Disclosed are carpet products comprising at least one flexible substrate and at least one coating layer associated with the at least one flexible substrate. The coating layer is formed from an aqueous composition comprising: A) an emulsifier-stabilized vinyl acetate/ethylene (VAE) emulsion copolymer dispersion wherein the VAE copolymer therein comprises co-monomers which include at least vinyl acetate copolymerized with ethylene and optionally also with other additional functional and/or non-functional co-monomers; and B) at least one particulate filler material selected from particulate inorganic compounds and particulate plastic material. The vinyl acetate/ethylene copolymer in the copolymer dispersion has a particle size, dₚ₅₀, ranging from about 50 to about 500 nm as determined by Laser Aerosol Spectroscopy. Such carpet products maintain their integrity and appearance after multiple machine washing operations. Some of these carpet products which have backing coated with certain of the coating compositions used herein also exhibit desirable non-slip properties.
WASHABLE CARPET PRODUCTS WITH COATING LAYERS FORMED FROM VINYL ESTER/ETHYLENE COPOLYMER DISPERSIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is based on the U.S. Provisional Patent Application having Ser. No. 61/373,091;Filed Aug. 12, 2010 and the U.S. Provisional Patent Application having Ser. No. 61/481,445;Filed May 2, 2011. The benefit of the filing dates of both of these provisional patent applications is claimed under the Paris Convention and under 35 USC §119 (e). The disclosures of both of these provisional patent applications are incorporated herein by reference.

FIELD

[0002] The present development relates to carpet products having coating layers therein which comprise a filler-containing, emulsifier- and/or colloid-stabilized vinyl ester/ethylene-based copolymer dispersion as a small particle size emulsion binder. Such carpet products exhibit desirable washability characteristics and preferably can also be especially effective for use as or in non-slip carpet applications such as for bathroom rugs or gymnasium mats.

BACKGROUND

[0003] Most conventional carpets comprise a primary backing with yarn tufts in the form of cut or uncut loops extending upwardly from this backing to form a pile surface. For tufted carpets, the yarn is inserted into a primary backing (frequently a woven or nonwoven substrate) by tufting needles and a pre-coat (i.e., a binder) is applied thereto.

[0004] Many residential and commercial carpets are also manufactured with a woven scrim (typically made from polypropylene) attached to the back of the carpet to provide dimensional stability to the carpet. These are dual layer products, where two coating layers (precoat for tuft anchorage and adhesive for scrim fixation) are added wet, and the scrim is added afterwards. After fixation of the scrim, the carpet is cured at 130-200°C for a certain time.

[0005] The physical properties of a binder coating are important to its successful utilization in a carpet product. In this regard, there are a number of important requirements which must be met by such coatings. The coating must be capable of being applied to the carpet and dried using the processes and equipment conventionally employed in the carpet industry for latex, e.g. emulsion, coating. The binder composition must also provide excellent adhesion to the pile fibers to secure them firmly in the backing. The coating will also typically have a high loading of fillers such as calcium carbonate, clay, aluminum trihydrate, barite, feldspar, cuttle, fly ash and/or recycled carpet backing. Further, coatings on carpet backing layers must preferably also be able to serve as non-slip substrates, thereby enabling the preparation of non-slip material for use in, for example, bathroom and rug carpet or gymnasium mat applications.

[0006] The binders in coating compositions for carpet materials are frequently emulsion polymers, i.e., latex dispersions, such as styrene-based emulsion copolymers like styrene-butadiene latex (SBL) materials or such as acrylic polymer latex dispersions. Copolymers of vinyl esters (such as vinyl acetate) and ethylene can also be used and can frequently have cost and performance advantages over rubber coatings or styrene-containing coatings such as SBL-based compositions. For example, vinyl ester copolymers can be used to provide carpet products which are desirably low in VOC (volatile organic compound) content and which do not contain potentially toxic materials such as 4-phenyl cyclohexene (4-PCH) and related compounds which can be found in styrene-based emulsion polymers.

[0007] Emulsion binders and carpet coating compositions based on vinyl ester/ethylene, e.g., vinyl acetate/ethylene (VAE), copolymers are disclosed, for example, in WO 2010/089142 and in U.S. Pat. Nos. 4,735,986; 5,026,765; 5,849,389; 6,359,076; 7,056,847; 7,582,699; 7,649,067 and in U.S. Patent Application Publication No. 2005/0287336. Some of these patent documents note that such VAE binders and coating compositions are compatible with polyvinyl chloride (PVC) plastisol which are frequently used as backing layers in such carpet products.

[0008] The vinyl ester/ethylene copolymers used in the binders and coating compositions described in the foregoing patent documents are prepared by polymerizing appropriate co-monomers in an aqueous emulsion. Such emulsions or dispersions can be stabilized by adding conventional surfactants (anionic, nonionic, cationic) as emulsifiers. Such emulsions or dispersions may also be stabilized by including protective colloids.

[0009] Notwithstanding the availability of a variety of carpet coating compositions based on stabilized vinyl ester/ethylene (e.g., VAE) latex emulsion/dispersions binders, it would be advantageous to identify and select specific types of relatively soft (as quantified by copolymer glass transition temperature (Tg), VAE-based, filler-containing, environmentally friendly binder emulsions/dispersions which exhibit a desirable balance of properties that make them especially useful in preparing textile structures such as carpets and carpet material. The present development provides carpet products of especially desirable washability characteristics, i.e., minimized loss of weight and integrity upon repeated washing, and preferably also carpet products and carpet components of desirable non-slip properties. Such carpet products can also be desirably low in VOC content. The carpet products described herein with their VAE-based binder coatings having a selected combination of features (e.g., specific co-monomers, cross-linkers, stabilizers, relatively small polymer particle sizes, Tg's, and fillers) can provide such a desirable balance of properties, especially when compared to carpet products using state-of-the-art SBL-based carpet coatings.

SUMMARY

[0010] The present development is directed to a carpet product comprising at least one flexible substrate and at least one coating layer associated with the at least one flexible substrate. Such a coating layer is formed from an aqueous composition comprising: A) an emulsifier-stabilized vinyl acetate/ethylene (VAE) copolymer dispersion, and B) at least one particulate filler material selected from particulate inorganic compounds and particulate plastic material. The vinyl acetate/ethylene copolymer in the copolymer dispersion comprises main co-monomers which include vinyl acetate, which is copolymerized with ethylene and optionally also with one or more additional different non-functional main co-monomer(s) which can be vinyl esters of C5-C18 monocarboxylic acids or C5-C18 esters of ethylenically unsaturated
mono-carboxylic acids or C₁₇-C₁₈ diesters of ethylenically unsaturated di-carboxylic acids.

[0011] The vinyl acetate/ethylene copolymer in the copolymer dispersion has a particle size, d₃₂, ranging from about 50 to about 500 nm as determined by Laser Aerosol Spectroscopy. In addition, the vinyl acetate/ethylene copolymer in the copolymer dispersion typically comprises from about 8 wt % to about 40 wt %, based on total main co-monomers therein, of ethylene and has a glass transition temperature, Tᵥ, of from about −25°C to about +15°C.

[0012] The copolymer dispersion is preferably stabilized with at least about 0.5 wt %, based on total main co-monomers in the copolymer, of one or more, preferably anionic and/or nonionic, emulsifiers and from about 0 wt % to about 3 wt %, based on total main co-monomers in the copolymer, of a protective colloid which, when used, is preferably polyvinyl alcohol. The vinyl acetate/ethylene copolymer in the copolymer dispersion will also preferably be substantially free of cross-linkable co-monomer moieties which generate formaldehyde upon formation of the coating or adhesive layer in the carpet product.

[0013] The carpet products herein will generally exhibit good washability characteristics in that they maintain their integrity and appearance well after multiple washings. Preferably, the carpet products herein will exhibit less than about 4.5% weight loss and less than about 40% tuft anchorage loss after 20 wash cycles in the Washability and Tuft Anchorage Tests described herein.

[0014] Certain embodiments of the carpet products herein will also exhibit good non-slip properties when the coated carpet backing of such carpets is in contact with the floor. Preferably these carpet products can exhibit non-slip properties such that a maximum drag force of about 6.0 Newtons or more are needed to move a sample of such carpet products when tested in accordance with TAPPI test 816 om-92.

DETAILED DESCRIPTION

[0015] The carpet products described herein will essentially comprise at least one flexible substrate and at least one coating or adhesive layer associated with the flexible substrates(s). The adhesive or coating layer(s) is/are formed from an aqueous composition containing a specific type of vinyl ester-based copolymer dispersion as the coating- or film-forming component thereof, together with a particulate filler material. The components and preparation of the layer-forming aqueous compositions, the copolymer dispersion and filler components thereof, the flexible, e.g., textile, substrate(s) and the preparation and characteristics of carpet products comprising all of these components are described in detail below:

Copolymer Dispersion

[0016] The film- or coating-forming component of the aqueous compositions applied to carpet flexible substrates(s) herein is a vinyl acetate-based copolymer comprising ethylene and optionally one or more additional non-functional main co-monomers. This vinyl acetate/ethylene copolymer is present in a copolymer dispersion prepared by the emulsion polymerization of appropriately selected co-monomers.

[0017] The primary co-monomer used in the preparation of the copolymer dispersion is vinyl acetate. This primary vinyl acetate co-monomer is generally present in the copolymer of the dispersion in amounts of from about 40% to about 80% by weight, more preferably from about 60% to 70% by weight, based on the total main co-monomers in the copolymer. The second essential co-monomer for incorporation into the copolymer of the dispersion is ethylene. The ethylene will generally comprise from about 8% to about 40% by weight, preferably 10% to about 32% by weight, most preferably from about 12% to about 30% by weight, based on the total main co-monomers in the copolymer.

