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(54) Title: FILM-TO-FILM LAMINATE, MADE BY USING AN AQUEOUS POLYMER DISPERSION AS ADHESIVE AGENT

(57) Abstract: A film-to-film laminate, comprising first and second sheets of film adhered by an adhesive agent comprising an adhesive polymer, which is produced from a monomer mixture, comprising: a) from 80 to 98% by weight of main monomers selected from C1 - to C12-alkyl (meth)acrylates and vinylaromatic monomers; b) from 1 to 10% by weight of vinyl acetate; c) from 0.2 to 5% by weight of hydroxyalkyl (meth)acrylates; d) from 0 to 3% by weight of (meth)acrylic acid; e) from 0 to 5 % by weight of further functional monomers; wherein the weight ratio of vinyl acetate to hydroxy substituted unsaturated monomers is from 1 :4 to 40:1. Also described is a method of forming said laminate and an aqueous polymer dispersion suitable as film-to-film lamination adhesive agent for forming said laminate. The adhesive agent preferably is a single-component adhesive agent.



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Film-to-film laminate, made by using an aqueous polymer dispersion as adhesive agent

Description

5 The present invention relates to film-to-film laminates, to a method of their manufacture and to the use of specific polymer dispersion as film-to-film lamination adhesive agent for forming said laminate. The adhesive agent comprises an adhesive polymer, which is produced from a monomer mixture, comprising main monomers selected from C1- to C12-alkyl (meth)acrylates and styrene; vinyl acetate; hydroxyalkyl (meth)acrylates; and
10 optionally (meth)acrylic acid; and further functional monomers in specific amounts and weight ratios.

There exists a high demand for low cost adhesives for film-to-film lamination with sufficiently good performance in the general purpose sector of flexible food packaging. Organic solvent based adhesive systems have been used but the desire to reduce organic solvent emissions and to improve handling has driven the demand for improved water-based adhesive systems. Particularly attractive have been acrylic polymer dispersion systems, also known as acrylic latex systems. Acrylic based adhesives are for example described in US 6,376,094 and in US 6,727,327. Often, the peel strength of
15 acrylic dispersion systems is unsatisfactory low for use as film-to-film laminating adhesives. One commonly used approach to increase peel strength to a sufficient level is to crosslink acrylic latex with a crosslinking system based on polyurethane chemistry, for example as described in EP 1770138 A1. This approach makes use of a two-component system which is relatively expensive and complex as it requires the additional process step of adding a crosslinking agent prior to lamination and the pot life is rather short. Thus, a need exists for low-cost, aqueous-based laminating adhesive systems with high peel strength and good handling properties for producing film-to-film laminates without the need for a crosslinking second component.

30 It has now been found that specific aqueous polymer dispersions can be used as film-to-film lamination adhesive agent. The present invention is directed to a film-to-film laminate, comprising a first and at least a second sheet of film adhered by an adhesive agent, said adhesive agent comprising an adhesive polymer, said adhesive polymer being produced from a monomer mixture, comprising:

- 35 a) from 80 to 98% by weight of main monomers selected from the group consisting of C1- to C12-alkyl acrylates, C1- to C12-alkyl methacrylates, vinyl aromatic monomers and mixtures thereof;
- b) from 1 to 10% by weight of vinyl acetate;
- c) from 0,2 to 5% by weight of hydroxy substituted unsaturated monomers, selected
40 from hydroxyalkyl acrylates, hydroxyalkyl methacrylates and mixtures thereof;
- d) from 0 to 3% by weight of unsaturated acid monomers, selected from acrylic acid, methacrylic acid and mixtures thereof;
- e) from 0 to 5 % by weight of functional monomers different from monomers a) to d);

wherein the sum of the monomers is 100% by weight and the weight ratio of vinyl acetate to hydroxy substituted unsaturated monomers is from 1:4 to 40:1.

5 The present invention is also directed to a flexible food packaging, comprising a laminate as described herein. The present invention is also directed to the use of an aqueous polymer dispersion as film-to-film lamination adhesive agent, wherein the aqueous polymer dispersion comprises an adhesive polymer as described herein.

10 The present invention is also directed to a method of forming a laminate, wherein an aqueous polymer dispersion as described herein is coated to at least one side of a first sheet of film, the coating is at least partially dried, a second sheet of film is attached to the coated side of the first sheet of film and the first and second sheet of film are bonded together by application of heat and pressure. The aqueous polymer dispersion comprises an adhesive polymer as described herein.

15 In a preferred embodiment of the invention, the adhesive agent is a single-component adhesive agent which is applied without one or more external crosslinking agents, i.e. it neither contains a crosslinking second component nor is it mixed with a crosslinking second component prior to use. This is a low-cost, one component, aqueous-based
20 laminating adhesive system with high peel strength and good handling properties for producing film-to-film laminates which does not need a crosslinking second component to provide a film-to-film laminate with sufficiently high peel strength.

