A carpet product includes in sequence a) a primary backing material having a back side and a face side, with carpet fibers extending from the face side to form a carpet pile and also passing through the primary backing material and forming loops on the back side; b) a primary coating layer on the loops, including a vinyl acetate ethylene copolymer and present at from 542 to 1085 g/m² (16 to 32 oz./yd²) on a dry solids basis; c) a secondary coating layer on the primary coating layer, including a styrene-butadiene copolymer; and d) a secondary backing material on the secondary coating layer and adhered thereby to the primary coating layer.
CARPET PRODUCT AND PROCESS FOR THE MANUFACTURING OF A CARPET PRODUCT

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority benefit of U.S. provisional patent application No. 61/895,149, filed 24 Oct. 2013, the entirety of which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to a carpet product and a process for manufacturing it.

BACKGROUND OF THE INVENTION

[0003] Carpets typically include a primary backing material to which carpet fibers are attached to form a carpet pile on the face side, and a primary coating layer on the back side of the primary backing material to fix the carpet fibers to the primary backing. To improve dimensional stability, a secondary backing material is often fixed to the primary backing material by means of a secondary coating layer.

[0004] The primary and secondary coating layers are typically formed from aqueous polymer dispersions, for example aqueous vinyl acetate ethylene copolymer dispersions and latices of carboxylated styrene butadiene copolymers.

[0005] U.S. Pat. No. 3,779,799 describes the use of an aqueous latex of carboxylated styrene butadiene copolymers, or alternatively of an aqueous dispersion of vinyl acetate ethylene copolymer, as the primary coating for the tufted primary backing material of carpets.

[0006] U.S. Pat. Nos. 4,735,986 and 5,084,503 describe carpet backing adhesives employing vinyl acetate ethylene dispersions stabilized with a mixture of polyvinyl alcohols. A high tuft lock is said to be obtained with such dispersions. It is also mentioned that such vinyl acetate ethylene dispersions are compatible with most styrene butadiene emulsions. The use of different types of coating materials for the primary and secondary coating layers is not disclosed.

[0007] U.S. patent application 2001/0046581 discloses a carpet comprising a primary backing with a yarn attached with an adhesive, with a woven secondary backing attached to the back side of the primary backing with the same adhesive. The second side of the secondary backing is coated with a thermoplastic polymer layer by melt bonding.

[0008] WO 2012/020321 A2 discloses carpet products with coating layers formed from vinyl ester ethylene copolymer dispersions. The vinyl ester ethylene copolymer dispersions have a particle size of 50 to 500 nm, and the dispersions are used to coat the primary backing material as well as for laminating the secondary backing material. Styrene-based emulsions are described as prior art binders for coating compositions for carpet materials, but these are said to be more expensive and have worse washability and are not used in the invention.

[0009] U.S. patent application 2008/0131146 describes a method for manufacturing carpets from recycled materials wherein EVA hotmelt, vinyl acetate ethylene emulsion, carboxylated styrene butadiene latex, styrene butadiene latex, acrylic latex, polyolefin hotmelt, polyolefin dispersion, or butadiene acrylate copolymers are described as adhesive backing materials for coating the primary backing materials.

[0010] WO 2010/129945 discloses a method for manufacturing carpets from recycled materials, using filler obtained from recycling of waste carpets. EVA hotmelt, vinyl acetate ethylene emulsion, carboxylated styrene butadiene latex, styrene butadiene latex, acrylic latex, polyolefin hotmelt, polyolefin dispersion, or butadiene acrylate copolymers are described as coating agents for coating the primary backing materials.

[0011] U.S. patent application 2013/0209726 describes a latex coating composition comprising a blend of a vinyl ester ethylene copolymer and a styrene butadiene copolymer. The blend may be used as a precoat binder, a skipcoat binder, or both.

[0012] Japanese patent application JP 59-214633 discloses coating a propylene woven fabric coated with an ethylene copolymer emulsion, e.g., a vinyl acetate ethylene copolymer emulsion (VAE), followed by drying. Pile yarns are then interwoven with the dry VAE-coated base fabric. A styrene butadiene rubber latex (SBR) is then applied to the dried VAE layer and the loops of pile yarn emerging from it. Then, a secondary base fabric of expanded polypropylene woven cloth bearing a wet coating of an ethylene copolymer emulsion, e.g., a VAE, is laid upon the wet SBR latex coating with the VAE and SBR coatings in contact, and bonded by heating and drying the VAE emulsion and SBR latex. In some embodiments, the VAE emulsion on the secondary base fabric is omitted.

[0013] Despite these advances, improved methods and materials would be beneficial for providing carpet having high tuft lock and high delamination resistance, yet easily processable at the elevated temperatures encountered on carpet coating lines.

SUMMARY OF THE INVENTION

[0014] In one aspect, the invention provides a carpet product including in sequence

[0015] a) a primary backing material having a back side and a face side, with carpet fibers extending from the face side to form a carpet pile and also passing through the primary backing material and forming loops on the back side;

[0016] b) a primary coating layer on the loops, including a vinyl acetate ethylene copolymer and present at from 542 to 1085 g/m² (16 to 32 oz/yd²) on a dry solids basis;

[0017] c) a secondary coating layer on the primary coating layer, including a styrene-butadiene copolymer, and

[0018] d) a secondary backing material on the secondary coating layer and adhered thereby to the primary coating layer.

[0019] In another aspect, the invention provides a process for making a carpet product, including in sequence

[0020] a) providing a primary backing material having a back side and a face side, with carpet fibers extending from the face side to form a carpet pile and also passing through the primary backing material and forming loops on the back side;

[0021] b) coating the loops with an aqueous primary coating composition including a vinyl acetate ethylene copolymer to form a wet primary coating layer providing from 542 to 1085 g/m² (16 to 32 oz/yd²) of coating on a dry solids basis;

[0022] c) coating a secondary backing material with an aqueous secondary coating composition including a styrene butadiene copolymer to form a wet secondary coating layer;

[0023] d) pressing the product of step c) against the product of step b) to contact the wet primary coating layer with the wet secondary coating layer; and

[0024] e) drying the product of step d).
DETAILED DESCRIPTION OF THE INVENTION

[0025] Surprisingly, the inventors have found that a specific combination of primary coating layer and secondary coating layer makes possible the production of carpet having high tuft lock and high delamination resistance, yet easily processable at the elevated temperatures encountered on carpet coating lines.