[0018] The vinyl acetate/ethylene copolymer of the copolymer dispersion can optionally comprise one or more additional non-functional main co-monomers besides vinyl acetate and ethylene. One type of such optional main non-functional co-monomer comprises vinyl ester co-monomers. Examples thereof are vinyl esters of mono-carboxylic acids having one to eighteen carbon atoms (except vinyl acetate), e.g., vinyl formate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl benzylate, vinyl-2-ethyl-hexanoate, vinyl esters of an [alpha]-branched carboxylic acid having 5 to 11 carbon atoms in the acid moiety, e.g., Versatic™ acids, and the vinyl esters of pivalic, 2-ethylhexanoic, lauric, palmitic, myristic, and stearic acid. Vinyl esters of Versatic™ acids, more particularly VeoVa™ 9, VeoVa™ 10, and VeoVa™ 11, are preferred.

[0019] Another type of optional main non-functional co-monomer which can be incorporated into the vinyl acetate/ethylene copolymer of the dispersion comprises esters of ethylenically unsaturated mono-carboxylic acids or diesters of ethylenically unsaturated di-carboxylic acids. Particularly advantageous co-monomers of this type are the esters of alcohols having one to eighteen carbon atoms. Examples of such non-functional, main co-monomers include methyl methacrylate or acrylate, butyl methacrylate or acrylate, 2-ethylhexyl methacrylate or acrylate, dibutyl maleate and/or dioctyl maleate.

[0020] Combinations of two or more of the foregoing optional non-functional main co-monomer types can be copolymerized into the vinyl acetate/ethylene copolymer. If present, such non-functional main co-monomers can comprise up to about 40 wt % based on total main co-monomers in the copolymer. More preferably, such non-functional main co-monomers can comprise from about 5 wt % to about 20 wt %, based on the total main co-monomers in the vinyl acetate/ethylene copolymer.

[0021] The vinyl acetate/ethylene emulsion copolymer used in the coatings for the carpet products herein can also optionally contain relatively minor amounts of other types of co-monomers besides vinyl acetate, ethylene or other main co-monomer types. Such other optional co-monomers will frequently be those which contain one or more functional groups and can serve to provide or facilitate cross-linking between copolymer chains within the copolymer dispersion-containing aqueous composition, or upon the drying or curing of films and coatings formed from such compositions.

[0022] Such optionally present, functional co-monomers can include ethylenically unsaturated acids, e.g. mono- or di-carboxylic acids, sulfonic acids or phosphonic acids. In place of the free acids, it is also possible to use their salts, preferably alkali metal salts or ammonium salts. Examples of optional functional co-monomers of this type include acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid, vinylsulfonic acid, vinylphosphonic acid, styrene sulfonic acid, monooesters of maleic and/or fumaric acid, and of itaconic acid, with monohydric aliphatic saturated alcohols of chain length C₇-C₁₆, and also their alkali
metal salts and ammonium salts, or (meth) acrylic esters of sulfoalkanols, an example being sodium 2-sulfoethyl methacrylate.

[0023] Other types of suitable optional functional co-monomers include ethylenically unsaturated co-monomers with at least one amide-, epoxy-, hydroxyl, trialkoxysilane- or carbonyl group. Particularly suitable are ethylenically unsaturated epoxide compounds, such as glycidyl methacrylate or glycidyl acrylate. Also suitable are hydroxyl compounds including methacrylic acid and acrylic acid \(C_1\)-\(C_2\) hydroxyalkyl esters, such as \(n\)-hydroxyethyl, \(n\)-hydroxypropyl or \(n\)-hydroxybutyl acrylate and methacrylate. Other suitable functional co-monomers include compounds such as diacetone acrylamide and acrylacetoxymethacrylamide and methacrylamide; and amides of ethylenically unsaturated carboxylic acids, such as acrylamide or meth acrylamide.

[0024] As noted, the emulsion copolymer used herein can optionally contain trialkoxysilane functional co-monomers. Alternatively, the emulsion copolymers used herein can be substantially free of silane-based co-monomers.

[0025] One type of functional co-monomer which should not be incorporated into the vinyl acetate/ethylene copolymers used herein comprises any co-monomer which contains cross-linkable moieties that generate formaldehyde upon formation of a coating layer from compositions containing such copolymers. Thus the vinyl acetate/ethylene copolymer in the copolymer dispersion should be substantially free of such co-monomers, which include, for example, common cross-linkers like N-methylolacrylamide (NMA) or even low formaldehyde versions of N-methylolacrylamide such as NMA-LF. Preferably also the vinyl acetate/ethylene copolymer in the copolymer dispersion should contain no halogenated co-monomers such as vinyl chloride co-monomers.

[0026] Optional functional co-monomers can be incorporated into the vinyl acetate/ethylene emulsion copolymers used herein in amount of up to about 5 wt%, based on total main co-monomers in the copolymer. More preferably, optional functional co-monomers can comprise from about 0.5 wt% to about 2 wt%, based on total main co-monomers in the copolymer.

[0027] The emulsion copolymer can be formed within the copolymer dispersion using emulsion polymerization techniques described more fully hereinafter. Within the copolymer dispersion, the copolymer will be present in the form of relatively small particles ranging in weight average particle size, \(d_w\), of from about 50 nm to about 500 nm, measured by laser aerosol spectroscopy. More preferably, the copolymer dispersion will be present in the form of particles ranging in weight average particle size, \(d_w\), of from about 120 nm to about 350 nm. Particle size can be determined by means of laser aerosol spectroscopy techniques.

[0028] Depending upon co-monomer type, solubility and the monomer feeding techniques employed, the vinyl acetate/ethylene based copolymer can be either homogeneous or heterogeneous in monomeric configuration and make-up. Homogeneous copolymers will have a single discrete glass transition temperature, \(T_g\), as determined by differential scanning calorimetry techniques. Heterogeneous copolymers will exhibit two or more discrete glass transition temperatures and might lead to core shell particle morphologies. Whether homogeneous or heterogeneous, the vinyl acetate-based copolymer used herein normally has a glass transition temperature, \(T_g\), which ranges between about -25°C. and +15°C., more preferably between about -20°C. and about +5°C. As is known, the \(T_g\) of the polymer can be controlled, for example, by adjusting the ethylene content, i.e., generally the more ethylene present in the copolymer relative to other co-monomers, the lower the \(T_g\).

Stabilizers for Polymer Dispersions

[0029] Both during polymerization and thereafter, the copolymer dispersion used to prepare the aqueous compositions that form the carpet adhesive or coating layers is stabilized in the form of an aqueous copolymer dispersion or latex. The copolymer dispersion therefore will be prepared in the presence of and will contain a stabilization system which generally comprises emulsifiers, in particular nonionic emulsifiers and/or anionic emulsifiers. Mixtures of nonionic and anionic emulsifiers can also be employed.

[0030] The amount of emulsifier employed will generally be at least 0.5 wt %, based on the total quantity of main co-monomers in the copolymer dispersion. Generally emulsifiers can be used in amounts up to about 8 wt %, based on the total quantity of main co-monomers in the copolymer dispersion. The weight ratio of emulsifiers nonionic to anionic may fluctuate within wide ranges, between 1:1 and 50:1 for example. The vinyl acetate/ethylene copolymer dispersion may further comprise small amounts of polymeric stabilizers (protective colloids).

[0031] Emulsifiers employed with preference herein are nonionic emulsifiers having allylene oxide groups and/or anionic emulsifiers having sulfate, sulfonate, phosphate and/or sulfonate groups. Such emulsifiers, if desired, can be used together with molecularly or disperse water-soluble polymers, preferably together with polyvinyl alcohol. Preferably also the emulsifiers used contain no alkylophenoles.

[0032] Examples of suitable nonionic emulsifiers include acyl, alkyl, oleyl, and alkylaryl ethoxylates. These products are commercially available, for example, under the names Genapol®, Lutensol® or Emulon®. They include, for example, ethoxylated mono-, di-, and tri-alkylenols (EO degree: 3 to 50, alkoy substituent radical: \(C_4\) to \(C_{12}\)) and also ethoxylated fatty alcohols (EO degree: 3 to 80, alkoy radical: \(C_4\) to \(C_{35}\)), especially \(C_{12}-C_{14}\) fatty alcohol (3-40) ethoxylates, \(C_{15}-C_{17}\) oxo-process alcohol (3-40) ethoxylates, \(C_{16}-C_{18}\) fatty alcohol (11-80) ethoxylates, \(C_{10}\) oxo-process alcohol (3-40) ethoxylates, \(C_{12}\) oxo-process alcohol (3-40) ethoxylates, polyoxyethyleneoxybenzene monosiloxane with 20 ethylene oxide groups, copolymers of ethylene oxide and propylene oxide having a minimum ethylene oxide content of 10% by weight, and the polyethylene oxide (4-40) ethers of oleyl alcohol. Particularly suitable are the polyethylene oxide (4-40) ethers of fatty alcohols, more particularly of oleyl alcohol, stearyl alcohol or \(C_{16}\) alkyl alcohols.

[0033] The amount of nonionic emulsifiers used in preparing the copolymer dispersions herein is typically about 1% to about 8% by weight, preferably about 1% to about 5% by weight, more preferably about 1% to about 4% by weight, based on the total main monomer quantity. Mixtures of nonionic emulsifiers can also be employed.

