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(54) Title: MICROSPHERE ACRYLIC COPOLYMER ADHESIVES AND PROCESS OF MANUFACTURING THEREOF

(57) Abstract: ABSTRACT An adhesive composition is provided, which comprises a plurality of elastic polymeric inherently tacky microspheres, wherein the synthesized particles are the reaction product of reactants comprising at least one C4-C14 monomer and at least one comonomer, chain transfer agent, multifunctional monomer and have an insoluble gel fraction in the range of 60-95% by weight with respect to the microspheres.

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MICROSPHERE ACRYLIC COPOLYMER ADHESIVES AND PROCESS OF MANUFACTURING THEREOF

This invention relates to a synthesis of suspension based acrylic adhesive microspheres and in particular to adhesive microspheres having variable adhesion properties. In some removable and repositionable product applications there is a need about a synthesis of an adhesive, which exhibits lower peel strength values and higher tack values (initial adhesion) while remaining removable and repositionable. Low peel strength and high tack are especially favored, when coating various low grammage, transparent papers or the like.

Microsphere adhesives are usually used for the purposes of manufacturing removable and repositionable products. The term "repositionable" means that the adhesive is capable to withstand repeated removal and adhesion of the product without substantial reduction of the adhesion capability. It is also desired that the product is completely removed from the surface without leaving any adhesive residue. The products where microsphere adhesives are applied are well known in common home and stationery environment and are normally used for temporary messaging. As examples of such products may serve e.g. self stick notes, which are manufactured by 3M Company and labeled as "Post-it", or also the so-called "TIX" product line offered and distributed by Aero Company.

Numerous published references can also be found in patent literature, which deal with the synthesis process as such and also refer to use of inherently tacky acrylic polymeric microspheres, which may either be solid or may have hollow particle morphology.

Preparation of solid microspheres by using alkyl acrylate monomers and ionic comonomers (e.g., sodium methacrylate) in the presence of an emulsifier via aqueous suspension polymerization is disclosed in US 3,691,140 (Silver). Another example of solid and inherently tacky microspheres prepared from non-ionic alkyl acrylate or (meth)acrylate monomer(s) is disclosed in US 4,166,152 (Baker et al.). Two surface active agents (an emulsifier and ionic suspension stabilizer) are used in such aqueous suspension polymerization. Said ionic suspension stabilizer is primarily used to prevent subsequent microsphere agglomeration. It is

also disclosed that by adding of an oil soluble and non ionic copolymerizable monomer (e.g., divinylbenzene) the tack of the microspheres can be varied. In both US 4,495,318 (Howard) and US 4,598,112 (Howard) similar types of microspheres are described, and a non-ionic or cationic emulsifier is applied in the polymerization process. Another process of preparing stabilized adhesive microspheres is disclosed in US 5,756,625 (Crandall et al.). All of the stated patents disclose utility as a "reusable adhesive".

The morphology of the microspheres and the impact of the particle morphology on adhesion properties (increasing the adhesion) are disclosed in US 5,053,436 (Delgado) and US 5,045,569 (Delgado). In these lastly mentioned patents the synthesis of hollow microspheres is described, which are prepared from alkyl acrylate or (meth)acrylate monomer(s) and optionally by adding a polar comonomer in the presence of an emulsifier, which results in formation of internal voids in the microspheres. Due to the hollow core of the microspheres, the adhesive exhibits an increased resistance to adhesive transfer and increased adhesion. Among others it is also disclosed that the composition of the hollow microspheres may also contain various crosslinking agents such as multifunctional (meth)acrylate crosslinking agent (e.g., 1,4 butanediol diacrylate or 1,6 hexanediol diacrylate) or other crosslinking agents (e.g., divinylbenzene). Similar void microspheres (having multiple small voids) and impact of such morphology on adhesion are disclosed in US 4,988,567 (Delgado). Such multiple small voids should enhance the adhesive properties.