25 Although not necessary for sufficient peel strength, the adhesive agent according to the invention may nevertheless optionally be formulated as two-component system, for example if specific additional effects are desired such as for example better heat resistance of the laminate and better resistance to chemicals, e.g. to components migrating from packed food into the adhesive between the films. The second component comprises at least one crosslinking agent. Suitable crosslinking agents are water dispersible oligomeric or polymeric isocyanates, aziridines or water dispersible or water soluble
30 silanes. Typical mixing ratios are 100 parts by weight of aqueous adhesive polymer dispersion to 1 to 7 parts by weight of crosslinker.

35 The terms „film“ and „sheet of film“ as used herein mean materials which may be manufactured in the form of films or foils such as polymeric films or metal foils, including metallized films and surface treated films. The term „film-to film laminate“ means a structure of two or more films which are laminated together by the use of a laminating adhesive. The term lamination adhesive as used herein means a material that is able to bond together two substrates by application of pressure and heat. Lamination adhesives are distinguished from pressure sensitive adhesives by higher peel strength and
40 by lower quick stick. The term „(meth)acryl...“ and similar terms as used herein mean „acryl... or methacryl...“.

The main monomers a) of the adhesive polymer comprise at least one monomer selected from the group consisting of C1- to C12-alkyl acrylates, C1- to C12-alkyl methacrylates, vinyl aromatic monomers and mixtures thereof. Examples of C1- to C12-alkyl acrylates and of C1- to C12-alkyl methacrylates are methyl methacrylate, methyl acrylate, ethyl acrylate, ethyl methacrylate, isopropyl methacrylate, n-butyl acrylate, n-butyl methacrylate, isobutyl methacrylate, tert-butyl acrylate, tert-butyl methacrylate, n-hexyl acrylate, 2-ethylhexyl acrylate, octyl acrylate, decyl acrylate and dodecyl acrylate. A combination of n-butyl acrylate and methyl methacrylate is especially preferred. The vinylaromatic compounds preferably have up to 20 carbon atoms. Examples are vinyltoluene, alpha- and p-methylstyrene, alpha-butylstyrene, 4-n-butylstyrene, 4-n-decylstyrene and, preferably, styrene. The main monomers a) are preferably selected from n-butyl acrylate, methyl methacrylate and styrene.

The amount of C1- to C12-alkyl (meth)acrylates is preferably from 60 to 98% by weight and the amount of vinylaromatic monomers is preferably from 0 to 30% or from 1 to 30% by weight, based on the total amount of monomers.

The amount of vinyl acetate monomer b) is from 1 to 10% by weight, preferably from 2 to 8% by weight, based on the total amount of monomers.

The hydroxy substituted unsaturated monomers c) are hydroxyalkyl (meth)acrylates, i.e. monoesters of acrylic acid or of methacrylic acid with alkanediols. Examples are hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate and hydroxybutyl methacrylate. Those hydroxyalkyl (meth)acrylates which exist as different isomers can be used in any of their isomers or in a mixture of two or more isomers. Most preferred are hydroxyethyl acrylate and hydroxypropyl acrylate.

The amount of hydroxy substituted unsaturated monomers c) is from 0,2 to 5% by weight, preferably from 0,5 to 4% by weight, based on the total amount of monomers.

The weight ratio of the amount of vinyl acetate monomer b) to hydroxy substituted unsaturated monomers c) is from 1:4 to 40:1, preferably from 1:2 to 10: 1.

The unsaturated acid monomers d) are selected from acrylic acid, methacrylic acid and mixtures thereof. Acrylic acid is preferred. The amount of unsaturated acid monomers d) is from 0 to 3% by weight, preferably from 0,5 to 3% by weight, based on the total amount of monomers.

The adhesive polymer is preferably composed exclusively of monomers a) to d) but may optionally contain further functional monomers e) in amounts of from 0 up to 5% or from 0,1 to 5% by weight, based on the total amount of monomers.

- 5 Further monomers d) are for example acetoacetoxyethyl methacrylate (AAEM), vinylsilanes, alkanediol diacrylates such as e.g. butanediol diacrylate, hydroxyalkyl (meth)acrylamides such as e.g. hydroxymethyl (meth)acrylamide and similar compounds.
- 10 For some applications of the laminates, e.g. applications with food contact such as food packaging, it is desired for safety, health or toxicological reasons that no acrylonitril is used for producing the adhesive polymer. As the performance properties can be achieved by monomer mixtures according to the invention without the need for acrylonitril, it is one aspect of the invention, that the monomer mixture does not contain acrylonitril.
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It has been found, that it is beneficial to work with no chain transfer agent to achieve more cohesion of the adhesive, better heat and chemical resistance and better converting properties such as easier cutting of laminate rolls, less or no edge bleeding etc.