[0034] Examples of suitable anionic emulsifiers include sodium, potassium, and ammonium salts of linear aliphatic carboxylic acids of chain length \(C_{12}-C_{20}\), sodium hydroxyoctadecanesulfonate, sodium, potassium, and ammonium salts of hydroxy fatty acids of chain length \(C_{12}-C_{20}\), and their sulfonation and/or sulfoxidation and/or acetylation products, alkyl sulfates, including those in the form of triethanolamine
salts, alkyl(C$_{10}$-C$_{20}$) sulfonates, alkyl(C$_{10}$-C$_{20}$) arylsulfonates, dimethyl-diaryl (C$_4$-C$_8$) ammonium chloride, and their sulfonation products, lignosulfonic acid and its calcium, magnesium, sodium, and ammonium salts, resin acids, hydrogenated and dehydrogenated resin acids, and their alkali metal salts, dodecylated sodium diphenyl ether sulfonate, sodium lauryl sulfate, sulfated alkyl or aryl ethoxylate with EO degree between 1 and 10, for example ethoxylated sodium lauryl ether sulfate (EO degree 5) or a salt of a bis-ester, preferably of a bis-C$_{12}$C$_{18}$ alkyl ester, of a sulfonated dicarboxylic acid having 4 to 8 carbon atoms, or a mixture of these salts, preferably sulfonated salts of esters of succinic acid, more preferably salts, such as alkali metal salts, of bis-C$_{4}$-C$_{18}$ alkyl esters of sulfonated succinic acid, or phosphates of polyethoxylated alkanols.

[0035] The amount of anionic emulsifiers used can typically range from about 0.1% to about 3.0% by weight, preferably from about 0.1% to about 2.0% by weight, more preferably from about 0.5% to about 1.5% by weight, based on the total main monomer quantity. Mixtures of anionic emulsifiers can also be employed.

[0036] Along with emulsifiers, the vinyl ester/ethylene copolymer dispersions employed in accordance with the invention may comprise as part of the stabilizer system protective colloids, preferably polyvinyl alcohols and/or their modifications. Protective colloids, if present, are generally present only in comparatively low concentrations, as for example at up to about 3% by weight, such as 0.2 to 2% by weight, based on the total amount of the main monomers used. Certain vinyl acetate/ethylene copolymer dispersions employed herein can preferably contain no protective colloids or only up to about 1% by weight of protective colloids, based on the total amount of the main co-monomers employed in the vinyl acetate/ethylene copolymer.

[0037] Examples of suitable protective colloids include water-soluble or water-dispersible polymeric modified natural substances, such as cellulose ethers, examples being methyl-, ethyl-, hydroxyethyl- or carboxymethylcellulose; water-soluble or water-dispersible polymeric synthetic substances, such as polyvinylpyrrolidone or polyvinyl alcohols or their copolymers (with or without residual acetyl content), and polyvinyl alcohol which is partially esterified or acetylated or etherified with saturated radicals and also with different molecular weights.

[0038] The protective colloids can be used individually or in combination. In the case of combinations, the two or more colloids can each differ in their molecular weights or they can differ in their molecular weights and in their chemical composition, such as the degree of hydrolysis, for example.

[0039] In addition to the emulsifiers and, if appropriate, protective colloids that are used during the emulsion polymerization of the copolymers herein, it is also possible for the vinyl acetate/ethylene copolymer dispersions used herein to contain subsequently added water-soluble or water-dispersible polymers as hereinafter described. Additional emulsifiers may also be added to the dispersions post-polymerization.

Copolymer Dispersion Preparation

[0040] The copolymer dispersions comprising the vinyl acetate/ethylene copolymer dispersions herein can be prepared using emulsion polymerization procedures which result in the preparation of polymer dispersions in aqueous latex form. Such preparation of aqueous polymer dispersions of this type is well known and has already been described in numerous instances and is therefore known to the skilled artisan. Such procedures are described, for example, in U.S. Pat. No. 5,849,389, and in the Encyclopedia of Polymer Science and Engineering, Vol. 8, p. 659 ff (1987). The disclosures of both of these publications are incorporated herein by reference in their entirety.

[0041] The polymerization may be carried out in any manner known per se in one, two or more stages with different monomer combinations, giving polymer dispersions having particles with homogeneous or heterogeneous, e.g., core shell or hemispherical, morphology. Any reactor system such as batch, loop, continuous, cascade, etc., may be employed.

[0042] The polymerization temperature generally ranges from about 20°C to about 150°C, more preferably from about 50°C to about 120°C. The polymerization generally takes place under pressure if appropriate, preferably from about 2 to about 150 bar, more preferably from about 5 to about 100 bar.

[0043] In a typical polymerization procedure involving, for example, vinyl acetate/ethylene copolymer dispersions, the vinyl acetate, ethylene, and other co-monomers can be polymerized in an aqueous medium under pressures up to about 120 bar in the presence of one or more initiators and at least one emulsifying agent, optionally along with protective colloids like PVOH. The aqueous reaction mixture in the polymerization vessel can be maintained by a suitable buffering agent at a pH of about 2 to about 7.

[0044] The manner of combining the several polymerization ingredients, i.e., emulsifiers, co-monomers, catalyst system components, etc., can vary widely. Generally an aqueous medium containing at least some of the emulsifier(s) can be initially formed in the polymerization vessel with the various other polymerization ingredients being added to the vessel thereafter.

[0045] Co-monomers can be added to the polymerization vessel continuously, incrementally or as a single charge addition of the entire amounts of co-monomers to be used. Co-monomers can be employed as pure monomers or can be used in the form of a pre-mixed emulsion. Ethylene as a co-monomer can be pumped into the polymerization vessel and maintained under appropriate pressure therein.

[0046] As noted, the polymerization of the ethylenically unsaturated monomers will generally take place in the presence of at least one initiator for the free-radical polymerization of these co-monomers. Suitable initiators for the free-radical polymerization, for initiating and continuing the polymerization during the preparation of the dispersions, include all known initiators which are capable of initiating a free-radical, aqueous polymerization in heterophase systems. These initiators may be peroxides, such as alkali metal and/or ammonium peroxodisulfates, or azo compounds, more particularly water-soluble azo compounds.

[0047] As polymerization initiators, it is also possible to use what are called redox initiators. Examples thereof are tert-butyl hydroperoxide and/or hydrogen peroxide in combination with reducing agents, such as with sulfur compounds, an example being the sodium salt of hydroxymethanesulfonic acid, Britrogil FF6 and FF7, Renogil C, sodium sulfite, sodium disulfite, sodium thiosulfate, and acetone-bisulfite adduct, or with ascorbic acid, sodium erythorbate, or with reducing sugars.

[0048] The amount of the initiators or initiator combinations used in the process varies within what is usual for aqueous polymerizations in heterophase systems. In general
the amount of initiator used will not exceed 5% by weight, based on the total amount of the co-monomers to be polymerized. The amount of initiators used, based on the total amount of the co-monomers to be polymerized, is preferably 0.05% to 2.0% by weight.

[0049] In this context, it is possible for the total amount of initiator to be included in the initial charge to the reactor at the beginning of the polymerization. Preferably, alternatively, a portion of the initiator is included in the initial charge at the beginning, and the remainder is added after the polymerization has been initiated, in one or more steps or continuously. The addition may be made separately or together with other components, such as emulsifiers or monomer emulsions. It is also possible to start the emulsion polymerization using a seed latex, for example with about 0.5 to about 15% by weight of the dispersion.

[0050] In addition to the emulsion polymerized vinyl acetate/ethylene copolymer, the copolymer dispersions used herein can additionally contain copolymers formed from C<sub>4</sub>-C<sub>8</sub> esters of (meth)acrylic acids, C<sub>4</sub>-C<sub>8</sub> esters of other ethylenically unsaturated mono-carboxylic acids, or C<sub>4</sub>-C<sub>8</sub> diesters of ethylenically unsaturated di-carboxylic acids. Such additional copolymers can comprise, for example, from about 0.5 to about 20 parts by weight based on total copolymers in the copolymer dispersion and can include copolymers formed from ethyl acrylate, butyl acrylate (BuA), 2-ethylhexyl acrylate (2-EHA), dibutyl maleate, dioctyl maleate or combinations of these esters.

[0051] The molecular weight of the various copolymers in the copolymer dispersions herein can be adjusted by adding small amounts of one or more molecular weight regulator substances. These regulators, as they are known, are generally used in an amount of up to 2% by weight, based on the total co-monomers to be polymerized. As regulators, it is possible to use all of the substances known to the skilled artisan. Preference is given, for example, to organic thio compounds, silanes, allyl alcohols, and aldehydes.

[0052] The copolymer dispersions as prepared herein will generally have a viscosity which ranges from about 100 mPas to about 5000 mPas at 45-55% solids, more preferably from about 200 mPas to about 4000 mPas, most preferably 400-3000 mPas measured with a Brookfield viscometer at 25°C, 20 rpm, with appropriate spindle. Viscosity may be adjusted by the addition of thickeners and/or water to the copolymer dispersion. Suitable thickeners can include polyacrylates or polyurethanes, such as Borchigel L75® and Tafigel PUR 60®. Alternatively, the copolymer dispersion may be substantially free of thickeners.

[0053] Following polymerization, the solids content of the resulting aqueous copolymer dispersions can be adjusted to the level desired by the addition of water or by the removal of water by distillation. Generally, the desired level of polymeric solids content after polymerization is from about 40 weight percent to about 70 weight percent based on the total weight of the polymer dispersion, more preferably from about 45 weight percent to about 55 weight percent.

[0054] The aqueous copolymer dispersions used to form the coating layer-forming compositions herein can be desirably low in Total Volatile Organic Compound (TVOC) content. A volatile organic compound is defined herein as a carbon containing compound that has a boiling point below 250°C (according to the ISO 11890-2 method for polymer dispersions TVOC content determination) at atmospheric pressure. Compounds such as water and ammonia are excluded from VOCs.

