by EMS), certain copolyamides 6/66 (such as Cniamid CF 815 by Caffaro), certain copolyamides of polyamide 6 and a partially

aromatic polyamide (such as Durethan® CI31F and CI31FKS by Bayer) or certain terpolyamides such as those based on polyamide 6, polyamide 11, and polyamide 66 (such as those sold by Bayer under the trade name Durethan® KU 2-2153 or KU 2-2153F), are examples of suitable polyamides.

- 5 The second outer layer in the protective laminate of the present invention comprises a thermoplastic polyurethane, or a blend of thermoplastic polyurethanes.

The thermoplastic polyurethane of the second outer layer may be of the ether or of the ester type. In case a blend of polyurethanes is employed, each polyurethane component may independently be of the ether or ester type.

- 10 These polymers tend to be sticky and are suitable blended with anti blocking agents. They can be used in blends in order to adjust the polymer flow viscosity and surface tackiness as desired.

- In a preferred embodiment of the present invention said second outer layer will essentially consist of said thermoplastic polyurethane or blend of thermoplastic polyurethanes, optionally
15 containing up to 10 %, preferably up to 7 %, and more preferably up to 5 % of a masterbatch of the desired additives in a thermoplastic compatible resin, such as the same or another polyurethane resin or any other resin compatible therewith.

- The overall thickness of the protective laminate according to the present invention is typically comprised between about 25 and about 80 μm , preferably between about 30 and
20 about 70 μm and even more preferably between about 35 and about 60 μm .

The thickness of the first outer layer is generally at least 5 μm , preferably at least 7 μm and even more preferably at least 9 μm . As this polymer is the least expensive one, when the bulk of the laminate has to be increased this is the layer that is generally increased in thickness.

- 25 The second outer layer has a thickness that is generally comprised between about 5 and about 20 μm , preferably between about 7 and about 15 μm and even more preferably between about 8 and about 14 μm .

Thin polyamide core layers are generally sufficient to provide the laminate with the desired mechanical properties. Typical thicknesses are between about 5 μm and about 25 μm , preferably between about 10 and about 18 μm .

If present, tie layers will have a thickness of few microns, e.g., from about 2 to about 10 μm , preferably from about 3 to about 8 μm and even more preferably from about 4 to about 6 μm .

The thermoplastic protective laminate according to the present invention is obtained by coextrusion. The film is not stretched or oriented, at least intentionally. A slight orientation, so-called accidental orientation, may be present depending on the production method employed.

A preferred method of manufacture thereof is the hot blown method.

Alternatively it is possible also to use the cast extrusion method, either through a round or preferably through a flat die.

The new protective laminate according to the present invention is then suitable employed in the manufacture of a molded carpet as known in the area.

Fig. 1, 2, and 3 represent a schematic cross-sectional view of alternative molded carpets that can be manufactured using the protective laminate according to the present invention.

In particular, with reference to Figure 1, the tufted carpet, made up by the combination of (1), (2), and (3), wherein (1) represents a layer of carpet pile or of fleece, (2) is a layer of fleece or cotton weave, and (3) is a layer of latex or hot melt or polyethylene bond, is charged from the roll onto a feeder machine and sprinkled on the reverse side with polyethylene powder (200-400 g/m^2). The powder is melted into a film by a heat treatment forming layer (4) and a heavy layer (7) is laminated thereto. Then, the protective laminate of the invention is fixed with the polyethylene side to the heavy layer. After shaping in an extra operational step, polyurethane foam is applied under pressure to the free polyurethane side. Instead of a heavy layer, that is a non-woven material obtained from several resins, often recycle materials, fleece or a textile molding compound can be used as layer (7).

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Alternatively, as illustrated in Figure 2, the molded carpet does not contain a heavy layer (7) and the protective laminate (5) is directly adhered with the polyethylene outer layer to the sintered polyethylene layer (4).

Still alternatively, as illustrated in Figure 3, the protective laminate (5) of the present invention is directly adhered with the polyethylene outer layer to the latex or hot melt layer (3) without the intermediate sintered polyethylene layer (4).

The advantages of this overall method are many:

- the elasticity of the new thermoplastic laminate, influenced by the polyurethane layer, improves puncture resistance and the molding capacity of the carpet structure:
- compared to the conventional polyethylene/polyamide laminates on the market, appreciable reductions in thickness are possible with the protective laminate of the invention:
- the use of the new laminate eliminates the problems caused by the curling of the polyethylene/polyamide conventional structures around the swell and the connecting part that does not lie flat.