- 20 Therefore, preferred adhesive polymers are those obtainable by polymerizing the monomer mixture mentioned above in the absence of molecular weight regulators (chain transfer agents). The K value of the adhesive polymer is preferably at least 70, for example 70 to 100 (K value according to Fikentscher, determined in a 1% by weight solution of the polymer in Tetrahydrofuran).

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The glass transition temperature T_g of the adhesive polymers of the invention is preferably in the range from -25 to 0°C , in particular in the range from -20 to -10°C . In this context it proves useful to estimate the glass transition temperature T_g of the dispersed polymer. According to Fox (T.G. Fox, Bull. Am. Phys. Soc. (Ser. II) 1, 123 [1956] and Ullmanns Enzyklopädie der technischen Chemie, Weinheim (1980), pp. 17, 18), for the glass transition temperature of copolymers at high molecular masses, it holds in good approximation that

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$$1/T_g = X_1/T_{g1} + X_2/T_{g2} + \dots x_n/T_{gn}$$
where $X_1, X_2, \dots, X_n$ are the mass fractions of the monomers 1, 2, $\dots$, n ; and $T_{g1}, T_{g2}, \dots, T_{gn}$ are the glass transition temperatures of the homopolymers of each of the monomers 1, 2, $\dots$, n in degrees Kelvin. The latter are known, for example, from Ullmann's Encyclopedia of Industrial Chemistry, VCH, Weinheim, Vol. A 21 (1992) p. 169 or from J. Brandrup, E. H. Immergut, Polymer Handbook 3rd edition, J. Wiley, New York 1989.

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In one aspect of the invention, the adhesive polymer is produced from a monomer mixture, comprising

- a) from 80 to 98% by weight of main monomers selected from the group consisting of C1- to C10-alkyl acrylates, C1- to C10-alkyl methacrylates, styrene and mixtures thereof;
- b) from 2 to 10% by weight of vinyl acetate;
- 5 c) from 0,5 to 5% by weight of hydroxy substituted unsaturated monomers, selected from hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate and hydroxybutyl methacrylate, including isomers of these monomers;
- d) from 0,5 to 3% by weight of unsaturated acid monomers, selected from acrylic acid and methacrylic acid;
- 10 e) from 0 to 5% by weight of functional monomers different from monomers a) to d); wherein the sum of the monomers is 100% by weight and the weight ratio of vinyl acetate to hydroxy substituted unsaturated monomers is from 1:2 to 20:1, and said monomer mixture does not comprise acrylnitril and wherein said adhesive polymer is produced without the use of a molecular weight regulator and wherein said adhesive
- 15 polymer has a glass transition temperature of from minus 25°C to 0°C.

Preferably, the adhesive agent is in the form of an aqueous dispersion of the adhesive polymer. Therefore, another embodiment of the invention is a polymer dispersion suitable as film-to-film lamination adhesive agent for forming laminates as described herein. This aqueous polymer dispersion comprises an adhesive polymer as defined above. It has been found advantageous for the adhesive polymer particles in the polymer dispersions of the invention to have an average particle diameter in the range from 50 to 1000 nm. The particle size can be determined by using an ultracentrifuge or by

20 photon correlation spectroscopy; on particle size determination see W. Mächtle, *Angew. Makromolekulare Chemie* 185 (1984), 1025-1039 and W. Mächtle, *op. cit.* 162 (1988), 35-42). In the case of formulations with high solids contents, e.g., >50% by weight based on the total weight of the formulation, it is advantageous on grounds of viscosity for the weight-average particle diameter of the polymer particles in the dispersion to be at least 100 nm. The average particle diameter will preferably not exceed 600 nm. It has also been found advantageous for the particle diameters of the individual polymer particles to vary over a wide range, and in particular for the size distribution to have two or more maxima, i.e. polymer dispersions having bimodal or polymodal polymer particle size distribution. The solids content of the polymer dispersions of the invention is typically in the range from 40 to 70% by weight. For the use in accordance with the invention it is of advantage if the solids content is as high as possible, i.e., at least 50% by weight.