[0055] The aqueous copolymer dispersions used herein will generally contain less than 0.5% TVOC by weight based on the total weight of the aqueous copolymer dispersion. Preferably, the aqueous copolymer dispersion will contain less than 0.3% TVOC by weight based on the total weight of the aqueous copolymer dispersion. These values can be determined according to ISO 11890-2, described hereinafter in the Test Methods section.

[0056] The aqueous copolymer dispersions used herein will generally also emit a relatively small amount of its TVOC content when exposed to the atmosphere. In particular, the copolymer dispersions herein will emit TVOC materials to the extent of no more than about 15 times the Toluene D8 standard, when films formed from such dispersions are tested in accordance with the procedures of ISO 16000-9, described hereinafter in the Test Methods section. More preferably, the copolymer dispersions herein will emit TVOC materials to the extent of no more than about 10 times the Toluene D8 standard.

[0057] Where appropriate, the vinyl acetate/ethylene copolymer dispersions used herein can also optionally comprise a wide variety of conventional additives which are typically used in the formulation of binders and/or adhesives. Such optional additives may be present in the copolymer dispersion from the beginning of or during polymerization, may be added to the dispersion post-polymerization or, as such as in the case of fillers, may be used in connection with preparation of the aqueous coating compositions from the copolymer dispersions as hereinafter described.

[0058] Typical conventional optional additives for the copolymer dispersions herein can include, for example, film-forming assistants, such as white spirit, Texanol®, TixB®, butyl glycol, butyl diglycol, butyl dipropylene glycol, and butyl tripropylene glycol; wetting agents, such as AMP 90®, TegoWet.280®, Fluowet PE®; defoamers, such as mineral oil defoamers or silicone defoamers; UV protectants, such as Tinuvin 1130®; agents for adjusting the pH; plasticizers, such as dimethyl phthalate, dibutyl phthalate, diisobutyl adipate, Consol B®, Plastilit 306®, and Trizet®; subsequently added stabilizing polymers, such as polyvinyl alcohol or cellulose ethers; and other additives and auxiliaries of the kind typical for the formulation of binders and adhesives. The amounts of these additives used in the VAE copolymer dispersions herein can vary within wide ranges and can be selected by the specialist in view to the desired area of application.

**Aqueous Coating Compositions**

[0059] The copolymer dispersions as hereinbefore described are combined with filler material and additional water to form aqueous coating compositions for the carpet products herein. Such a coating composition can then be applied to the textile substrate(s) which form the carpet products herein. Upon drying, the applied aqueous coating compositions then provide the coating layer(s) within the carpet products. The carpet product can comprise only one or more than one coating layer.

[0060] In general, the carpet products herein will always contain a binder coating layer to secure the carpet fibers to a primary backing substrate. The carpet products herein can then optionally also comprise a second or additional layer.
which may be an adhesive layer to secure a secondary backing substrate to the coated primary backing.

[0061] In one embodiment, the carpet product can comprise both a coating and an adhesive layer which are formed from the same type of aqueous coating compositions as described herein. Alternatively, the carpet products herein can comprise both a coating layer as described herein and a different type of adhesive layer which may also be formed from the same type of compositions as the coating compositions herein or may be formed from a completely different conventional adhesive coating composition.

[0062] The aqueous coating compositions used herein will also contain a particulate filler material selected from particulate inorganic compounds and particulate plastic materials. Thus, the filler employed can be essentially any filler suitable for use in carpet manufacture. Such fillers are widely commercially available.

[0063] Filler examples include inorganic, e.g., mineral, fillers or pigments such as fly ash and ground glass and those known in the art, such as calcium carbonate, clay, kaolin, talc, barites, feldspar, titanium dioxide, calcium aluminum pigments, satin white, zinc oxide, barium sulfate, gypsum, silica, mica, and diatomaceous earth. Particulate plastic material such as synthetic polymer pigments, hollow polymer pigments and recycled carpet backing may also be employed, as can mixtures of any of the foregoing filler types. The preferred filler material is calcite carbonate.

[0064] The particulate filler material can generally range in average particle size between about 200 nm and 1000 µm, more preferably between about 1 µm and 500 µm, most preferably 10 µm-300 µm. Preferred coating compositions used to prepare carpet products in accordance with the present invention are loaded with filler to yield an aqueous coating composition comprising from about 10 to about 70 weight percent, more preferably from about 20 to about 50 weight percent, and more preferably from about 20 to about 50 weight percent of dry polymer and from about 30 to about 90 weight percent, preferably about 40 to about 80 weight percent, and most preferably 50 to 80 weight percent of filler based on total weight of solids in the aqueous composition, depending in part on the type and form of the carpet being constructed.

[0065] Such coating compositions can contain in addition to the copolymer dispersions and filler materials hereinafter described, a variety of additional conventional additives in order to modify the properties thereof. Among these additives may include thickeners, rheology modifiers, dispersants, flame retardants, colorants, biocides, anti-foaming agents, etc. These optional additives are largely the same as those hereinafter described with respect to the copolymer dispersions herein.

[0066] The coating compositions hereinafter described form the coating, i.e., binder, layer(s) in the carpet products herein which will also comprise at least one flexible substrate. Such flexible substrates can, for example, be selected from nonwovens, wovens, unidirectional weaves, knitted fabrics and pile fabrics. Thus the carpet products herein can be conventional tufted carpet, non-tufted carpet or needle-punched carpet. Such carpet products can be prepared by applying and drying the emulsion copolymer-containing aqueous compositions using equipment which is readily available in most carpet mills.

[0067] Pile carpet products comprise a primary backing with pile yarns extending from the primary backing substrate to form pile tufts. Pile or tufted carpet can be prepared by a) tufting or needle-fining yarn into a woven or non-woven backing substrate; b) applying the aqueous carpet coating composition as described herein to the rear of the backing such that the yarn is embedded in the carpet coating composition; and c) drying the resultant carpet construction. In producing such tufted carpets, it is also possible, but not necessary, to apply a secondary backing to the primary backing either before or after drying of the carpet coating, depending upon the type of backing employed. For tufted carpets, the primary backing substrate can be non-woven polypropylene, polyethylene or polyester or woven jute, polypropylene or polyamide (synthetic and natural).

[0068] The carpet products herein can also be non-tufted carpets wherein the fibers are embedded into a coating or binder composition which has been coated onto a woven or non-woven substrate. Non-tufted carpets also may be prepared by a) coating an aqueous composition such as hereinbefore described onto a substrate; b) embedding the carpet fibers in the substrate; and c) drying the resultant carpet construction. In forming a non-tufted carpet, the carpet coating can be thickened and applied to a scrim surface. The fibers then are directly embedded into the wet coating using conventional techniques and then dried. These non-tufted carpets also may be advantageously prepared utilizing a secondary backing that can provide additional dimensional stability.

[0069] In preparing the carpet products herein, the aqueous composition is applied in a manner such that it penetrates the fibers of the carpet yarn to yield better adhesion, fiber bundle integrity, anti-fuzzing properties and suitable tuft-bind values. Suitable carpet performance properties can be achieved by applying an amount of the aqueous coating/binder composition ranging from about 100 g/m² to about 3000 g/m², more preferably from about 200 g/m² to about 2000 g/m², most preferably from about 400 g/m² to about 1500 g/m² (dry basis).

Certain Carpet Product Embodiments

[0070] In one specific carpet product embodiment, the carpet product will comprise a textile fabric structure treated with a selected type of vinyl acetate/ethylene (VAE) copolymer dispersion. The textile fabric structure in such a carpet product can be in the form of a fabric selected from wovens, nonwovens, unidirectional weaves, knitted fabrics or pile fabrics. Specifically, the carpet product can comprise a pile fabric which is coated with a coating composition based on the selected type of VAE copolymer dispersion with the coating being on the far side of the pile (tread side). Alternatively, the carpet product can be in the form of a carpet wherein a secondary backing layer is bonded to the pile fabric layer on the far side of the tread side. The bonding between the two layers is effected through the VAE copolymer dispersion-based coating. Such textile fabric structures can have a weight per unit area of from about 1000 to about 3000 g/m².

[0071] The selected VAE copolymer dispersions used to treat the textile fabric structure in order to form such a carpet product embodiment can comprise from about 70 to about 80 phr (parts per hundred of monomers) of vinyl acetate and from about 20 to about 30 phr, preferably from about 20 to 24 phr, of ethylene. This copolymer will have a glass transition temperature, T_g, of from about 0°C to about -10°C.
C., more preferably between about -3°C and -6°C, and a mean particle diameter, d_m, within the dispersion of about 150 to 200 nm.

[0072] Such a selected VAE copolymer can also comprise up to about 10 phm of further co-monomers which are copolymerizable with the vinyl acetate and ethylene co-monomers. Such further co-monomers can include ethylenically unsaturated acids, or the salts thereof, ethylenically unsaturated monomers having at least one amide, epoxy, hydroxyl, N-methyl, trialkoxysilane or carbonyl group, and combinations of two or several monomers from any of these further monomer types. Alternatively, such further co-monomers can include vinyl esters which are not vinyl acetate, alpha-olefins which are not ethylene, vinyl aromatics, esters of ethylenically unsaturated monocarboxylic acids, and diesters of ethylenically unsaturated dicarboxylic acids.

[0073] The VAE copolymer dispersion used to make this carpet embodiment is stabilized with at least about 1 wt % of emulsifiers and about 0 wt % to about 2 wt % of a protective colloid based on polyvinyl alcohol. Preferably the emulsifiers used are selected from anionic and nonionic surfactants but contain no alklyphenylethoxylates (APEs). These VAE copolymer dispersions can have a viscosity of from about 400 to about 1600 mPa.s measured with a Brookfield viscometer at 25°C. Such dispersions can also have a solids content of from about 45 wt % to about 55 wt %.