Furthermore, in DE 3544882 A1 (Nichiban) a synthesis of a crosslinked microspheres derived from 90 to 99.5 weight percent of (meth)acrylate ester and 10 to 0.5% by weight of vinyl type monomer (e.g., acrylic acid) is presented. The crosslinking reaction is achieved via reaction with an oil soluble crosslinking agent. As also disclosed therein such microspheres may also contain other monomers (e.g., acetate, styrene, acrylonitrile, methacrylonitrile, etc.), which are added in the monomer mixture in order to prevent cohesion failure of the adhesive when peeling the face material from the substrate. The microspheres are prepared via dispersing of a copolymer solution in water, which was synthesized by using other known methods of polymerization (e.g., bulk, solution, emulsion or suspension). In the last two cases (emulsion and suspension polymerization) there is no need to prepare a new water dispersion and the product may be used as a synthesized one

Still further, preparation of partially crosslinked microspheres is disclosed in US 5,714,237 (Coopridner et al.). The microspheres are the product of reactants comprising at least one alkyl (meth)acrylate monomer and optionally at least one comonomer and they have a portion of soluble fraction in range about 30-98% of the microspheres. A chain transfer agent modifier was added in order to vary the portion of soluble fraction in above mentioned range. Similar process for preparing of a repositionable adhesive is also disclosed in US 5,571,617 (Coopridner et al.). The distinct difference is in the used selection of comonomers. In latter case, the employed comonomers have a polar nature.

An aqueous suspension polymerization procedure for the synthesis of the elastic micro-balls is disclosed in US 4,735,837 (Miyasaka et al.). In this case the synthesized micro-balls are used as an adhesive coating for production of a detachable adhesive sheet, where micro-balls partially protrude from the surface of the adhesive layer. They are synthesized using (meth)acrylate monomer and an α -olefinic carboxylic acid monomer. After the polymerization procedure, the micro-balls are dispersed and mixed in solvent together with the adhesive. The disclosed ratio between micro-balls and adhesive is from about 1:10 to about 10:1. In this range, the micro-balls are found to be completely covered with the adhesive, what is necessary for the adhesion process.

A method of producing a pressure sensitive microsphere adhesives is disclosed in JP 63 260,973 (Sekisui). The tacky microspheres are prepared by means of a suspension polymerization of an acrylate or (meth)acrylate monomer, a water soluble comonomer and an oil soluble multifunctional crosslinking agent having at least two polymerizable double bonds (amount ranging from 0.01 to 0.5% by weight). As mentioned therein, a high degree of crosslinking in the microspheres negatively influences the adhesion properties.

US 5,215,818 (Silver et al.) further describes a synthesis of microspheres via aqueous suspension polymerization process and the use thereof in aerosol adhesive systems. The monomers used in the synthesis may e.g. be alkyl acrylate monomers with added ionic comonomers (e.g., sodium methacrylate), which are primarily used for enhancing of suspension stability due to comonomer zwitterionic nature.

Suspension polymerization process of synthesis inherently tacky (meth)acrylate microspheres with absence of an ionic comonomer or an ionic suspension stabilizer (intended for

preventing coagulation of the suspension) is described in US 4,786,696 (Bohnel). A combination of (meth)acrylate monomer and small amounts of vinyl comonomer (e.g. acrylic acid used for the purposes of modification of tack) are used in this process. Due to the absence of surface active agents, agitation of the reaction mixture prior to the initiation of the reaction is needed in order to create a suspension of monomer droplets in continuous phase. In such case an average diameter of synthesized microspheres rates between 5 and 70 micrometers. The absence of stabilizer in the suspension influences the adhesion properties of a dried adhesive coating, and consequently, such microspheres exhibit high tack values.

Adding a water insoluble polymeric thickening agent in the continuous phase for the aqueous suspension polymerization that yields bead-type polymers is disclosed in US 3,620,988 (Cohen). The product of the described method is a mixture of a high solid suspension, which consist of a crosslinked polymer (derived from higher alkyl acrylate) as well as of a tackifier.

Application of a protective colloid (comprising casein a main ingredient) for synthesis of aqueous suspension microspheres with application of one or more alkyl (meth)acrylate esters, α -monoolefin carboxylic acids, and one or more other vinyl monomers is disclosed in US 4,645,783 (Kinoshita) and US 4,656,218 (Kinoshita). Such products are used for coating of a so called "repeatably usable and releasable sheet".