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The aqueous polymer dispersions employed in accordance with the invention can be prepared by free-radical aqueous emulsion polymerization of said monomers. The emulsion polymerization is customarily conducted in an aqueous polymerization medium in the presence of at least one free-radical polymerization initiator and, if desired,

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of a surface-active substance. Suitable free-radical polymerization initiators in principle include both peroxides, such as hydrogen peroxide, organic peroxides such as tert-butyl hydroperoxide, alkali metal and ammoniumperoxodisulfates, for example, and azo compounds. It is preferred to use redox initiator systems, which are composed of at least one organic reducing agent and at least one peroxide and/or hydroperoxide, an example being tert-butyl hydroperoxide and a sulfur compound, such as the sodium salt of hydroxymethanesulfinic acid, sodium sulfite, sodium disulfite, sodium thiosulfate or acetone bisulfite adduct, or hydrogen peroxide with ascorbic acid. For this purpose it is also possible to use redox initiator systems containing a small amount of a metal compound which is soluble in the polymerization medium and whose metallic component is able to exist in a plurality of valence states, an example being ascorbic acid/iron(II) sulfate/hydrogen peroxide, in which the ascorbic acid can in many cases also be replaced by the sodium salt of hydroxymethanesulfinic acid, acetone bisulfite adduct, sodium sulfite, sodium hydrogen sulfite or sodium disulfite, and the hydrogen peroxide by organic peroxides, such as tert-butyl hydroperoxide, alkali metal peroxodisulfates and/or ammonium peroxodisulfate. Likewise preferred initiators are peroxodisulfates, such as sodium peroxodisulfate or ammonium peroxodisulfate. Preferably, the amount of free-radical initiator systems employed, based on the total amount of monomers to be polymerized, is from 0.1 to 2% by weight. The initiator can either be all included in the initial charge to the polymerization vessel or else added continuously or in stages at the rate at which it is consumed in the course of the free-radical aqueous emulsion polymerization. In each individual case it will depend, in a manner known to the skilled worker, both on the chemical nature of the initiator system and on the polymerization temperature. Preferably, a portion is included in the initial charge and the remainder is supplied to the polymerization vessel at the rate at which it is consumed.

Surface-active substances suitable for conducting the emulsion polymerization are the emulsifiers and protective colloids commonly employed for such purposes. The surface-active substances are customarily used in amounts of up to 10% by weight, preferably from 0.1 to 5% by weight and, in particular, from 0.5 to 4% by weight, based on the monomers to be polymerized. The surface-active substances can remain in the polymer dispersions and can therefore also be a constituent of the laminating adhesives of the invention. Examples of suitable protective colloids are polyvinyl alcohols, starch derivatives and cellulose derivatives, or vinylpyrrolidone copolymers. A detailed description of further suitable protective colloids can be found in Houben-Weyl, Methoden der organischen Chemie, Volume XIV/1, Makromolekulare Stoffe [Macromolecular substances], Georg-Thieme-Verlag, Stuttgart 1961, pp. 411-420. Mixtures of emulsifiers and/or protective colloids can also be used. As surface-active substances it is preferred to employ exclusively emulsifiers, whose relative molecular weights, unlike those of the protective colloids, are usually below 2000. They can be anionic, cationic or else nonionic in nature. The anionic emulsifiers include alkali metal and ammonium salts of alkyl sulfates (alkyl: C8-C12), of dialkyl esters of sulfdsuccinic acid (alkyl: C4-C10), of

sulfuric monoesters with ethoxylated alkanols (EO units: 2 to 50, alkyl: C12 to C18) and with ethoxylated alkylphenols (EO units: 3 to 50, alkyl: C4-C10), of alkylsulfonic acids (alkyl: C12-C18) and of alkylarylsulfonic acids (alkyl: C9 to C18). The anionic surface-active substances also include mono- and dialkyl derivatives of sulfonylphenoxybenzenesulfonic salts, especially their sodium, potassium or calcium salts. The alkyl groups in these compounds generally have 6 to 18 and especially 6, 12 or 16 carbon atoms. Use is frequently made of technical mixtures comprising a proportion of from 50 to 90% by weight of the monoalkylated product. These compounds are common knowledge, for example, from U.S. Pat. No. 4,269,749, and are obtainable commercially, for example, as Dowfax(R) 2A1 (trademark of the Dow Chemical Company). Suitable nonionic emulsifiers are araliphatic or aliphatic nonionic emulsifiers, examples being ethoxylated mono-, di- and trialkylphenols (EO units: 3 to 50, alkyl: C4-C9), ethoxylates of long-chain alcohols (EO units: 3 to 50, alkyl: C8-C36), and also polyethylene oxide/polypropylene oxide block copolymers. Preference is given to ethoxylates of long-chain alkanols (alkyl: C10-C22, average degree of ethoxylation: 3 to 50) and, of these, particular preference to those based on oxo alcohols and naturally occurring alcohols having a linear or branched C12-C18 alkyl radical and a degree of ethoxylation of from 8 to 50. Further suitable emulsifiers can be found in Houben-Weyl, Methoden der organischen Chemie, Volume XIV/1, Makromolekulare Stoffe [macromolecular substances], Georg-Thieme-Verlag, Stuttgart, 1961, pp. 192-208. The surface-active substances used to prepare the polymer dispersions of the invention preferably include at least one anionic emulsifier. It has been found advantageous for the stability of the polymer dispersions of the invention, especially to mechanical loads such as shear forces, that the anionic emulsifiers used to prepare the dispersions of the invention can include at least one salt of a dialkyl ester of sulfosuccinic acid (linear or branched C4-C10 and, in particular, C8 alkyl radical), preferably an alkali metal salt and in particular the sodium salt.