Carpet Washability and Non-Slip Characteristics

[0074] The carpet products herein have especially desirable washability and, in some instances, especially desirable non-slip characteristics as well. Washability refers to the ability of a movable carpet product such as one, for example, in the form of an area rug, a throw rug, a runner, a carpet tile, a tapestry or wall hanging, a door mat, an automobile floor mat or a gymnasium mat to maintain its integrity upon being washed in a machine washing operation. Maintenance of carpet integrity includes the propensity of the carpet product not to lose weight upon being subjected to one or multiple machine washings. Carpet integrity after one or more washings further involves the propensity of the carpet to maintain its original appearance, its hand feel, the integrity of its backing and its anchorage of tufted yarn and fibers (pile) within the carpet backing.

[0075] Carpet washability can be determined by test procedures which involve weighing of carpet product test samples before and after washing operations. A suitable test procedure for determining carpet weight loss upon washing is set forth in the Test Methods section hereinafter. Generally, the carpet products herein will exhibit a weight loss of less than about 4.5% after 20 washings in this washability test. More preferably, the carpet products herein will exhibit a weight loss of less than about 3.6% after 20 washings.

[0076] Carpet washability can also be quantified by making tuft anchorage measurements both before and after carpet washing operations. Carpet tuft anchorage is a conventionally determined parameter in the carpet industry. A procedure for determining the extent of tuft anchorage is also set forth hereinafter in the Test Methods section. Generally, the carpet products herein will exhibit a loss of tuft anchorage of less than about 40% after 20 washings in this tuft anchorage test. More preferably, the carpet products herein will exhibit a tuft anchorage loss of less than about 25% after 20 washings.

[0077] The resistance of carpet products to detergent action upon washing can also, of course, be determined by simple visual observation of the effect of one or more washing operations on samples of the carpet product. Suitable procedures for visual grading of carpet products on a scale of 1 to 4 for their appearance and integrity before and after washing are also set forth hereinafter in the Test Methods section. Preferred carpet products herein will have a washability grade of 3 or less after 20 washing operations.

[0078] Carpet products herein having a backing surface coated with VAE copolymer-based coating compositions, wherein the VAE copolymer has a relatively low glass transition temperature, can also provide especially desirable non-slip performance. Non-slip performance refers to the propensity of a movable, weight-bearing carpet product to resist movement along or across the surface, e.g., the floor, which it covers when the carpet is subjected to a lateral force parallel to its plane. Resistance to this kind of lateral movement, i.e., slippage, is provided by the frictional drag which the weighted coated backing exerts on the surface which the carpet product covers. Non-slip propensity can be determined objectively by measuring the maximum force needed to drag a weighted carpet sample across a test surface. A procedure for making these kinds of measurements to determine carpet non-slip performance is also set forth in the Test Methods section hereinafter. Non-slip carpet embodiments herein will generally exhibit a maximum drag force in this test of at least about 6.0 Newtons, even after washing. More preferably, non-slip carpet embodiments herein will exhibit a maximum drag force of at least about 7.0 Newtons in this test.

Additional Carpet Characteristics

[0079] The carpet products herein, with the specific type of vinyl acetate/ethylene-based copolymer dispersions used in forming coating layers, also have especially desirable, environmentally friendly characteristics. The copolymer dispersions used, by virtue of containing no cross-linking groups which generate formaldehyde (e.g., no NMA or NMA-L,F), and by virtue of their low TVOC content and TVOC emission, do not cause potentially problematic materials of this type to be emitted from the carpet products herein. The carpet products herein are furthermore preferably substantially free of halogenated co-monomers, polyvinyl chloride and bitumen, which are types of materials which typically have been used in commercial carpet products. Finally, since the carpet products herein do not utilize SBL, coatings or binders, the carpet product will also be substantially free of potentially toxic components such as 4-phenylcyclohexene (4-PCH), 4-vinylcyclohexene (4-VCH), styrene, and ethylbenzene.

[0080] The carpet products which contain the coating layers formed from aqueous compositions containing the copolymer dispersions and fillers herein can have a weight per unit area of from about 100 g/m² to about 3000 g/m², more
preferably from about 200 g/m² to about 2000 g/m², most preferably from about 400 g/m² to about 1500 g/m² (dry basis).

EXEMPLARY

The carpet products herein can be in the form of rugs or mats which can be used as area floor coverings. Alternatively, the carpet products herein can be in the form of carpet tiles or even in the form of wall-to-wall carpeting.

EXAMPLES

The carpet products herein and the copolymer dispersion-containing coating compositions used to make such carpet products are more particularly described with reference to the following non-limiting Examples. The several test methods employed in connection with these Examples are described as follows:

Test Methods

Copolymer Dispersion Particle Size Determination

The size of solid particles within the copolymer dispersions used herein can be determined by laser aerosol spectroscopy (LAS). This LAS method is described in the publication "Characterization and Quality Assurance of Polymer Dispersions"; October 1992, Dr. J. Paul Fischer. The method uses a Nd:YVO4 Laser (Millenia II) supplied with Spectra Physics with a laser power of 2 W and a wave length of 532 nm. The detector is a Bi-alkali Photocathode Typ 4517 supplied by Burle (formerly RCA). The scattered light of the spray dried single particles will be detected at 40°. The evaluation of the data is done with a multi channel analyser by TMCA with 1024 channels.

To make the particle size determination, 0.2 ml of a dispersion sample is diluted in 100 ml of deionized and filtered water (conductivity of 18.2 µS/m). The sample is spray dried over a Beckmann nozzle and dried with nitrogen gas. The single particles are neutralized with beta radiation (KBr-85) and then investigated by single particle laser scattering. After evaluation the number and mass mean values within the range of 80 nm to 550 nm and mean particle size values d50, d90, d10, and d_w/d_0 are obtained.

Copolymer Glass Transition Temperature (T_g) Determination

The glass transition temperature, T_g, can be obtained by using a commercial differential scanning calorimeter Mettler DSC 820 at 10 K/min. For evaluation, the second heating curve is used and the DIN mid point calculated.

Emission of Total Volatile Organic Compounds (TVOC) From Copolymer Dispersion Films (ISO 16000-9)

The extent of emission of the Total Volatile Organic Compound (TVOC) content of a copolymer dispersion sample is determined using the general procedures of ISO-16000-9, which test method is incorporated herein by reference. In such a procedure, 2 grams of the copolymer dispersion are weighed into an alumina dish with a diameter of 4.2 cm. The dispersion is dried at room temperature (23 C/50% humidity) overnight to form a film which is then tested in a micro chamber having a diameter of 4.5 cm and a volume of 40 ml. A continuous air flow (100 ml/minute of clean dry air not reconditioned for humidity) is passed through the chamber and the film sample therein is allowed to equilibrate for a period of 20 min to chamber conditions (25° C.).

After 20 minutes, the air flow is directed to an absorption device which is a Tenax tube spiked with 111 ng of Toluene D8 which is used as an absorption standard. The volatile organic compounds (VOCs) in the air flow from the film sample are absorbed onto the Tenax tube for a period of 60 minutes. The Tenax tube is then analyzed via GC-MS for the amount of VOCs absorbed onto it.

The result of the GC-MS measurements are used to give an amount of VOCs absorbed relative to the Toluene D8 standard. If the amount of the toluene standard in the absorbed in the Tenax tube is taken as 1, the amount of VOCs absorbed in the Tenax tube is reported as the number of multiples of 1 represented by the VOCs emitted from the copolymer dispersion film.

Washability of Carpet Samples

The "washability" of carpet samples can be determined by measuring the weight loss of test samples after washing them in a commercial washing machine. Two carpet samples (22x26.5 cm/sutured with cotton web; approximately 20±3 g per sample) for each tested copolymer dispersion are washed together. The samples are packed separately in washing bags (40x50 cm with zipper) to avoid the contact between the backings during the wash cycles. All samples are washed twenty times and after each cycle the weights of the samples are measured.

The washing machine used is a Siemens Vario Perfect E14-32. For each cycle, 15 g of washing powder are used. The washing powder used is Professional Clean and Cleaver (15-30% phosphates, 5-15% oxygen bleach, <5% nonionic tensides, <5% soap, fragrance, enzymes, and brightener). The following conditions are applied for every wash cycle: washing program: "Pflegeleicht", tumbling speed 600 rpm and temperature 40° C. After each washing cycle, the samples are dried overnight at 23° C. and 50% humidity.

The samples are weighed after each wash cycle. The results are the average of the total weight loss in gram [g] after every 5th wash cycle, for the two samples washed for each applied copolymer dispersion tested. Results can be calculated as the percentage of weight lost from each sample tested after every 5 washing cycles. Additionally the non-slip properties of the carpet samples are also determined in connection with this washability testing. The test method for determining non-slip properties of the washed carpet samples is described hereinafter.

Non-Slip Properties of Carpet Samples (TAPPI 816 om-92)

The non-slip properties of carpet samples can be determined by using a modified version of the TAPPI 816 om-92 test method, which test method is incorporated herein by reference. This test method determines the maximum force in Newtons [N] needed to drag a weighted carpet
sample over a glass plate. The non-slip properties are measured initially and after every 5th wash cycle in the Washability test described above.