The present invention also provides a process for the preparation of a carpet comprising an upper fibrous layer, an intermediate protective laminate and a polyurethane foam layer, wherein the polyurethane foam layer is formed on the surface of the protective laminate which is not bonded to the upper fibrous layer, wherein the protective laminate comprises (i) a first outer layer facing the upper fibrous layer and comprising an ethylene homo- or co-polymer, (ii) a core layer comprising a polyamide, and (iii) a second outer layer comprising a thermoplastic polyurethane.

The present invention also provides a carpet for the automotive industry comprising an upper fibrous layer, an intermediate thermoplastic protective laminate and a polyurethane foam layer wherein the polyurethane foam layer is formed on the surface of the protective laminate which is not bonded to the upper fibrous layer, wherein the protective laminate comprises (i) a first outer layer facing the upper fibrous layer and comprising an ethylene homo- or co-polymer, (ii) a core layer comprising a polyamide, and (iii) a second outer layer comprising a thermoplastic polyurethane.

Unless indicated otherwise, all percentages are by weight.

EXAMPLES

LDPE/tie/PA/tie/TPU

10 General resin descriptions are shown in Table 1.

TABLE I

| RESIN | TRADE NAME | SUPPLIER | DENSITY (g/cm ³) | T _m (°C) | MFI (g/10 min) |
|--|---------------------|---------------|------------------------------|---------------------|----------------|
| • LDPF | Quantum NA345-013 | Quantum Chem. | 0.922 | 125 | 3.2 |
| • tie (anhydride grafted LLDPE) | Tymor L203 | Norton Int. | 0.91 | 130 | 2.6 |
| • PA | Chamid CF 815 | Caffaro | 1.12 | 195 | 3.5 |
| Nylon 6/66 | | | | | |
| • TPU ₁ (ether type) | Elastollan 806-10 | BASF | 1.12 | ~120 | 2.3 |
| • TPU ₁ (ester type) | Elastollan 883-50 | BASF | 1.19 | ~120 | 3.0 |
| • TPU ₁ (ether type) | Elastollan 1154-D10 | BASF | 1.17 | ~120 | 1.9 |
| • TPU ₄ | | | | | |
| TPU ₁ plus 5% of antiblock Elastollan Konz. 978 | concentrate by BASF | | | | |
| • TPU ₄ | | | | | |
| TPU ₁ plus 9% of antiblock Elastollan Konz. 978 (BASF). | | | | | |

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The temperature profiles for the TPU were established so that to keep the polymer melt below the critical temperature of 230°C.

Both TPU and PA resins were pre-dried for at least 4 hours at 85-90°C in a convection oven prior to extrusion. The coextrusion system was also equipped with an enclosed feeder and a dry/inert gas purge to prevent moisture absorption by the TPU from the atmosphere.

The film layers were added starting with LDPE at the bottom of the die and ending with the TPU on the outside of the bubble at the top of the die.

Layer target thickness was 15 µm/5 µm/15 µm/5 µm/10 µm for the LDPE tie PA tie TPU layers respectively.

The obtained films were cooled with a standard air ring, slit on both edges and separated to provide two single ply films that were wound with the TPU layer on the outside of the roll.

The reference to any prior art in this specification is not, and should not be taken as, an acknowledgment or any form of suggestion that that prior art forms part of the common general knowledge in Australia.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A thermoplastic laminate suitable for use as protective laminate in the manufacture of a polyurethane padded carpet comprising
 - (i) a first outer layer comprising an ethylene homo- or copolymer
 - (ii) a core layer comprising a polyamide
 - (iii) a second outer layer comprising thermoplastic polyurethane
2. The thermoplastic laminate of claim 1, further comprising a tie layer or tie layers bonding the core layer to an outer layer or both outer layers respectively.
3. The thermoplastic laminate of claim 1 or 2, wherein the first outer layer comprises an ethylene homo- or co-polymer selected from the group consisting of polyethylene and ethylene- α -olefin copolymer.
4. The thermoplastic laminate of claim 3, wherein the first outer layer comprises an ethylene homo- or co-polymer selected from the group consisting of polyethylene of low, medium or high density and ethylene- α -olefin copolymer of low or medium density.
5. The thermoplastic laminate of any one of the preceding claims wherein the core layer comprises a polyamide with a melting temperature below 220°C.
6. The thermoplastic laminate of claim 5, wherein the core layer comprises a polyamide with a melting temperature below 210°C.
7. The thermoplastic laminate of any one of the preceding claims wherein the second outer layer comprises thermoplastic polyurethane of the ether or of the ester type.
8. A thermoplastic laminate suitable for use as protective laminate in the manufacture of a polyurethane padded carpet, substantially as hereinbefore described with reference to the Examples.