The emulsion polymerization takes place in general at from 30 to 130, preferably from 50 to 100 °C. The polymerization medium can consist either of water alone or else of mixtures of water with water-miscible organic liquids such as methanol, ethanol, n-propanol, isopropanol, n-butanol, tert-butanol, tetrahydrofuran, formamide, or dimethylformamide, the proportion of said liquids usually being less than 10% by weight based on the polymerization medium. It should be borne in mind here that the presence of alcohols during the polymerization may result in a reduction in molecular weight. Preferably, water alone is used as polymerization medium.

The emulsion polymerization can be conducted either as a batch process or in the form of a feed process, including stages or a gradient procedure. Preference is given to the feed process, in which the monomers in pure or emulsified form are supplied to the polymerization zone continuously, in stages or under a concentration gradient, with the polymerization being maintained. The individual components can be added to the reac-

tor, in the case of the feed process, from above, from the side or from below, through the reactor floor. Besides the seed-free preparation route, a defined polymer particle size can be established by conducting the emulsion polymerization by the seed latex process or in the presence of seed latex prepared in situ. In the case of the seed latex process, the polymerization is customarily conducted in the presence of from 0.001 to 3% by weight and, in particular, from 0.01 to 1.5% by weight of a seed latex (solids content of the seed latex, based on total monomer amount), preferably with seed latex included in the initial charge (initial charge seed). The latex generally has a weight-average particle size of from 10 to 100 nm and, in particular, from 20 to 50 nm. Examples of its constituent monomers are styrene, methyl methacrylate, n-butyl acrylate and mixtures thereof.

In order to remove the residual monomers after polymerization it is common to carry out physical deodorization, by distilling off the volatile monomers with steam, for example, or chemical deodorization in any order. For example, after the end of the emulsion polymerization i.e. after a monomer conversion of at least 95%, or after the residual monomer content has been lowered to a level <5% by weight by physical deodorization, further initiator is added, such as a redox initiator.

The adhesive polymer dispersions of the invention are used in accordance with the invention in aqueous adhesive formulations for producing film-to-film laminates; i.e., in aqueous laminating adhesive formulations for bonding at least two film or foil substrates of large surface area. The present invention therefore also provides a method for producing film-to-film laminates in which an aqueous adhesive formulation is used which comprises at least one of the polymer dispersions of the invention. In this context, the aqueous polymer dispersions can be used as they are or after formulation with auxiliary agents. Examples of auxiliary agents are wetting agents, thickeners, protective colloids, light stabilizers, biocides, defoamer etc. Typical wetting agents are the anionic surface-active substances mentioned above, e.g. one or more salts of a dialkyl esters of sulfosuccinic acid (linear or branched C4-C10 and, in particular, C8 alkyl radical), preferably an alkali metal salt and in particular the sodium salt. With the adhesive formulations of the invention there is no need to add plasticizing resins (tackifiers) or other plasticizers. In the method of the invention for producing film-to-film laminates, the aqueous adhesive polymer dispersion of the invention, or an appropriately formulated preparation (formulation), is applied, for example by coating, to at least one side of a first sheet of film. The coating may have a layer thickness of from 0.1 to 20 g/m², preferably from 1 to 7 g/m². Conventional coating processes can be used such as for example roll coating, reverse roll coating, gravure roll coating, reverse gravure roll coating, brush coating, wire-wound rod (Meyer rod) coating, spray coating, air knife coating, meniscus coating, curtain coating or dipping. The coating is at least partially dried, e.g. by evaporation of the dispersion water for a short time, preferably after from 1 to 60 seconds. The coated first substrate can then be laminated with a second substrate.

A second sheet of film is attached to the coated side of the first sheet of film and the first and second sheet of film are bonded together by application of heat and pressure. The temperature can be, for example, from 30 to 200, preferably from 30 to 100°C, and the pressure can be, for example, from 100 to 3000, preferably from 300 to 2000 kN/m².

In one embodiment, the adhesive agent is applied as a one component agent, i.e. without one or more separate crosslinking agents, especially without the use of isocyanate crosslinking compounds. Optionally, at least one of a first and second sheet of film can be printed or metallized on its respective side which is coated with the adhesive agent.

Examples of suitable substrates are polymer films, especially those of polyethylene (PE), oriented polypropylene (OPP), cast polypropylene (CPP), polyamide (PA), polyethylene terephthalate (PET), polyacetate, cellophane, metallized films (i.e. polymer films (vapor-)coated with metal, e.g. aluminum) or metal foils, such as those of aluminum. Said foils or films can be bonded to one another, or to a foil or film of a different type, e.g., polymer films to metal foils, different polymer films to one another, etc. Said foils and films can also be printed with printing inks, for example.