[0093] Two samples (22×26.5 cm/sutured with cotton web approximately 20×3 g per sample) for every carpet type to be tested are used. The carpet sample is put with its back against a piece of glass on the plate (60×30 cm). The carpet sample is oriented in the machine direction. Then a weight (1.18 kg/8x 5x4 cm) is applied in the middle of the carpet sample. The carpet sample is put at the far end of the plate with its longest side toward the testing device and having a contact area of 40 cm². The testing device used is a LF Plus universal testing machine from Lloyd Instruments. The sample is dragged with a speed of 150 mm/min over the glass plate for a distance of 10 cm. During the dragging procedure, the force needed to move the carpet in Newtons [N] is measured. The Maximum Force is determined between 10 and 90 mm. The results provided are the average of 2 measurements.

Tuft Anchorage of Carpet Samples (ISO 4919)

[0094] Eight carpet samples (4 washed and 4 unwashed) having dimensions of 11×26.5 cm for each type of binder coating to be tested are prepared and stored for a minimum of 24 hours at 23°C and 50% humidity prior to measurement. The strength of the tuft anchorage in such samples is then measured according to ISO 4919, which test method is incorporated herein by reference.

[0095] The testing machine used is made by Lloyd Instruments and is called LF Plus universal testing machine. The test program works with a preload of 0.5 N force and a testing speed of 100 mm/min. The carpet sample is clamped to a mounting which is a stainless steel tray of 10x10 cm/ hole (05 cm) horizontal. A hook is attached to one tuft and this hook is used to pull the tuft until it separates from the carpet sample.

[0096] The maximum break force of the tufts is measured. The breakpoint should be reached within 2 to 10 seconds. For each carpet sample, 20 tufts are tested to give the average for the maximum break force. The break force is measured in Newtons (N).

Visible Evaluation of Carpet Sample Appearance and Hand Feel

[0097] Carpet samples can also be visually evaluated for their backing appearance and hand feel. The unwashed carpet samples are compared with these same samples which are then washed 20 times important criteria for evaluation include the integrity of the backing, the visible weight loss of the carpet sample combined with the embedding of the fibers as well as the softness of the backed carpet samples both initially and after 20 washes.

[0098] The results of these visible evaluations are expressed on a scale of 1 to 4. The backing integrity is judged as follows: 1—closed backing; 2—some weight loss and uncoated fibers are visible; 3—more weight loss and more uncoated fibers are visible; and 4—in addition to a visible weight loss and uncoated fibers, cracks appear in the backing surface. The Hand feel is also judged as follows: 1—soft; 2—slightly stiffer; 3—stiff; and 4—very stiff. Two samples for every type of carpet sample to be evaluated (two samples unwashed and two samples washed) are judged by these criteria.

Example 1
Polymer Dispersion Preparation

[0099] Into a pressure reactor fitted with an anchor stirrer (running at 150 rpm), a heating jacket, dosage pumps and having a volume of 6.4 liters, a water based solution of the following components is added:

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (deionized)</td>
<td>24490 g</td>
</tr>
<tr>
<td>Allyl polyglycol ether (28 mols of Ethylene Oxide) - nonionic emulsifier</td>
<td>1375 g</td>
</tr>
<tr>
<td>Allyl sulfate (15% in deionized water of an anionic emulsifier)</td>
<td>2164 g</td>
</tr>
<tr>
<td>Sodium acetate (anhydrous)</td>
<td>82 g</td>
</tr>
<tr>
<td>Sodium vinylsulfonate (30%)</td>
<td>549 g</td>
</tr>
<tr>
<td>Sodium disulfate</td>
<td>15.0 g</td>
</tr>
<tr>
<td>Molb's Salt</td>
<td>6.07 g</td>
</tr>
</tbody>
</table>

Example 2
Polymer Dispersion Preparation

[0100] The reactor is purged with nitrogen to eliminate oxygen. Out of a total amount of (25316 g of vinyl acetate + 325 g Glycidyl methacrylate). 5.0% of the (vinyl acetate + Glycidyl methacrylate) is added to the water phase in the reactor. The ethylene valve is opened, and the reactor is pressurized to 15 bar at ambient temperature (ca. 10000 g of ethylene) and is then closed again (total amount of ethylene: 7140 g). The reactor temperature is ramped up to 65°C. At 35°C, a First Initiator which is sodium peroxydisulfate (145 g in 575 g of deionized water) is added quickly (over ca. 8 minutes) into the reactor.

[0101] At 65°C, the (vinyl acetate + Glycidyl methacrylate) feed is started and is the remaining 95% of the vinyl acetate + Glycidyl methacrylate is introduced into the reactor in 300 minutes. At the same time the ethylene valve is opened again until the rest of the ethylene is fed into the reactor. After 270 minutes of vinyl acetate + Glycidyl methacrylate feeding time, a Second Initiator feed (35 g of sodium peroxydisulfate in 575 g of deionized water) is started for approximately 30 minutes. After the vinyl acetate + Glycidyl methacrylate feed is finished, the reactor temperature is ramped up to 85°C within 30 minutes. This temperature is maintained for another 40 minutes. The reactor is then cooled down to approximately 40°C. A final redox treatment can be made at this point by introducing Brüggolit FF 6 (a sodium salt of a sulfonic acid derivative, obtained from L. Brüggemann KG) (33 g in 312 g of deionized water) and afterwards Trigonox AW 70 (70 g).

[0102] The Example 2 VAE copolymer dispersion has the following characteristics:

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids content:</td>
<td>54.0%</td>
</tr>
<tr>
<td>pH:</td>
<td>4.2</td>
</tr>
<tr>
<td>Viscosity Brookfield (25°C, Spindel 3, 20 rpm):</td>
<td>600 mPas</td>
</tr>
<tr>
<td>Residual vinyl acetate:</td>
<td>&gt;0,1%</td>
</tr>
<tr>
<td>Glass transition temperature, Tg (10 K/min, mid point):</td>
<td>-9°C</td>
</tr>
<tr>
<td>Particle size distribution (LAS):</td>
<td>d₅₀ = 149 nm</td>
</tr>
<tr>
<td></td>
<td>d₃₂/d₈₉ = 1.2</td>
</tr>
<tr>
<td>TVOC (ISO 11890-2)</td>
<td>980 ppm</td>
</tr>
</tbody>
</table>

Example 2
Polymer Dispersion Preparation

[0103] Into a pressure reactor fitted with an anchor stirrer (running at 150 rpm), a heating jacket, dosage pumps and
having a volume of 68.6 liters, a water based solution of the following components is added:

19738 g Water (deionized)
1786 g Polyvinyl alcohol solution (29%) in deionized water, i.e., partially hydrolyzed [88 hydrolysis (mole %)] that forms a 4% solution viscosity of 4.50 cP at 20°C.
3149 g Polyvinyl alcohol solution (15%) in deionized water, i.e., partially hydrolyzed [88 hydrolysis (mole %)] that forms a 4% solution viscosity of 8.50 cP at 20°C.
80 g Sodium acetate (anhydrous)
542 g Sodium vinylsulfonate (30%)
931 g Alkyl polyglycol ether (28 mols of Ethylene Oxide)-nonionic emulsifier
0.33 g Mohr’s Salt

The polyvinyl alcohol is dissolved 15%/29% in deionized water at 90°C for 2 hours. The reactor is purged with nitrogen to eliminate oxygen. Out of a total amount of (28753 g of vinyl acetate, 5% of the vinyl acetate is added to the water phase in the reactor.

The ethylene valve is opened and the reactor is pressurized to 15 bar at ambient temperature (ca. 1000 g of ethylene) and is then closed again (total amount of ethylene: 3828 g). The reactor temperature is ramped up to 65°C. At 35°C, 9% of a First Initiator (reducing agent), which is sodium metabisulfite (44 g in 1043 g of deionized water), is added quickly (over ca. 1-2 minutes) into the reactor. At 50°C, 5% of a Second Initiator (oxidizing agent), which is Trigonox AW-70, (29 g of t-butyl hydroperoxide in 2196 g of deionized water), is added quickly (over ca. 1-2 minutes) into the reactor.

At 65°C, the vinyl acetate feed is started and is introduced into the reactor according to the following profile: 55% in 120 minutes and the remaining 40% in an additional 150 minutes. At the same time, the ethylene valve is opened again until the rest of the ethylene is fed into the reactor. At the same time, all initiator feeds are introduced according to the following profile: 51% of the First Initiator and 55% of the Second Initiator in 120 minutes and the remaining 40% of each initiator in an additional 150 minutes. At 50 minutes before the end of the vinyl acetate feed, the reactor temperature is ramped up over 50 minutes to 85°C. After all of the vinyl acetate and the First and Second Initiators have been introduced, feed of a Third Initiator (33 g of sodium peroxodisulfate in 763 g of deionized water) is started for approximately 10 minutes. The reactor temperature of 85°C is maintained for 1 hour. The reactor is then cooled down to approximately 40°C. A final redox treatment can be made at this point by introducing Brüggemli FT 6 (a sodium salt of a sulfonic acid derivative, obtained from L. Brüggemann KG) (33 g in 489 g of deionized water) and afterwards Trigonox AW 70 (95 g).

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### Example 3

**Comparative SBL Latex (Litex T 5260)**

Litex® T 5260 is a commercial product of Polymer Latex and is a styrene-butadiene latex.