Structural Carpet Components

[0026] The primary backing material typically comprises any material recognized in the art for use as a carpet backing. Specific examples typically include woven or nonwoven fabrics made from one or more of natural or synthetic fibers or yarns including jute, wool, polypropylene, polyethylene, polyimide, polyesters, nyon, or various copolymers.

[0027] The primary backing has a face side and a back side. Carpet fibers (yarn) are attached to the primary backing, extending from the face side to form the carpet face. The fibers can be made with uncut yarn loops, cut yarn loops (a pile of single yarns), or a combination of cut and uncut yarns. The fibers can be made from wool, cotton, nylon, acrylic resin, polyester, polypropylene and blends thereof. As the fiber material is not critical, other fiber material would be readily apparent to one of skill in the art, i.e., any material recognized in the art for use as a carpet fiber. A tufting method can be used to fix fibers to the primary backing material. In a typical case, carpet fibers extend from the face side to form a carpet pile and pass through the primary coating material to form loops on the back side. Typically, the primary backing will have a basis weight in a range from 102 g/m² (3 to 10 oz./yd²), more typically in a range from 136 to 237 g/m² (4 to 7 oz./yd²). The combination of primary backing and carpet fibers (yarn) will typically have a basis weight in a range from 339 to 1017 g/m² (10 to 30 oz./yd²).

[0028] The secondary backing side is oriented toward and attached to the back side of the primary backing, with the primary and secondary coating layers interposed. The secondary backing can be made of a variety of materials. Typically, it will be made of one or more of the materials mentioned above for making the primary backing. In most cases the secondary backing will not have carpet pile fibers passing through it, and will not have carpet pile fibers directly adhered or otherwise directly attached to it. Here the term "directly" means without any intervening woven or nonwoven fabric layer(s). Typically, the secondary backing will have a basis weight in a range from 33.9 to 203 g/m² (1 to 6 oz./yd²). More typically, the range will be in a range from 102 to 170 g/m² (3 to 5 oz./yd²).

[0029] The primary coating layer will typically be present at a loading level in a range from 542 to 1085 g/m² (16 to 32 oz./yd²) on a dry solids basis. More typically, the amount will be in a range from 610 to 881 g/m² (18 to 26 oz./yd²). The secondary coating layer will typically be present at a loading level in a range from 203 to 305 g/m² (6 to 9 oz./yd²) on a dry solids basis. More typically, the amount will be in a range from 237 to 271 g/m² (7 to 8 oz./yd²).

[0030] Generally, the primary backing material, the secondary backing material, the primary coating layer and the secondary coating layer are each independently coextensive with one or more of the others. Most typically, they are all mutually coextensive.

Vinyl Acetate Ethylene Copolymer Dispersion

[0031] The vinyl acetate ethylene copolymer comprises vinyl acetate units in an amount of 79 to 98 wt%, based on the total weight of comonomers. Preferably the vinyl acetate content is in the range of 75 to 95 wt%, most preferably the vinyl acetate content is in the range of 80 to 95 wt%, in each case based on the total weight of comonomers.

[0032] The copolymer comprises ethylene in an amount of 2 to 30 wt%, based on the total weight of comonomers. The amount is preferably 5 to 15 wt%, most preferably 10 to 12 wt%, in each case based on the total weight of comonomers.

[0033] Most preferred copolymers are those of ethylene and vinyl acetate without further comonomers. Nonetheless, in some embodiments the copolymer may include up to 30 wt%, preferably up to 10 wt%, in each case based on the total weight of comonomers, of other non-functional monomer units selected from the group consisting of vinyl chloride, (meth)acrylic acid esters and vinyl esters other than vinyl acetate. Suitable other vinyl esters are those of carboxylic acids with 3 to 12 carbon atoms such as vinyl propionate, vinyl butyrate, vinyl 2-ethylhexanoate, vinyl laurate, 1-methyl vinyl acetate, vinyl pivalate and vinyl esters of α-branched monocarboxylic acids with 9 to 11 carbon atoms, such as VeOVA™991R, VeOVA™910R, or VeOVA™913R (available from Hexion Specialty Chemicals, Inc., Columbus, Ohio). Suitable methacrylic or acrylic acid esters are esters of straight-chain or branched alcohols having 1 to 15 carbon atoms, for example methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, butyl acrylate (α-, iso- and tert-), n-butyl methacrylate, 2-ethylhexyl acrylate and norbornyl acrylate. Methyl acrylate, methyl methacrylate, butyl acrylate and 2-ethylhexyl acrylate are preferred. Such non-functional monomers may be introduced for example to adjust glass transition temperature or hydrophobicity.

[0034] In some embodiments, auxiliary monomers (functional monomers) may be copolymerized in an amount up to 10 wt%, preferably 0.5 to 10 wt%, most preferably 0.1 to 2 wt%, in each case based on the total weight of comonomers. Examples of auxiliary monomers are ethylenglycidyl unsaturated monocarboxylic and dicarboxylic acids, typically acrylic acid, methacrylic acid, fumaric acid and maleic acid; ethylenically unsaturated carboxamides and carbonitriles, typically acrylamide and acrylonitrile; monoesters and diesters of fumaric and maleic acid, such as the diethyl and disopropyl esters, and also maleic anhydride, ethylenically unsaturated sulfonic acids and their salts, typically vinylsulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid. Such auxiliary monomers may for example improve dispersion stability.