One embodiment of the invention is a laminate made by using an aqueous adhesive polymer dispersion as described above and wherein the material of a first sheet of film is selected from oriented polypropylene, cast polypropylene, polyethylene, polyethylene terephthalate and polyamide and wherein the material of a second sheet of film is selected from oriented polypropylene, cast polypropylene, polyethylene, polyethylene terephthalate, polyamide and metal foils. In another embodiment of the invention the first sheet of film and/or the second sheet of film are printed or metallized on their respective side which is coated with the adhesive agent. The thickness of the base films may for example be from 5 to 100 µm, preferably from 5 to 40 µm.

An advantage of the invention is that substrates of very different kinds can be bonded to one another, i.e., laminated, with the adhesive polymer dispersions of the invention ensuring good adhesion of the adhesive formulation to the substrates and resulting in high strength of the bonded composite.

While surface modification of the base films prior to adhesive coating is not required, better results may be obtained if the surface or surfaces of the base films are modified before application of the adhesive agent of the present invention. Conventional surface modification techniques include corona treatment, which is the most common and most preferred procedure for modifying the surface of the polymer base film to enhance coating adhesion. The corona treatment or other surface modification should be sufficient to permit wetting out of the coating. Corona treatment of about 10 watt per square

meter per minute is typically sufficient to achieve the desired results. Alternatively or in addition, primer or other intermediate layers can optionally be used between the polymer film and the barrier coating. Further, the laminates may include additional functional layers such as barrier layers, printed layers, colored layers or protective layers.

- 5 The functional layers may be located on the outer surface of the laminates or on the inside, between base substrate and adhesive coating.

Examples

10 Substances:

Disponil® FES 77: 32% by weight aqueous solution of sodium salt of fatty alcohol polyether sulfate (Cognis)

Dowfax® 2A1: 45% by weight aqueous solution of dodecylphenoxybenzenedisulfonic acid sodium salt (Dowchemical).

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General polymerization procedure

Procedures for emulsion polymerization are generally known (see e.g. WO 98/23656).

An emulsion was formed in deionized water with monomers according to table 1, 0,4 pphm NaOH (parts by weight per hundred parts monomers) and 1 pphm Disponil®

- 20 FES 77. The monomer emulsions of examples D2 to D5 additionally contained 0,2 pphm Dowfax® 2A1. The monomers were polymerized using a total of 0,5% by weight (with respect to the total weight of monomers) of sodium peroxodisulfate, dissolved in deionized water. A polymerization reactor was charged in a nitrogen atmosphere with 250 g of deionized water. The initial charge was heated to 90°C and 10% of the total
- 25 amount of the initiator solution was added to the initial charge. Then addition of the monomer emulsion and addition of the remainder of the initiator solution were added in parallel. The monomer emulsion was added in 3 hours, the remainder of the initiator solution was added in 3,5 hours, beginning simultaneously. The pH can be adjusted by aqueous ammonia. The mixture was subsequently cooled to room temperature and
- 30 filtered through a 125µm sieve.

Table 1: monomer mixtures of exemplary and comparative adhesive polymers

example	monomers [pphm]							solids [%]	pH
	nBA	MM A	S	VAc	AA	HEA	HPA		
CE1	78	20			2			56,3	4,8
CE2	73	20		5	2			54,8	5
CE3	76	20			2	2		56,1	4,8
D1	71	20		5	2	2		56,4	5,1
D2	71	20		5	2	2		57,9	6,1
D3	71		20	5	2	2		56,1	5,8
D4	71	20		5	2		2	57,9	6

D5	71		20	5	2		2	55,4	5,8
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pphm: parts per hundred monomers

nBA: n-butyl acrylate; MMA: methyl methacrylate; S: styrene; VAc: vinyl acetate; AA: acrylic acid; HEA: hydroxyethyl acrylate; HPA: hydroxypropyl acrylate (isomeric mixture of 2-hydroxy-n-propyl acrylate and 2-hydroxy isopropyl acrylate)

- 5 CE1-3: comparative examples; D1-D5: inventive examples

Performance testing of film-to-film lamination adhesives

- 10 The adhesive polymer dispersions were knife-coated in a dry layer thickness of 2 g/m² (solids) onto various commercially available polymer films and dried. The coated polymer films were laminated to a second polymer film in a calender at 70°C and under a pressure of 6.5 bar. The film-to-film laminates were subsequently stored at room temperature for 24 hours. The peel strength for separating the laminated films was determined. For this purpose the film-to-film laminates were cut into strips 15 mm wide. The strips were subsequently subjected to peeling in a universal peel strength tester machine from Zwick (model 1120.25.01) at a rate of 100 mm/min and an angle of 180°, and the force required for this (in newtons) was measured. The results are compiled in Table 2.