**Characterization of this comparative copolymer dispersion Litex T 5260 is given as follows:**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids Content</td>
<td>52.0%</td>
</tr>
<tr>
<td>pH</td>
<td>8.7</td>
</tr>
<tr>
<td>Viscosity Brookfield (25°C, Spindel 3, 20 rpm)</td>
<td>398 mPas</td>
</tr>
<tr>
<td>Glass transition temperature (10 K/min, mid point)</td>
<td>-20.1°C</td>
</tr>
<tr>
<td>Particle size distribution (LAS)</td>
<td>d&lt;sub&gt;43&lt;/sub&gt; = 146 nm, d&lt;sub&gt;90&lt;/sub&gt;/d&lt;sub&gt;2&lt;/sub&gt; = 1.1</td>
</tr>
<tr>
<td>TVOC (ISO 11890-2)</td>
<td>339 ppm</td>
</tr>
</tbody>
</table>

### Example 4

**TVOC—Emission—Copolymer Dispersion Films**

Copolymer Dispersions of Examples 1, 2 and 3

**The two types of copolymer dispersions as described in Examples 1, 2 and 3 are formed into films and tested for their propensity to emit volatile organic compounds when tested in accordance with the procedures of ISO 16000-9 as described in the Test Methods section above. Results are given as multiples of the Toluene D8 standard represented by the TVOC (Total volatile organic compounds) emitted. Results are shown in Table 1.**

<table>
<thead>
<tr>
<th>Copolymer Dispersion Type</th>
<th>Example No.</th>
<th>Present Development or Comparative</th>
<th>TVOC (Total volatile organic compounds) [No. of Multiple Times Toluene Standard]</th>
</tr>
</thead>
<tbody>
<tr>
<td>VAE</td>
<td>Example 1</td>
<td>Present Development</td>
<td>12.4</td>
</tr>
<tr>
<td></td>
<td>Example 2</td>
<td>Development</td>
<td>5.4</td>
</tr>
<tr>
<td>SBL</td>
<td>Example 3</td>
<td>Standard - 111 ng</td>
<td>20.0</td>
</tr>
<tr>
<td>Toluene D8</td>
<td></td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

**The Table 1 results for the TVOC emissions measurements of the copolymer dispersion films show that the Example 1 VAE dispersion film gives slightly lower TVOC emission than the comparative Example 3 SBL dispersion**
film. The TVOC emission of Example 2 is much lower than that of comparative Example 3.

Example 5

Carpet Sample Preparation

Based on Copolymer Dispersions of Examples 1, 2 and 3

Carpet samples are prepared in the lab by using a foam box to coat a base substrate having fibrous tufts inserted therein and by then curing the applied coating to embed the tufts in the base substrate. The base substrate is a woven polypropylene tufting base. Tufts are made of polypropylene yarn inserted into the tufting base such that the amount of tufts plus base material comprises 500 g/m².

The coating compositions which are used are prepared from the Copolymer Dispersions of Examples 1, 2 and 3. These coating compositions contain, in addition to the Example 1, 2 or 3 copolymer dispersion, a filler material which is calcium carbonate. These aqueous coating compositions all have the following formulation based on the dry copolymer amount: 40% Copolymer Dispersion (dry) formulated with 60% calcium carbonate (Manufacturer Omnia, tradenname Omnicalc 5 GU)

The copolymer dispersion and calcium carbonate filler are premixed with IKA RE 166 stirrer to form a smooth and homogenous mixture. This mixture is foamed up using a Moulinex Supermix 170 device to a volume of 350±50 ml. The foam density (500±100 g/l) is measured with a pycnometer (Erichson Pycnometer Typ 290). A foam box (stainless steel/adjustable gap 0-15 mm/25x5.4x5 cm) is put on the carpet weighed base and is then filled with the mixture. The foam box is dragged slowly and continuously over the back of the carpet sample to form an even film. After coating, the carpet sample is dried for 30 minutes at 110°C (Gallencamp Oven 300 Plus). The carpet samples are stored in a climate room for a minimum of 24 hours at 23°C and 50% humidity. The samples are weighed to determine that the coating add-on is 550±100 g/m².

After conditioning, the carpet samples are cut to a size of 22x26.5 cm (edges sutured with a cotton web to prevent decomposition) and used in the washability, non-slip, tuft anchorage and visual evaluation testing as hereinafter described.

Example 6

Carpet Sample Washability Testing

Based on Copolymer Dispersions of Examples 1, 2 and 3

The several carpet samples prepared as described in Example 4 above are tested for weight loss after washing in accordance with the testing procedure described for the Washability of Carpet Samples Test in the Test Methods section above. The weight loss in grams for each type of carpet sample tested is determined after every five wash cycles and the percentage of weight lost after every five wash cycle is calculated and reported. Results are set forth in Table 2.

<table>
<thead>
<tr>
<th>Carpet Sample Copolymer Type</th>
<th>Weight loss after 5 washes [%]</th>
<th>Weight loss after 10 washes [%]</th>
<th>Weight loss after 15 washes [%]</th>
<th>Weight loss after 20 washes [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>VAE Example 1</td>
<td>Present Development</td>
<td>2.3</td>
<td>2.8</td>
<td>3.0</td>
</tr>
<tr>
<td>VAE Example 2</td>
<td>Present Development</td>
<td>1.5</td>
<td>1.7</td>
<td>1.8</td>
</tr>
<tr>
<td>SBL Example 3</td>
<td>Comparative</td>
<td>2.5</td>
<td>3.5</td>
<td>4.0</td>
</tr>
</tbody>
</table>

The Table 2 data show that the carpet sample with a coating based on the VAE copolymer of Example 1 exhibits comparable weight loss to the carpet sample with a coating based on SBL copolymer of Example 3. The carpet sample with a coating based on the VAE copolymer of Example 2 shows slightly better washability compared to the carpet with a coating based on the SBL coating of Example 3.

Example 7

Non-Slip Testing of Carpet Samples

Based on Copolymer Dispersions of Examples 1, 2 and 3

The several carpet samples prepared as described in Example 5 above are tested for their non-slip properties, both initially and after washing, in accordance with the testing procedure described for the Non-Slip Properties of Carpet Samples (TAPP 816 on-92) in the Test Methods section above. The non-slip properties are measured as the maximum force of dragging a sample over the glass plate in Newtons [N]. Results are the average of two samples and are set forth in Table 3.
The results in Table 3 indicate that the carpets with VAE-based coatings with copolymer dispersions of Examples 1 and 2 show comparable initial non-slip properties compared to carpets with coatings based on the SBL of Example 3.

Carpet with Example 1 VAE-based coating shows better non-slip properties after 5, 10, 15 and 20 washes compared to carpet with Example 3 SBL-based coating. Carpet with Example 2 VAE-based coating shows comparable non-slip properties after 5, 10, 15 and 20 washes to carpet with Example 3 SBL-based coating.

Example 8
Tuft Anchorage for Carpet Samples
Based on Copolymer Dispersions of Examples 1, 2 and 3

The several carpet samples prepared as described in Example 5 above are tested for their tuft anchorage properties, both initially and after 20 wash cycles, in accordance with the testing procedure described for the Tuft Anchorage of Carpet Samples (ISO 4919) in the Test Methods section above. Tuft Anchorage testing determines maximum break force which is measured in Newtons (N). Tuft Anchorage test results are shown in Table 4.

Table 3
Carpet Non-Slip Properties Initially & After 5, 10, 15 and 20 Washes

<table>
<thead>
<tr>
<th>Carpet Sample</th>
<th>Copolymer or Comparative</th>
<th>Present</th>
<th>Max. Force after 5 Washes</th>
<th>Max. Force after 10 Washes</th>
<th>Max. Force after 15 Washes</th>
<th>Max. Force after 20 Washes</th>
</tr>
</thead>
<tbody>
<tr>
<td>VAE</td>
<td>Example 1</td>
<td>Present</td>
<td>8.1</td>
<td>9.1</td>
<td>10.9</td>
<td>9.3</td>
</tr>
<tr>
<td>VAE</td>
<td>Development</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VAE</td>
<td>Example 2</td>
<td>Present</td>
<td>5.0</td>
<td>6.8</td>
<td>5.7</td>
<td>5.7</td>
</tr>
<tr>
<td>SBL</td>
<td>Example 3</td>
<td>Development</td>
<td>7.1</td>
<td>5.5</td>
<td>4.4</td>
<td>4.8</td>
</tr>
</tbody>
</table>

The Table 5 results show that carpet samples with coatings based on the copolymers of Examples 1, 2 and 3 all initially have a closed backing without cracks and an even appearance. After 20 washes, the backing of samples with coatings of the VAE-based copolymers of Examples 1 and 2 shows less visible weight loss, fewer uncoated fibers and fewer cracks compared to the carpet samples with coatings based on the SBL of Example 3.

Example 9
Visual Evaluation of Carpet Samples
Based on Copolymer Dispersions of Examples 1, 2 and 3

The several carpet samples prepared as described in Example 5 above are also visually evaluated in accordance with Visible Evaluation of Carpet Sample Appearance and Hand Feel criteria set forth above in the Test Methods section. The carpet samples are evaluated on a scale of 1 to 4 for both backing integrity and hand feel (softness), both initially and after 20 wash cycles. Results of the visible evaluation of the carpet samples are shown in Table 5. In the Table 5, a scale grade of 1 is good and 4 is bad.

Table 4
Carpet Sample Tuft Anchorage - Initial and After 20 Washes

<table>
<thead>
<tr>
<th>Carpet Sample</th>
<th>Copolymer Type</th>
<th>Present Development</th>
<th>Tuft Anchorage Initial [N]</th>
<th>Tuft Anchorage After 20 Washes [N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>VAE</td>
<td>Example 1</td>
<td>Present</td>
<td>10.9</td>
<td>10.9</td>
</tr>
<tr>
<td>VAE</td>
<td>Development</td>
<td>Present</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VAE</td>
<td>Example 2</td>
<td>Present</td>
<td>29.9</td>
<td>21.1</td>
</tr>
<tr>
<td>SBL</td>
<td>Example 3</td>
<td>Development</td>
<td>27.5</td>
<td>10.8</td>
</tr>
</tbody>
</table>

The Table 5 results show that carpet samples with coatings based on the copolymers of Examples 1, 2 and 3 all initially have a closed backing without cracks and an even appearance. After 20 washes, the backing of samples with coatings of the VAE-based copolymers of Examples 1 and 2 shows less visible weight loss, fewer uncoated fibers and fewer cracks compared to the carpet samples with coatings based on the SBL of Example 3.