[0035] Further examples of such auxiliary monomers are crosslink-forming functional comonomers. Examples for precrosslinking comonomers are polyethylenically unsaturated comonomers, examples being divinyl adipate, diallyl maleate, allyl methacrylate or triallyl cyanurate. Examples of postcrosslinking comonomers are acrylamidoglycolic acid (AGA), methacrylamidoglycolic acid methyl ester (MAGME), N-methylolacrylamide (NMA), N-methylolmethacrylamide (NMMA), N-methylolallylcarbamate, allyl ethers such as the isobutoxy ether or esters of N-methylolacrylamide or of N-methylolmethacrylamide or of N-methylolallylcarbamate.

[0036] Also suitable as auxiliary monomers are ethylenically unsaturated, hydrolyzable silicon compounds. For
example compounds of the general formula $\text{R}^1\text{Si}((\text{OR}^2)_{1-3})$, where $\text{R}$ has the definition $\text{C}_1\text{C}_2$ alkyl radical, $\text{C}_3\text{C}_4 \text{C}_5 \text{C}_6 \text{C}_7 \text{C}_8 \text{C}_9 \text{C}_{10} \text{C}_{11}$ alkyl radical or halogen (e.g., Cl or Br). $\text{R}^1$ has the definition $\text{CH}_2\text{CH}=(\text{CH}_2)_{1-3}$. $\text{R}^2$ is unbranched or branched, optionally substituted alkyl radical or acyl radical having 1 to 12 carbon atoms, which may optionally be interrupted by an ether group, and $\text{R}^3$ stands for $\text{H}$ or $\text{CH}_3$. Preference is given to $\text{γ}$-acycloxy- and $\text{γ}$-methacryloxy-ox- propyltri(alkoxy)alkanes, vinyllaklyldioklosylsilanes, and vinyllaklyldioklosylsilanes, having $\text{C}_3\text{C}_4 \text{C}_5 \text{C}_6 \text{C}_7 \text{C}_8 \text{C}_9 \text{C}_{10} \text{C}_{11}$ alkyl groups and optionally $\text{C}_1\text{C}_2$ alkyl radicals, and also $\text{α}$-silanes, with examples of $\text{C}_1\text{C}_2 \text{C}_3 \text{C}_4$ alkyl groups that can be used being methoxy, ethoxy, methoxyethene, ethoxyethene, meth- oxypropylene glycol ether and/or ethoxypolypropylene glycol ether radicals. Ethynaphenically unsaturated, hydroxylizable silicon compounds that are most preferred are vinyltrimethoxysilane, vinyllaklyldioklosylsilane, 3-methacryloxypropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, and $\text{α}$-methacryloxyethyltrimethoxysilane.

[0037] Further examples for auxiliary monomers are ethy- naphenically unsaturated compounds containing epoxyoxide groups, such as, for example, glycidyl methacrylate, glycidyl acry- late, allyl glycidyl ether, vinyl glycidyl ether, vinylocylcohex- aene oxide, limonene oxide, myrcene oxide, carpyllene oxide, and styrenes and vinyloluenes substituted by a glycidyl radical on the aromatic moiety, and also vinyl benzoxides substituted by glycidyl radicals on the aromatic moiety. Preference is given to glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether, and vinyl glycidyl ether.

[0038] While some applications may favor the inclusion of additional monomers in the VAE copolymer, for example such as those listed above, it may nonetheless in some cases be advantageous to exclude certain monomers, depending on the specific needs of a given application. In other cases, these monomers may be included up to a limit of 1.0 wt% of the VAE copolymer. The exclusion or limited monomers may include any one or more of the following: i-butoxy methy- lacrylamide; acrylamidoglycolic acid; acrylamidobutylalde- hyde; dialkyl acetals of acrylamidobutylaldehyde; glycidyl-containing compounds (e.g., glycidyl (meth)acrylate, triglycidyl isocyanurate, etc.); ethynaphenically unsaturated phosphates, phosphonates or sulfates; ethynaphenically unsatur- ated silicon compounds; (meth)acrylamide or N-substituted (meth)acrylamides; (meth)acrylic esters; vinyl ethers; acry- lonitrile; butadiene; styrene; vinyl acetals; divinyl benzene and/or other olefinically unsaturated hydrocarbons other than ethylene; halogenated monomers (e.g., vinyl chloride); and esters of allyl alcohol. In some embodiments of the invention, only VAE copolymers not containing further comonomer units or auxiliary monomers are used.

[0039] In each case the data is in % by weight are based on the total weight of comonomers and summing up to 100% by weight.

[0040] The monomers are preferably selected so as to give copolymers with a glass transition temperature $T_g$ of $-30^\circ$C to $+30\,^\circ$C, preferably $-5\,^\circ$C to $+20\,^\circ$C, and most preferably $0\,^\circ$C to $18\,^\circ$C. The glass transition temperature $T_g$ of the copoly- mers may be determined in a known manner by means of differential scanning calorimetry (DSC) according to ASTM D3418-03.

[0041] The $T_g$ may also be calculated approximately in advance by means of the Fox equation. According to Fox T. G., Bull. Am. Physic Soc. 1, 3, page 123 (1956), it holds that: $T_g = x_1 T_{g1} + x_2 T_{g2} + \ldots + x_n T_{g_n}$, where $x_n$ is the mass fraction (wt% 100%) of the monomer $n$ and $T_{g_n}$ is the glass transition temperature, in kelvins, of the homopolymer of the monomer $n$. $T_g$ values for homopolymers are listed in the Polymer Handbook, 2nd Edition, J. Wiley & Sons, New York (1975). [0042] The vinyl acetate ethylene copolymer can be pre- pared by an aqueous emulsion polymerization using conventional emulsion polymerization procedure. Preferably at a temperature in a range from 40°C to 150°C, more preferred 50°C to 120°C and most preferred 60°C to 100°C. The polymerization pressure is generally between 40 and 100 bar absolute, preferably between 45 and 90 bar absolute, and most preferred between 45 and 85 bar absolute, depending on the ethylene feed. [0043] Polymerization may be initiated using a redox ini- tiator combination such as is customary for an aqueous emulsion polymerization. Examples of suitable oxidation initiators are hydrogen peroxide, tert-butyl peroxide, tert-butyl hydroperoxide, potassium peroxodiphosphate, tert-butyl per- oxopivalate, cumene hydroperoxide, isopropylbenzene monohydroperoxide, azobisisobutyronitrile, and the sodium, potassium, and ammonium salts of peroxodisulfuric acid. Preference is given to the sodium, potassium, and ammonium salts of peroxodisulfuric acid and to hydrogen peroxide. The stated initiators are used in general in an amount of 0.01 wt% to 2.0 wt%, based on the total weight of the comonomers.