Table 2: Peel strength test results for single-component adhesives

Example	Film A	Film B	Peel strength [N/15 mm]
CE1	printed OPP	PE	1,5
CE2	printed OPP	PE	1,7
CE3	printed OPP	PE	1,7
D1	printed OPP	PE	2,0
D2	printed OPP	PE	1,9
D3	printed OPP	PE	1,9
D4	printed OPP	PE	2,2
D5	printed OPP	PE	1,9
CE1	printed PET	met. PET	0,7
CE2	printed PET	met. PET	0,7
CE3	printed PET	met. PET	0,8
D1	printed PET	met. PET	1,0
D2	printed PET	met. PET	0,9
D3	printed PET	met. PET	0,9
D4	printed PET	met. PET	0,9
D5	printed PET	met. PET	0,9

- 20 OPP: oriented polypropylene; PE: polyethylene; PET: polyethylene terephthalate; met.: metallized.

For same film substrates, film-to-film lamination adhesives D1 to D5 according to the invention show significantly higher peel strength than comparative adhesives C1 to C3.

Examples of two component adhesives

- 5 100 parts by weight of acrylic dispersion D1, D2, D3, D4 or D5 are mixed with 2 parts by weight of a water dispersible isocyanate crosslinker, e.g. Basonat® F 200 WD (polyfunctional aliphatic isocyanate). Within the pot life time of maximum 6 hours, this mixture is processed by coating onto a polymeric film (printed or unprinted OPP or PET). The coated polymer films can be laminated to a second polymeric film (PE or unmetallized or metallized PET) in a calender at 70°C and under a pressure of 6.5 bar.
- 10

Patent Claims

1. A film-to-film laminate, comprising a first and at least a second sheet of film adhered by an adhesive agent, said adhesive agent comprising an adhesive polymer, said adhesive polymer being produced from a monomer mixture, comprising:
 - a) from 80 to 98% by weight of main monomers selected from the group consisting of C1- to C12-alkyl acrylates, C1- to C12-alkyl methacrylates, vinylaromatic monomers and mixtures thereof;
 - b) from 1 to 10% by weight of vinyl acetate;
 - c) from 0,2 to 5% by weight of hydroxy substituted unsaturated monomers, selected from hydroxyalkyl acrylates, hydroxyalkyl methacrylates and mixtures thereof;
 - d) from 0 to 3% by weight of unsaturated acid monomers, selected from acrylic acid, methacrylic acid and mixtures thereof;
 - e) from 0 to 5 % by weight of functional monomers different from monomers a) to d);wherein the sum of the monomers is 100% by weight and the weight ratio of vinyl acetate to hydroxy substituted unsaturated monomers is from 1:4 to 40:1.
2. Laminate according to the preceding claim, wherein said hydroxy substituted unsaturated monomers are selected from hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate and hydroxybutyl methacrylate including isomers of these monomers.
3. Laminate according to any of the preceding claims, wherein said main monomers a) are selected from the group consisting of methyl methacrylate, n-butyl acrylate and styrene.
4. Laminate according to any of the preceding claims, wherein said monomer mixture does not comprise acrylonitril and/or wherein said adhesive polymer is produced without the use of a molecular weight regulator.
5. Laminate according to any of the preceding claims, wherein said adhesive polymer has a glass transition temperature of from minus 25°C to 0°C.
6. Laminate according to any of the preceding claims, wherein the material of said first sheet of film is selected from oriented polypropylene, cast polypropylene, polyethylene, polyethylene terephthalate and polyamide and wherein the material of said second sheet of film is selected from oriented polypropylene, cast polypropylene, polyethylene, polyethylene terephthalate, polyamide and metal foils and wherein optionally at least one of the first and second sheets of film can be printed or metalized on its respective side which is coated with the adhesive agent.