Application of primers is reasonable in process of coating the microspheres due to poor anchorage of the microspheres to the substrate. However, the microspheres may also be mixed with finer polymer particles (usually prepared by emulsion polymerization of one or more vinyl monomers), which leads to efficiently improvement of anchorage onto the face material as well as onto the substrate.

US 3,857,731 (Merrill) and EP 209,337 (Smith & McLaurin) both relate to microspheres transfer process. In the first case (US 3,857,731) utilization of binder material together with microspheres of the Silver patent (US 3,691,140) is disclosed. The function of said binder material is to provide sockets in which microspheres are held. Preferably, the microspheres are derived from at least one alkyl acrylate or methacrylate ester. When bearing in mind EP 209,337 the microspheres are composed of non-ionic monomers alone or together with a proportion of ionic comonomers. Ionic comonomers are first dissolved in an organic cosolvent. Given that the microspheres comprise an adhesion promoting monomer (which

remains unreacted during polymerization) the subsequent binding of the microspheres thorough an electrostatic interaction is possible. Another polymerization process for synthesis of removable pressure sensitive adhesive with reduced adhesive transfer is disclosed in US 5,663,241 (Takamatsu et al.). Products of a mono-olefinically unsaturated monomer comprise an aldehyde or ketone group and a base monomer. By addition of a polyhydrazine the adhesives with improved properties can be provided.

Synthesis of removable adhesives is also feasible on the basis of a combination of suspension and emulsion polymerization, which is e.g. described in US 5,326,842 (Knudsen et al.). In the first stage microspheres are synthesized via suspension polymerization process (with application of chain transfer agent), upon which the suspension polymerization is followed by an emulsion polymerization, which provides stability of the produced dispersion.

A method of making of pressure sensitive adhesive film having different adhesive properties is disclosed in US 6,017,624 (Delgado). This kind of adhesive film provides different levels of peel adhesion and moreover excels in high shear strength and good tensile properties, and is used for production of unsupported PSA films. In such a case microspheres are synthesized via suspension polymerization process by using isooctyl acrylate and acrylic acid as monomers. PSA films are prepared by using acetone dispersion of the produced hollow microspheres or by a combination of hollow microsphere dispersion and solvent borne acrylate PSA creating a two layer laminate. Also a blend of both PSA's is prepared and coated on a primed polyester backing. Other examples of preparing microsphere adhesives with lower adhesion to coated papers are disclosed in US 6,905,763 (Crandall et al.) and US 6,296,942 (Crandall et al.)

US 5,719,247 (Delgado et al.) discloses a process of preparing a tack free elastomeric acrylate microspheres via suspension polymerization using standard alkyl acrylate ester monomers, by which also a multifunctional crosslinking agent is used. As stated therein, the shear storage modulus is reduced and the microspheres become tacky, when too much alkyl acrylate ester is used or also, if there is a lack of the multifunctional crosslinking agent.

US 7,022,745 (Guo et al.) refers to a process for forming solid pressure sensitive adhesive polymer microspheres. Presented is a copolymerization process, in which a non-ionic monomer of an alkyl acrylate or alkyl (meth)acrylate ester of a non-tertiary alcohol and an acid

monomer copolymerizable with the non ionic monomer in presence of an electrolyte (e.g., alkali metal, alkaline earth metal or ammonium salt of an inorganic acid) are used.

All these known patent documents disclose a synthesis and preparation of tacky or tack free acrylic microspheres, where the adhesion properties are changed by using either various acrylic monomers and comonomers, by different emulsifiers or suspension stabilizers in order to change the morphology of the microspheres, or by addition of various modifiers such as chain transfer agents or multifunctional monomers. All these documents are however silent with respect to a synthesis of acrylate microspheres, where both, multifunctional crosslinking agent and chain transfer agent, would be used at the same time. Combination of both modifiers in the synthesis results in an acrylic microsphere adhesive, having low peel values and high tack. There is a need to obtain such acrylate microspheres, which would possess low peel values while retaining or even improving the tack values, and could on such a basis be particularly useful for the purposes of coating various low grammage papers, and which can be easily deformed when peeling the coated backing from the substrate.