[0044] The stated oxidizing agents, more particularly hydrogen peroxide or the salts of peroxodisulfuric acid, may also be used on their own as thermal initiators.

[0045] Suitable reducing agents are ammonium or alkali metal sulfites and bisulfites, as for example sodium sulfite, the derivatives of sulfoxylic acid such as zinc sulfoxylates or alkal alkali metal formaldehyde sulfoxylates, such as sodium hydroxyethanesulfinate (Brüggolit). It is preferred to use a non-formaldehydederiving redox initiation system. In general, suitable non-formaldehyde generating reducing agents for redox pairs include, as non-limiting examples, those based on ascorbic acid or its salts, or erythorbate (iso- ascorbic acid) or its salts, or tartaric acid or its salts, or bisulfite salts particularly sodium bisulfite, as known in the art, or disodium glycic acid sulfonate hydrate, which is available as a commercial reducing agent known as BRUG- GOLITE FT8M manufactured by Bruggeman Chemical of Heilbronn, Germany. It is preferred to use disodium glycic acid sulfonate hydrate, or sodium sulfite, or ascorbic acid or its salts, or erythorbic acid (iso-ascorbic acid) or its salts. The amount of reducing agent is preferably 0.01 wt% to 3 wt%, based on the total weight of the comonomers.

[0046] Regulating substances may be used during the poly- merization to control the molecular weight of the copolymer. In a preferred embodiment no regulating substances are used. If regulators are used, they are employed typically in amounts between 0.01 wt% to 5.0 wt%, based on the total weight of the monomers to be polymerized, and are metered separately or else as a premix with reaction components. Examples of such substances are n-dodecyl mercaptan, tert-dodecyl mercap- tian, mercaptopropionic acid, methyl mercaptopropionate, isopropanol, and acetaldehyde.

[0047] One or more emulsifiers and/or one or more protec- tive colloids are used to stabilize the aqueous dispersion of the vinyl acetate ethylene copolymers.

[0048] Suitable emulsifiers are nonionic, anionic or cat- ionic emulsifiers. Preferably nonionic or anionic emulsifiers are used, or mixtures of nonionic and anionic emulsifiers. The
amount of emulsifier is preferably 0.5 to 10 wt. %, more preferably 1 to 5 wt. %, in each case based on the total amount of comonomers.

Suitable nonionic emulsifiers are, for example, acyl, alkyl, and oleyl ethoxylates. These products are available commercially, for example, under the name GENAPOL® or LUTENSO®. Suitable nonionic emulsifiers also include ethoxylated branched or unbranched fatty alcohols (aliphatic alcohols), preferably having a degree of ethoxylation of 5 to 80 ethylene oxide units and C₈ to C₁₆ alkyl radicals. Other suitable nonionic emulsifiers include C₁₂-C₁₅ oxo-process alcohol ethoxylates having a degree of ethoxylation of 3 to 30 ethylene oxide units, C₁₂-C₁₅ fatty alcohol ethoxylates having a degree of ethoxylation of 11 to 90 ethylene oxide units, C₁₀ oxo-process alcohol ethoxylates having a degree of ethoxylation of 3 to 11 ethylene oxide units, C₁₃ oxo-process alcohol ethoxylates having a degree of ethoxylation of 3 to 20 ethylene oxide units, polyoxyethylene sorbitan monooleate having 20 ethylene oxide units, copolymers of ethylene oxide and propylene oxide with a minimum content of at least 10 wt. % of ethylene oxide, and polyethylene oxide ethers of oleyl alcohol having a degree of ethoxylation of 4 to 20 ethylene oxide units.

Preferred are ethoxylated branched or unbranched aliphatic alcohols, particularly having a degree of ethoxylation of 3 to 80 ethylene oxide units and C₈ to C₁₆ alkyl radicals. Preferred nonionic emulsifiers are also C₁₂-C₁₅ oxo-process alcohol ethoxylates having a degree of ethoxylation of 3 to 30 ethylene oxide units, and C₁₂-C₁₅ aliphatic alcohol ethoxylates having a degree of ethoxylation of 11 to 90 ethylene oxide units. Particularly preferred are C₁₃-C₁₅ aliphatic alcohol ethoxylates having a degree of ethoxylation of 3 to 20 ethylene oxide units. Preferably the copolymer dispersion is free of alkylphenol ethoxylates and esters thereof.

Examples of suitable anionic emulsifiers are sodium, potassium, and ammonium salts of straight-chain aliphatic carboxylic acids having 12 to 20 C atoms; sodium hydroxystearatesulfonate; sodium, potassium, and ammonium salts of hydroxyl-fatty acids having 12 to 20 C atoms and the sulfonation and/or acetylation products thereof; sodium, potassium, and ammonium salts of alkyl sulfates, also as triethanolamine salts, and sodium, potassium, and ammonium salts of alkyl sulfates having in each case 10 to 20 C atoms and of alkylaryl sulfonates having 12 to 20 C atoms; dimethyldiallylammonium chloride having 8 to 18 C atoms and its sulfonation products; sodium, potassium, and ammonium salts of sulfosuccinic esters with aliphatic saturated monohydric alcohols having 4 or 16 C atoms, and sulfosuccinic 4-esters with polyethylene glycol ethers of monohydric alcohols having 10 to 12 C atoms, more particularly their disodium salts, and of bis cyclicsulpho sulfosuccinate, more particularly its sodium salt; ligninsulfonic acid and also its calcium, magnesium, sodium, and ammonium salts; and resin acids or hydrogenated or dehydrogenated resin acids, and alkali metal salts of any of these.