7. Laminate according to any of the preceding claims, wherein said adhesive polymer being produced from a monomer mixture, comprising:
- a) from 80 to 98% by weight of main monomers selected from the group consisting of C1- to C10-alkyl acrylates, C1- to C10-alkyl methacrylates, styrene and mixtures thereof;
 - b) from 2 to 10% by weight of vinyl acetate;
 - c) from 0,5 to 5% by weight of hydroxy substituted unsaturated monomers, selected from hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate and hydroxybutyl methacrylate including isomers of these monomers;
 - d) from 0,5 to 3% by weight of unsaturated acid monomers, selected from acrylic acid and methacrylic acid;
 - e) from 0 to 5 % by weight of functional monomers different from monomers a) to d);
- wherein the sum of the monomers is 100% by weight and the weight ratio of vinyl acetate to hydroxy substituted unsaturated monomers is from 1:2 to 20:1, and said monomer mixture does not comprise acrylnitril and wherein said adhesive polymer is produced without the use of a molecular weight regulator and wherein said adhesive polymer has a glass transition temperature of from minus 25°C to 0°C.
8. Laminate according to any of the preceding claims, wherein said adhesive agent is a single-component adhesive agent which is applied without external crosslinking agent.
9. Flexible food packaging, comprising a laminate according to any of claims 1-8.
10. An aqueous polymer dispersion suitable as film-to-film lamination adhesive agent for forming laminates according to claim 1, said aqueous polymer dispersion comprising an adhesive polymer, said adhesive polymer being produced from a monomer mixture, comprising:
- a) from 80 to 98% by weight of main monomers selected from the group consisting of C1- to C12-alkyl acrylates, C1- to C12-alkyl methacrylates, vinylaromatic monomers and mixtures thereof;
 - b) from 1 to 10% by weight of vinyl acetate;
 - c) from 0,2 to 5% by weight of hydroxy substituted unsaturated monomers, selected from hydroxyalkyl acrylates, hydroxyalkyl methacrylates and mixtures thereof;
 - d) from 0 to 3% by weight of unsaturated acid monomers, selected from acrylic acid, methacrylic acid and mixtures thereof;
 - e) from 0 to 5 % by weight of functional monomers different from monomers a) to d);

wherein the sum of the monomers is 100% by weight and the weight ratio of vinyl acetate to hydroxy substituted unsaturated monomers is from 1:4 to 40:1.

- 5 11. Aqueous polymer dispersion according to the preceding claim, wherein said polymer dispersion has a solids content of from 40 to 70% by weight.
- 10 12. Aqueous polymer dispersion according to any of claims 10 to 11, wherein said hydroxy substituted unsaturated monomers are selected from hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate and hydroxybutyl methacrylate including isomers of these monomers.
- 15 13. Aqueous polymer dispersion according to any of claims 10 to 12, wherein said main monomers a) are selected from the group consisting of methyl methacrylate, n-butyl acrylate and styrene.
- 20 14. Aqueous polymer dispersion according to any of claims 10 to 13, wherein said monomer mixture does not comprise acrylonitril and/or wherein said adhesive polymer is produced without the use of a molecular weight regulator.
- 25 15. Aqueous polymer dispersion according to any of claims 10 to 14, wherein said adhesive polymer has a glass transition temperature of from minus 25°C to 0°C.
- 30 16. Aqueous polymer dispersion according to any of claims 10 to 15, wherein said adhesive polymer being produced from a monomer mixture, comprising:
a) from 80 to 98% by weight of main monomers selected from the group consisting of C1- to C10-alkyl acrylates, C1- to C10-alkyl methacrylates, styrene and mixtures thereof;
b) from 2 to 10% by weight of vinyl acetate;
c) from 0,5 to 5% by weight of hydroxy substituted unsaturated monomers, selected from hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate and hydroxybutyl methacrylate including isomers of these monomers;
d) from 0,5 to 3% by weight of unsaturated acid monomers, selected from acrylic acid and methacrylic acid;
e) from 0 to 5 % by weight of functional monomers different from monomers a) to d);
wherein the sum of the monomers is 100% by weight and the weight ratio of vinyl acetate to hydroxy substituted unsaturated monomers is from 1:2 to 20:1, and said monomer mixture does not comprise acrylonitril and wherein said adhesive polymer is produced without the use of a molecular weight regulator and wherein said adhesive polymer has a glass transition temperature of from minus 25°C to 0°C.
- 40

17. Use of an aqueous polymer dispersion according any of claims 10 to 16, as a single-component film-to-film lamination adhesive agent which is applied without external crosslinking agent.
- 5
18. A method of forming a laminate, wherein an aqueous polymer dispersion according to any of claims 10 to 16 is coated to at least one side of a first sheet of film, the coating is at least partially dried, a second sheet of film is attached to the coated side of the first sheet of film and the first and second sheet of film are bonded together by application of heat and pressure.
- 10
19. A method according to the preceding claim, wherein the material of said first sheet of film is selected from oriented polypropylene, cast polypropylene, polyethylene, polyethylene terephthalate and polyamide and wherein the material of said second sheet of film is selected from oriented polypropylene, cast polypropylene, polyethylene, polyethylene terephthalate, polyamide and metal foils and wherein optionally at least one of the first and second sheets of film can be printed or metallized on its respective side which is coated with the adhesive agent.
- 15

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2010/060231

A. CLASSIFICATION OF SUBJECT MATTER

INV. B32B7/12 C09J133/08 C09J133/10 C08F220/18
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B32B C08F C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

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Further documents are listed in the continuation of Box C.



See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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INTERNATIONAL SEARCH REPORT

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PCT/EP2010/060231

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