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9. A process for the preparation of a carpet comprising an upper fibrous layer, an intermediate protective laminate and a polyurethane foam layer, wherein the polyurethane foam layer is formed on the surface of the protective laminate which is not bonded to the upper fibrous layer, wherein said protective laminate comprises (i) a first outer layer facing the upper fibrous layer and comprising an ethylene homo- or co-polymer, (ii) a core layer comprising a polyamide, and (iii) a second outer layer comprising a thermoplastic polyurethane.
10. The process of claim 9, wherein the protective laminate is a thermoplastic laminate according to any one of claims 2 to 8.
11. A process for the preparation of a carpet substantially as hereinbefore described with reference to the Examples.
12. A carpet for the automotive industry comprising an upper fibrous layer, an intermediate thermoplastic protective laminate and a polyurethane foam layer, wherein the polyurethane foam layer is formed on the surface of the protective laminate which is not bonded to the upper fibrous layer, wherein said protective laminate comprises (i) a first outer layer facing the upper fibrous layer and comprising an ethylene homo- or co-polymer, (ii) a core layer comprising a polyamide, and (iii) a second outer layer comprising a thermoplastic polyurethane.
13. A carpet according to claim 12, wherein the protective laminate is a thermoplastic laminate according to any one of claims 2 to 8.

DATED this 21st day of July, 2004

Cryovac, Inc.

by DAVIES COLLISON CAVE

Patent Attorneys for the Applicant(s)

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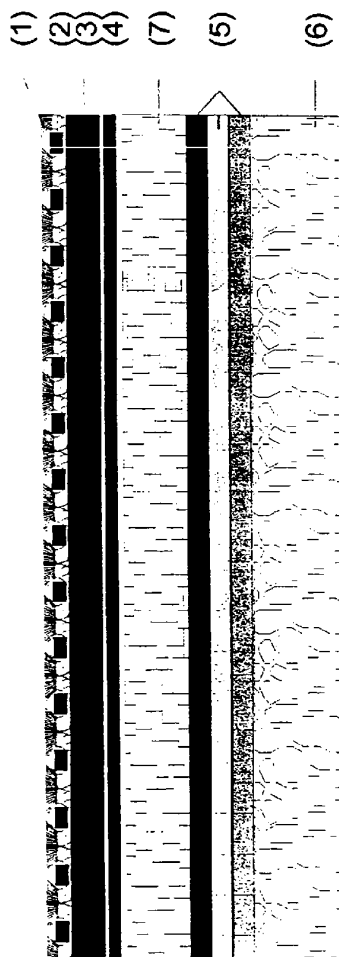


Fig. 1

SUBSTITUTE SHEET (RULE 26)

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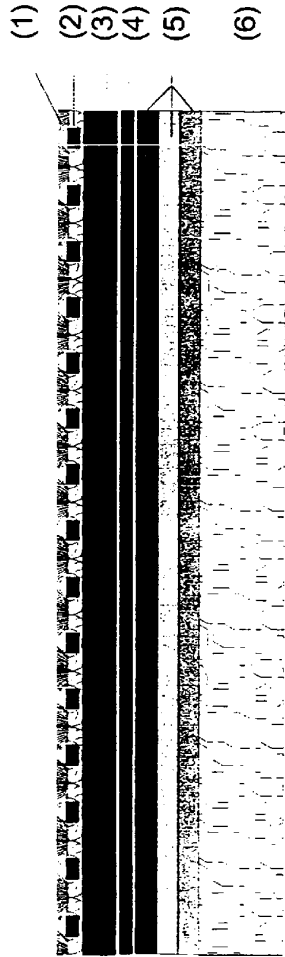


Fig. 2

SUBSTITUTE SHEET (RULE 26)

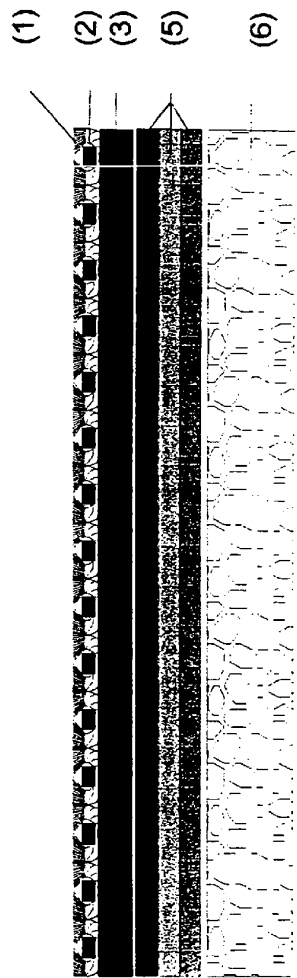


Fig. 3

SUBSTITUTE SHEET (RULE 26)