The most preferred anionic emulsifiers are the sodium, potassium, and ammonium salts of alkyl sulfates and of alkylaryl sulfonates having in each case 10 to 20 C atoms, and also of alkylaryl sulfonates having 12 to 20 C atoms, and of sulfosuccinic esters with aliphatic saturated monohydric alcohols having 4 to 16 C atoms.

Suitable protective colloids include polyvinyl alcohols; polyvinyl acetals; polyvinylpyrrolidones; polysaccharides in water-soluble form such as starches (amylose and amylopectin), cellulosics and their carboxymethyl, methyl, hydroxyethyl, hydroxypropyl derivatives; proteins such as casein or caseinate, soya protein, gelatine; lignosulfonates, synthetic polymers such as poly(meth)acrylic acid, copolymers of (meth)acrylates with carboxyl-functional comonomer units, poly(meth)acrylamide, polyvinylsulfonic acids, and the water-soluble copolymers thereof; melamine-formaldehyde sulfonates, napthalene-formaldehyde sulfonates, styrene-maleic acid copolymers, and vinyl ether-maleic acid copolymers.

Preference is given to using partially hydrolyzed (degree of hydrolysis: 80 to 95 mol %) and/or fully hydrolyzed (degree of hydrolysis: 98 to 100 mol %) polyvinyl alcohols. Preferred partially hydrolyzed polyvinyl alcohols have a degree of hydrolysis of 80 to 95 mol % and a Hübner viscosity in 4% strength aqueous solution, of 1 to 30 mPas (method of Hübner at 20° C, DIN 53015). Most preferred are polyvinyl alcohols having a degree of hydrolysis of 85 to 94 mol % and a Hübner viscosity in 4% strength aqueous solution of 3 to 25 mPas (method of Hübner at 20° C, DIN 53015). As used herein, the “degree of hydrolysis” of a polyvinyl alcohol means the degree to which vinyl acetate monomer units have been hydrolyzed to alcohols.

Preferred embodiments employ a mixture of one or more partially hydrolyzed polyvinyl alcohol(s) and one or more fully hydrolyzed polyvinyl alcohol(s). Preferred fully hydrolyzed polyvinyl alcohols have a degree of hydrolysis of 98 to 99.95 mol % and a Hübner viscosity of 13 to 50 mPas (method of Hübner at 20° C, DIN 53015).

Both partially hydrolyzed and fully hydrolyzed polyvinyl alcohols may be hydrophobically modified, e.g., they may comprise hydrophobic comonomers, one example of which is ethylene.

The total amount of the protective colloid is preferably 1 to 5 wt. %, based on the total weight of comonomers. It is also a preferred embodiment to use a mixture of at least one emulsifier and at least one protective colloid.

The emulsifiers and protective colloids discussed above are all commercially available or obtainable by processes known to the skilled person.

Preparation of Aqueous Vinyl Acetate Ethylene Copolymer Dispersions.

In preparing the aqueous vinyl acetate ethylene copolymer dispersion, all of the protective colloid or all of the emulsifier may form an initial charge, or all of the protective colloid or all of the emulsifier may form a feed, or portions of the protective colloid or of the emulsifier may form an initial charge and the remainder may form a feed after the polymerization has been initiated. The feeds may be separate (spatially and chronologically), or all or some of the components may be fed after pre-emulsification. In a preferred embodiment all of the protective colloid and optionally all of the emulsifier are charged initially to the reactor.

All of the monomers may form an initial charge, or all of the monomers may form a feed, or portions of the monomers may form an initial charge and the remainder may form a feed after the polymerization has been initiated. The feeds may be separate (spatially and chronologically), or all or some of the components may be fed after pre-emulsification. In a preferred embodiment at least a part of the monomers, preferably 70 to 85 wt. %, is added in the initial charge.

Once the polymerization process has ended, post-polymerization may be carried out using known methods to
remove residual monomer, for example using post-polymerization initiated by a redox catalyst. Volatile residual monomers may also be removed by distillation, preferably at sub-atmospheric pressure, and, where appropriate, by passing inert entraining gases, such as air, nitrogen, or water vapor, through or over the material.

[0063] The solids content of suitable aqueous vinyl acetate ethylene copolymer dispersions is typically in a range from 45 wt % to 75 wt %. The particle size distribution may be monomodal or multimodal, and the mean particle diameter may range in size from 0.15 μm to 10 μm as measured by laser diffraction.

Styrene Butadiene Dispersions

[0064] The styrene butadiene copolymers comprise 20 to 79.9 wt %, preferably 50 to 65 wt % styrene and 20 to 79.9 wt %, preferably 35 to 50 wt % butadiene, based on the total amount of comonomers. Optionally 0.1 to 15 wt % of further auxiliary comonomers may be present, in each case based on the total weight of comonomers. Preferred auxiliary comonomers are ethylenically unsaturated mono-carboxylic acids, and/or di-carboxylic acids, their anhydrides, and their salts, and mixtures thereof; particularly acrylic acid, methacrylic acid, itaconic acid and/or malic acid and/or fumaric acid.

[0065] Additional suitable auxiliary comonomers are for example, allyl esters of (meth)acrylic acid, such as, for example, methyl methacrylate, ethylenically unsaturated carboxamides and carbonitriles, such as, for example, (meth) acrylonitrile; diesters of fumaric acid or malic acid; hydroxy alkyl (meth)acrylates; sulfite acid monomers, phosphonic acid monomers, crosslinking comonomers, such as, for example, divinyl benzene or divinyl adipates; postcrosslinking comonomers, such as acrylamidoglycolic acid (AGA), allyl methacrylates or allyl N-methylol carbamates; epoxide-functional comonomers, such as glycidyl (meth)acrylates; and silicon-functional comonomers, such as alkoxysilane containing (meth)acrylates or vinyl monomers.