Example 10
Carpet with coatings based on the VAE copolymer of Example 1 show a much softer initial hand feel compared to the carpet samples with coatings based on the SBL of Example 3 which feel quite stiff. The samples with coatings based on the VAE of Example 2 feel still unwashed,
although this stiffness is comparable to samples with coatings based on the SBL of Example 3.

[0127] After 20 washes, Example 1-based coatings still have the same smooth hand feel as they do initially. Example 3-based coatings have lost their initial stiffness after 20 washings and then have the same soft touch as Example 1-based coatings. The hand feel of the Example 2 based coating is the same after 20 washes.

1. A carpet product comprising at least one flexible substrate and at least one coating or adhesive layer associated with said at least one flexible substrate, said coating or adhesive layer being formed from an aqueous composition comprising:

A) an emulsifier-stabilized vinyl acetate/ethylene copolymer dispersion wherein the vinyl acetate/ethylene copolymer therein comprises co-monomers which include a vinyl acetate co-monomer copolymerized with ethylene and wherein the vinyl acetate/ethylene copolymer dispersion has a particle size, \( d_p \), ranging from 50 to 500 nm as determined by Laser Aerosol Spectroscopy; and

B) at least one particulate filler material selected from particulate inorganic compounds and particulate plastic material.

1. A carpet product comprising at least one flexible substrate and at least one coating or adhesive layer associated with said at least one flexible substrate, said coating or adhesive layer being formed from an aqueous composition comprising:

A) an emulsifier-stabilized vinyl acetate/ethylene copolymer dispersion wherein the vinyl acetate/ethylene copolymer therein comprises co-monomers which include a vinyl acetate co-monomer copolymerized with ethylene; and

B) at least one particulate filler material selected from particulate inorganic compounds and particulate plastic material;

wherein the carpet product exhibits no more than 4.5% weight loss after 20 wash cycles in the Washability Test described herein.

3. The carpet product according to claim 2 wherein the vinyl acetate/ethylene copolymer dispersion has a particle size, \( d_w \), ranging from 50 to 500 nm as determined by Laser Aerosol Spectroscopy.

4. The carpet product according to claim 1 wherein said vinyl acetate/ethylene copolymer comprises one or more additional different non-functional main co-monomer(s) based on vinyl esters of C1-C18 mono-carboxylic acids or C1-C18 esters of ethylenically unsaturated mono-carboxylic acids or C1-C18 diesters of ethylenically unsaturated di-carboxylic acids.

5. The carpet product according to claim 1 wherein said vinyl acetate/ethylene copolymer in the copolymer dispersion is substantially free of cross-linkable co-monomer moieties which generate formaldehyde upon formation of said coating or adhesive layer.

6. (canceled)

7. The carpet product according to claim 1 wherein said vinyl acetate/ethylene copolymer in the copolymer dispersion comprises from 8 wt % to 40 wt %, based on total main co-monomers therein, of ethylene.

8. (canceled)

9. The carpet product according to claim 1 wherein said vinyl acetate/ethylene copolymer in the copolymer dispersion has a glass transition temperature, \( T_g \), of from \(-25^\circ \) C. to \(+15^\circ \) C.

10. (canceled)

11. (canceled)

12. The carpet product according to claim 1 wherein the vinyl ester copolymer of the copolymer dispersion comprises up to 5 wt %, based on total main monomers therein, of additional functional co-monomers copolymerizable with said main co-monomers, said additional functional co-monomers being selected from ethylenically unsaturated acids, or the salts thereof, ethylenically unsaturated monomers having at least one amide, epoxy, hydroxyl, trialkoxysilane or carboxyl group, and combinations of two or more co-monomers from any of said additional functional co-monomer types.

13. The carpet product according to claim 1 wherein the vinyl ester/ethylene copolymer of the copolymer dispersion comprises an additional ethylenically unsaturated cross-linking co-monomer having an epoxy group.

14. The carpet product according to claim 13 wherein the cross-linking co-monomer in the vinyl acetate/ethylene copolymer of the copolymer dispersion is selected from glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether, vinyl glycidyl ether, and combinations of said cross-linking co-monomers.

15. (canceled)

16. (canceled)

17. (canceled)

18. (canceled)

19. (canceled)

20. (canceled)

21. The carpet product according to claim 1 wherein said copolymer dispersion is stabilized with at least 0.5 wt %, based on total main co-monomers in said copolymer, of one or more emulsifiers and from 0 wt % to 3 wt %, based on total main co-monomers in said copolymer, of a protective colloid.

22. (canceled)

23. (canceled)

24. (canceled)

25. (canceled)

26. (canceled)

27. The carpet product according to claim 1 wherein the particulate filler in the aqueous composition comprises from 10 wt % to 70 wt % of the dispersion and is selected from particulate calcium carbonate and particulate plastic material.

28. The carpet product according to claim 1 which is substantially free of polyvinyl chloride and bitumen.

29. The carpet product according to claim 1 which is substantially free of 4-phenylcyclohexene (4-PCH), 4-vinylcyclohexene (4-VCH), styrene, and ethylbenzene.

30. The carpet product according to claim 1 which comprises at least one binder coating and at least one adhesive layer, each of which is different in composition from the other.

31. The carpet product according to claim 1 wherein the flexible substrate therein is selected from nonwovens, woven, unidirectional weaves, knitted fabrics and pile fabrics.

32. (canceled)

33. (canceled)

34. (canceled)

35. (canceled)

36. (canceled)
37. The carpet product according to claim 1 which is in the form of a woven non-slip carpet or a tufted non-slip carpet, said carpet types being coated with the vinyl ester/ethylene copolymer-containing dispersion on the far side of the tread side.

38. (canceled)

39. A carpet product comprising at least one flexible substrate and at least one coating or adhesive layer associated with said at least one flexible substrate, said coating or adhesive layer being formed from an aqueous composition comprising:
   A) an emulsifier-stabilized copolymer dispersion comprising a vinyl acetate/ethylene copolymer; and
   B) at least one particulate filler material selected from particulate calcium carbonate and particulate plastic material;

   wherein
   i) said vinyl acetate/ethylene copolymer in the copolymer dispersion has an ethylene content of from 8 wt % to 40 wt % based on total main co-monomers therein and a glass transition temperature, Tg, of from -20°C to +5°C;
   ii) said vinyl acetate/ethylene copolymer in the copolymer dispersion comprises no cross-linkable moieties which generate formaldehyde upon formation of said coating or adhesive layer;
   iii) said vinyl acetate/ethylene copolymer in the copolymer dispersion has a particle size, dp, ranging from 120 to 350 nm as determined by Laser Aerosol Spectroscopy;
   iv) said copolymer dispersion is emulsifier-stabilized with a combination of at least 0.5 wt %, based on total monomers in said copolymer, of one or more anionic and/or nonionic emulsifiers and up to 3 wt %, based on total co-monomers in said copolymer, of a polyvinyl alcohol protective colloid;
   v) said copolymer dispersion has a Brookfield viscosity ranging from 200 mPa·s to 4000 mPa·s;
   vi) said carpet product is substantially free of polyvinyl chloride and bitumen; and
   vii) said carpet product exhibits no more than 4.5% weight loss after 20 wash cycles in the Washability Test described herein.

40. A carpet product comprising a textile fabric structure treated with a vinyl acetate/ethylene copolymer dispersion, the copolymer in said dispersion comprising from 70 to 80 pphm of vinyl acetate and from 20 to 30 pphm of ethylene, wherein the copolymer has a glass transition temperature between 0°C and -10°C, possesses a mean particle diameter dw of 150 to 200 nm and is stabilized with at least 1 wt % of emulsifiers and 0 wt % to 2 wt % of a protective colloid formed from polyvinyl alcohol or cellulose ether.

41. (canceled)

42. The carpet product according to claim 40 wherein the vinyl acetate/ethylene copolymer dispersion has a viscosity of from 400 to 1,600 mPa·s, measured with a Brookfield viscometer at 25°C.

43. (canceled)

44. The carpet product according to claim 40 wherein vinyl acetate/ethylene copolymer in the copolymer dispersion comprises further co-monomers copolymerizable with vinyl acetate and ethylene, which further co-monomers are selected from the group consisting of ethylenically unsaturated acids, or the salts thereof, ethylenically unsaturated monomers having at least one amide, epoxy, hydroxyl, N-methylol, triloxysilane or carbonyl group, and combinations of two or several monomers from any of said further monomer types.

45. The carpet product according to claim 40 wherein the vinyl acetate/ethylene copolymer in the copolymer dispersion comprises further co-monomers copolymerizable with vinyl acetate and ethylene, which further co-monomers are selected from the group consisting of vinyl esters which are not vinyl acetate, alpha-olefins which are not ethylene, vinyl aromatics, esters of ethylenically unsaturated monocarboxylic acids, and diesters of ethylenically unsaturated dicarboxylic acids.

46. (canceled)

47. The carpet product according to claim 40 wherein the copolymer dispersion has a solids content of from 45 to 55 wt %.

48. The carpet product according to claim 40 wherein the textile fabric structure comprises at least one fabric selected from the group consisting of nonwovens, wovens, unidirectional weaves, knitted fabrics and pile fabrics.

49. The carpet product according to claim 40 wherein textile fabric structure comprises a pile fabric which is coated with a coating composition based on the copolymer dispersion with the coating being on the far side of the tread side.

* * * * *