[0066] While some applications may favor the inclusion of additional monomers in the styrene butadiene copolymer, for example such as those listed above, it may nonetheless in some cases be advantageous to exclude certain monomers, depending on the specific needs of a given application. In other cases, these monomers may be included up to a limit of 1.0 wt % of the styrene butadiene copolymer. Monomers that may be excluded or limited include those mentioned above in this context with respect to the VAE copolymer.

[0067] The styrene butadiene copolymers can be prepared by aqueous emulsion or suspension polymerization, preferably emulsion polymerization, in conventional manner, employing conventional polymerization temperatures, preferably from 40 °C to 120 °C, and pressures, preferably with diene comonomer pressures up to 10 bar absolute.

[0068] The polymerization may be initiated using conventional amounts of one or more conventional water-soluble initiators such as sodium persulphate, or oil (monomer) soluble initiator, such as tert-butyl peroxide and cumene hydroperoxide, or a redox initiator combination, using a reducing agent such as sulfites and bisulfites. To control the molecular weight, conventional regulator substances or chain transfer agents, such as mercaptans, alkyls, and dimeric alpha methyl styrene can be used during the polymerization in conventional manner in conventional amounts of from 0.01 to 5.0 percent by weight, or, preferably, up to 3 percent by weight, based on the comonomers to be polymerized. The polymerization process preferably takes place in known manner in the presence of conventional amounts of one or more conventional emulsifier and/or protective colloid. Suitable emulsifiers and protective colloids are the same as described for preparing the vinyl acetate ethylene dispersion.

[0069] The solids content of the styrene butadiene copolymer dispersion is typically in a range from 45 wt % to 75 wt %.

Coating Compositions

[0070] To obtain the primary or secondary coating composition, the vinyl acetate ethylene copolymer dispersion or the styrene butadiene copolymer dispersion is combined with one or more fillers and one or more thickeners, and optionally further additives.

[0071] Any filler suitable for use in carpet manufacture may be used. Examples include mineral fillers or pigments including those known in the art, such as calcium carbonate, ground glass, clay, kaolin, talc, barites, feldspar, titanium dioxide, calcium aluminum pigments, satin white, synthetic polymer pigment, zinc oxide, barium sulphate, gypsum, silica, alumina trihydrate, mica, hollow polymer pigments, and diatomaceous earth. Mixtures of fillers can also be employed.

[0072] The amount of filler in the composition can vary depending upon the density of the filler and the coating properties desired. Typically, it will be from about 50 to about 800 dry weight parts filler, more typically from about 100 to about 600 dry weight parts, and most typically from about 250 to about 600 dry weight parts, in each case per 100 dry weight parts of copolymer solids.

[0073] One or more polymeric thickeners is typically included in the composition to provide sufficient viscosity for application according to conventional methods. Any polymeric thickener known in the carpet coating art may be used, for example hydroxyethyl cellulose and sodium polycarboxylate. Although any amount of polymeric thickener may be used, the inventors have found that typically no more than 6 wt % of thickener is needed, relative to the amount of aqueous dispersion of the copolymer, and thus in some embodiments of the invention no more than 6 wt % is used, relative to the amount of aqueous dispersion of the copolymer. In some embodiments, at most 5 wt % or at most 4 wt % is used, relative to the amount of aqueous dispersion of the copolymer. Typically, at least 1 wt % of thickener, or at least 2 wt %, is used, relative to the amount of aqueous dispersion of the copolymer.

[0074] The Brookfield RV viscosity of the resulting coating composition should be in a range from 7000 to 15000 mPas, measured with a Brookfield RV viscometer using spindle No. 5 at 25°C and 20 rpm.

[0075] Further conventional additives in carpet coating compositions are flame retardants or biocides or antioxidants. If a foamed coating is desired blowing agents can be added to the coating compositions.

Making the Carpet Product

[0076] The primary and secondary aqueous coating compositions can be applied in various ways. For example the coating compositions can be applied directly, such as with a roll over roller applicator, or with a doctor blade. Alternatively, they can be applied indirectly, such as with a pan applicator. Preferably a roll over roller applicator is used. The primary
coating coats at least the loops on the back side of the primary backing, and may also coat some or all of the back side of the backing itself.

[0077] The primary and secondary backing materials are brought together to bring the still-wet primary and secondary coating compositions into contact, typically with application of pressure, and heat is then applied to evaporate the water from the coatings. This may be done by passing the product through an oven, typically set at a temperature between about 100°C and 150°C. Upon cooling, the final product is obtained.

[0078] A significant advantage of carpet products obtained according to the invention is better delamination resistance compared with carpet products according to the state of the art.

EXAMPLES

[0079] The following polymer dispersions were used to prepare the carpet products. Vinyl acetate-ethylene copolymer dispersion (VAE):

[0080] An aqueous dispersion of a vinyl acetate ethylene copolymer with a solids content of about 60 wt % was used. The dispersion was costabilized with a protective colloid and a non-ionic surfactant. The copolymer composition was about 85 wt % vinyl acetate and about 15 wt % ethylene, with a glass transition temperature $T_g$ of about 2°C.

Styrene Butadiene Copolymer Dispersion (SBR):

[0081] An aqueous dispersion of a styrene butadiene copolymer with a solids content of about 55 wt % was used. The dispersion was stabilized with an anionic surfactant. The copolymer composition was about 65 wt % of styrene and about 35 wt % of butadiene, with a glass transition temperature $T_g$ of about 11°C.

Carpet Coating Compositions:

Filler:

[0082] Filler used was calcium carbonate (CARMEUSE™ MW 101 manufactured by Carmeuse Lime and Stone, Chatsworth, Ga.).

Froth Aid:

[0083] Froth aid used was ammonium lauryl sulphate (STANFAX® 238 manufactured by Royal Adhesives, Dalton, Ga.).

Thickener:

[0084] Thickener used was a sodium polyacrylate (PARAGUM® 277 manufactured by Royal Adhesives, Dalton, Ga.).

General Recipe for the Carpet Coating Compositions Used as Primary Coating Composition or Secondary Coating Composition in Testing:

<table>
<thead>
<tr>
<th>Material</th>
<th>Dry weight [grams]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersion</td>
<td>100</td>
</tr>
<tr>
<td>Filler</td>
<td>450</td>
</tr>
<tr>
<td>Froth Aid</td>
<td>0.33</td>
</tr>
</tbody>
</table>

[0085] *Thinner and water were admixed in amounts needed to obtain a carpet coating composition having a total solids content of about 81.5 wt % and a Brookfield viscosity (spindle No. 5, 20 rpm) of 6000 to 7000 cps.

[0086] The Uncoated Backing Materials Used in the Test were:

[0087] A nylon carpet greige goods (i.e., a backing with pile yarn tufted in but without a binder) with a 678 g/m² (20 oz/yd²) false weight level loop nylon with a straight stitch commercial style tufting construction was used as primary backing.

[0088] A polypropylene 5ick woven material with an average weight of 68 g/m² (2 oz/yd²) was used as secondary backing.

Preparation of Samples for Testing:

[0089] The primary and secondary coating compositions were admixed according to the general recipe with a lighting mixer. Thicker and water were admixed in an amount necessary for obtaining a total solids content of about 81.5 wt % and a Brookfield viscosity (spindle No. 5, 20 rpm) of 6000 to 7000 cps.

[0090] The primary coating composition was applied with a spatula having a 25.4 cm (10 in) blade to the backside of the nylon carpet material at a rate of 949 g/m² (28 oz/yd²) of primary coating solids.

[0091] The secondary backing was coated with the secondary coating composition with a draw-down bar at a 762 µm (30 mil) wet film thickness, resulting in about 237 g/m² (7 oz/yd²) of secondary coating solids. The wet coated secondary backing was pressed against the wet coating layer on the primary backing with a large stainless steel roller. The assembly was dried at 132°C (270°F) in a convection air oven for 20 minutes, and the resulting carpet product was allowed to stand at ambient temperature and humidity for at least two hours before testing.

Test Methods

Determination of $T_g$ According to ASTM D3418-03:

[0092] Glass transition temperatures of copolymers were measured calorimetrically using a TA Instruments Q20-1002 differential scanning calorimeter (DSC). The samples were prepared by casting a wet film of 254 µm (10 mil) thickness and drying the film at 105°C. Discs were cut from this dried film and 10 to 15 mg of the sample were loaded into an aluminum DSC pan. The pan was loaded into the calorimeter and heated to 105°C for 5 minutes to ensure that the sample is dry. The samples were then cooled to −60°C and equilibrated there for 2 minutes. The temperature was then increased at a rate of 20°C per minute to 100°C. The run conditions were consistent with section 10.2 of ASTM D3418. The onset $T_g$ is the value reported.

[0093] Carpet Tuft Bind values were determined according to ASTM D1335-05. This procedure is a method to calculate the force required to pull a loop or cut pile from a piece of carpet.
Equipment:
0094. Instron Model 2519-105 (1000 N capacity) equipped with 7.62 cm (3 inch) jaw clamps, desiccator for conditioning carpet samples, 3.8 mm cylindrical specimen holder and loop hook.

Test Procedure:
0095. Treatment of Samples for Testing Dry Tuft Bind:
0096. All samples for testing were cut into 17.15x17.15 cm (6.75x6.75 in) squares and placed in the desiccator with 25 to 35% humidity and 22 to 24°C for a minimum of 12 hours.

Additional Treatment of Samples for Testing Wet Tuft Bind:

Samples for Wet Tuft Bind are Prepared One at a Time According to the Following Procedure:
0097. After dry tuft binds are determined, the 17.15x17.15 cm (6.75x6.75 in) square is placed in a gallon container with 3.8 liter container that has been filled with cold tap water. The carpet sample is submerged into the water and allowed to soak for 10 minutes. After 10 minutes the sample is removed and placed on a paper towel for 30 seconds to soak up excess water. The carpet is then taken to be tested for tuft bind values as previously described.

Determination of Dry Tuft Bind and of Wet Tuft Bind:
0098. Samples were mounted over the 3.8 mm holder with rows or loops in line with the long axis of the holder. The carpet and cylinder (specimen holder) were then placed into the jaws of the Instron. Only loops with a minimum of 2.54 cm (1 inch) from the sample edge were tested.
0099. The loop hook was inserted in the loop to be pulled. By visual inspection it was insured that only one loop was hooked for testing.
0100. The tuft was pulled at a speed of 304.8 cm (12 in) per minute. The pull was continued until the tuft was separated from the primary backing.
0101. The maximum force needed to pull tuft was measured in pounds. A total of ten pulls were made, averaged, and are reported in Table 1.

Testing of Delamination Resistance:
0102. Carpet Delamination resistance was determined according to ASTM D3936-05. This procedure is a method to calculate the force required to separate the secondary backing material from the primary backing material.

Equipment:
0103. Instron Model 2519-105 (1000 N capacity) equipped with 7.62 cm (3.00 in) jaw clamps
Desiccator for Conditioning Carpet Samples

Test Procedure:
0104. Treatment of samples for testing Dry Delamination:
0105. All samples for testing were cut into strips 7.62 cm (3.00 in) wide in the warp direction and 30.48 cm (12.00 in) long in the machine direction and kept in the desiccator at 25% to 35% humidity and 22°C to 24°C for a minimum of 12 hours.
0106. Additional treatment of samples for testing Wet Delamination: Samples for wet delamination were prepared one at a time according to the following procedure:
0107. An untested strip of the dimensions described above was placed in a 3.8 liter (one gallon) container that had been filled with cold tap water. The carpet sample was submerged into the water and allowed to soak for 10 minutes. After 10 minutes the sample was removed and placed on a paper towel for 30 seconds to soak up excess water. The sample was then tested for delamination values as described below.

Determination of Dry Delamination and of Wet Delamination:
0108. The secondary backing was separated from the primary backing approximately 3.8 cm (1/2 in) in the long (machine) direction on each sample. The primary backing/pile was placed in the bottom jaw as straight as possible, and the secondary backing was placed in the top jaw for a 180° peel configuration as straight as possible. The two layers were pulled apart at a speed of 30.5 cm (12 in) per minute for a total of 17.8 cm (7 in) of jaw travel.
0109. No data were taken during the first and last inches of jaw travel, and the highest value obtained in each of the five central one-inch segments was recorded. The average of these five values was divided by 3 (the width of the sample in inches) to provide delamination strength in lb/in. Each such run was performed in triplicate, and the average of these for each type of carpet is reported in Table 1. The “% Retain” figures are the wet values as a percentage of dry.

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Coating Layer</td>
</tr>
<tr>
<td>VAE</td>
</tr>
<tr>
<td>Secondary Coating Layer</td>
</tr>
<tr>
<td>VAE</td>
</tr>
<tr>
<td>Dry Tuft Bind N(lb)</td>
</tr>
<tr>
<td>Wet Tuft Bind N(lb)</td>
</tr>
<tr>
<td>% Retain Tuft Bind</td>
</tr>
<tr>
<td>Dry Delamination Ncm(lb-in)</td>
</tr>
<tr>
<td>Wet Delamination Ncm(lb-in)</td>
</tr>
<tr>
<td>% Retain Delamination</td>
</tr>
</tbody>
</table>

0110. As seen in Table 1, the combination of VAE on the primary backing and SBR on the secondary backing according to the invention provided a 26% increase in Dry Delamination strength and a 27% increase in Wet Delamination strength, compared with the use of VAE on both backings.

1. A carpet product comprising in sequence
   a) a primary backing material having a back side and a face side, with carpet fibers extending from the face side to form a carpet pile and also passing through the primary backing material and forming loops on the back side;
   b) a primary coating layer on the loops, comprising a vinyl acetate ethylene copolymer as the only binder, wherein the vinyl acetate ethylene copolymer comprises no comonomers other than vinyl acetate and ethylene, and present at from 542 to 1085 g/m² (16 to 32 oz. yd²) on a dry solids basis;
c) a secondary coating layer on the primary coating layer, comprising a styrene-butadiene copolymer as the only binder; and

d) a secondary backing material on the secondary coating layer and adhered thereby to the primary coating layer.

2. The carpet product of claim 1, wherein the vinyl acetate ethylene copolymer comprises vinyl acetate units in an amount of 70 to 98 wt %, based on the total weight of comonomers.

3. The carpet product of claim 1, wherein the vinyl acetate ethylene copolymer comprises vinyl acetate units in an amount of 75 to 95 wt %, based on the total weight of comonomers.

4. The carpet product of claim 1, wherein the vinyl acetate ethylene copolymer comprises vinyl acetate units in an amount of 80 to 95 wt %, based on the total weight of comonomers.

5. The carpet product of claim 1, wherein the vinyl acetate ethylene copolymer comprises ethylene in an amount of 2 to 30 wt %, based on the total weight of comonomers.

6. The carpet product of claim 1, wherein the vinyl acetate ethylene copolymer comprises ethylene in an amount of 5 to 15 wt %, based on the total weight of comonomers.

7. The carpet product of claim 1, wherein the vinyl acetate ethylene copolymer comprises ethylene in an amount of 10 to 12 wt %, based on the total weight of comonomers.

8. The carpet product of claim 1, wherein the vinyl acetate ethylene copolymer in the primary coating layer is derived from a vinyl acetate ethylene copolymer dispersion stabilized only by one or more emulsifiers and one or more protective colloids.

9. The carpet product of claim 1, wherein the vinyl acetate ethylene copolymer in the primary coating layer is derived from a vinyl acetate ethylene copolymer dispersion stabilized only by one or more emulsifiers.

10. The carpet product of claim 1, wherein the vinyl acetate ethylene copolymer in the primary coating layer is derived from a vinyl acetate ethylene copolymer dispersion stabilized only by one or more protective colloids.

11. The carpet product of claim 10, wherein the one or more protective colloids consist of one or more polyvinyl alcohols.

12. The carpet product of claim 11, wherein the one or more polyvinyl alcohols comprise at least one partially hydrolyzed polyvinyl alcohol and at least one polyvinyl alcohol having a degree of hydrolysis of 98 to 100 mol %.

13. The carpet product of claim 1, wherein the styrene butadiene copolymer comprises 20 to 79.9 wt %, preferably 50 to 65 wt % styrene and 20 to 79.9 wt %, preferably 35 to 50 wt % butadiene, based on the total amount of comonomers.

14. The carpet product of claim 1, wherein the styrene butadiene copolymer comprises 0.1 to 15 wt % in total of auxiliary comonomers, based on the total weight of comonomers.

15. The carpet product of claim 14, wherein the auxiliary comonomers are selected from the group consisting of ethylenically unsaturated mono-carboxylic acids, ethylenically unsaturated di-carboxylic acids, the anhydrides or salts of either of these, and combinations of any of the foregoing.

16. A process for manufacturing the carpet product according to claim 1, comprising in sequence

   a) providing a primary backing material having a back side and a face side, with carpet fibers extending from the face side to form a carpet pile and also passing through the primary backing material and forming loops on the back side;

   b) coating the loops with an aqueous primary coating composition comprising a vinyl acetate ethylene copolymer as the only binder, wherein the vinyl acetate ethylene copolymer comprises no comonomers other than vinyl acetate and ethylene, to form a wet primary coating layer providing from 542 to 1085 g/m² (16 to 32 oz./yd²) of coating on a dry solids basis;

   c) coating a secondary backing material with an aqueous secondary coating composition comprising a styrene butadiene copolymer as the only binder to form a wet secondary coating layer;

   d) pressing the product of step c) against the product of step b) to contact the wet primary coating layer with the wet secondary coating layer, and

   e) drying the product of step d).

* * * * *