The proposed invention generally relates to removable and repositionable pressure sensitive adhesives. This invention provides partially crosslinked solid acrylate polymer microspheres, in which the amount of insoluble gel phase represents from about 60% to about 95% by weight with respect to the polymer, having low peel values while improving tack adhesion values without the addition of any adhesion modifiers after the polymerization process.

In particular, the present invention relates to a microsphere adhesive comprising:

- (a) a plurality of polymeric, partially crosslinked microspheres wherein the microspheres are obtained from the reaction between the reactants comprising at least one $C_4 - C_{14}$ alkyl (meth)acrylate monomer and at least one $C_4 - C_{14}$ alkyl (meth)acrylate comonomer;
- (b) a polymeric stabilizer in an amount from about 0.01% to about 2% by weight with respect to the monomer(s), preferably from about 0.01% to about 1 % by weight with respect to the monomer(s);
- (c) a surfactant in an amount from about 0.1% to about 3% by weight with respect to the polymerizable monomer(s), preferably from about 1% to about 3% by weight with respect to the polymerizable monomer(s);

- (d) a modifier, which is either one of the chain transfer agents or a multifunctional monomer or the like, and is available in an amount needed to provide the microspheres with a gel phase amount in the range from about 60% to about 95% by weight with respect to the polymer, preferably in the range of from about 70% to about 85% by weight with respect to the polymer.
- (e) an initiator in an amount from about 0.1% to about 2% by weight with respect to the polymerizable monomer(s) starting material, preferably from about 0.1% to about 1% by weight with respect to the polymerizable monomer starting material.

The term “(meth)acrylate” used in this application refers to both acrylate and methacrylate.

A microstructure of the polymer is one of the most pertinent parameters regarding the applicative properties of the microsphere pressure sensitive adhesives. Polymerization processes, in which the acrylic monomers are used, are often subjected to formation of a gel phase during the polymerization process [see e.g. O. Elizalde, G. Arzamendi, J. R. Leiza, J. M. Asua, *Ind. Eng. Chem. Res.* **2004**, *43*, 7401]. Recent studies show that the acrylate chain-growth kinetics is complicated by the intermolecular and intramolecular (backbiting) transfer to polymer. By these events, mid-chain radical structures of lower reactivity are formed [see e.g. R. Jovanović, M. A. Dube, *Ind. Eng. Chem. Res.* **2005**, *44*, 6668 or e.g. I. Gonzales, J. R. Leiza, J. M. Asua, *Macromolecules* **2006**, *39*, 5015 or also e.g. M. Van der Brink, M. Pepers, A. M. Van Herk, A.L. German, *Polym. React. Eng.* **2001**, *9*(2), 101 or also e.g. O. Kammona, E. G. Chatzi, C. Kiparissides, *J. Macromol. Sci. R. M. C.* **1999**, *C39*(1), 57]. These mechanisms have a significant effect to the rate of the acrylate polymerization, even though temperatures are low. As the consequence of intermolecular chain transfer to polymer, long chain branches are formed. The gel is formed, when intermolecular chain transfer to polymer is followed by termination by combination. The relative amounts of the sol and gel polymer phase as well as molar mass distribution of the sol fraction and the crosslinking density of the gel fraction are among the most important factors that influence the adhesive properties. The amount of gel may also be influenced by promoting the formation of crosslinked polymer structure either by application of multifunctional monomers, or by addition of crosslinking agent. Beside the sol phase molecular weight, the crosslinking may be considered as one of the most important factors in respect of the adhesion properties of the adhesive, because the mobility of the polymer molecules is extensively reduced by the chemical bond in the polymer structure. As known, formation of crosslinked polymer structure affects the peel

strength of the adhesive, due to the effect on the wettability of the PSA to the substrate [see e.g. J. Asahara, N. Hori, A. Takemura, H. Ono, *J. Appl. Polym. Sci.* **2003**, 87, 1493]. On the other hand said gel phase also consists of a highly entangled and coiled polymer molecules, which result from the differing molecular weight of the base polymer. Through the introduction of multifunctional monomer in the monomer mixture, the crosslinking reactions are preferred, which results in formation of crosslinked polymer structures and hence the formation of gel phase. With a combination of both, chain transfer agent and multifunctional monomer we may vary the amount of formed gel phase and as well the molecular weight of the sol phase what exerts in the measured adhesion properties.

Chain transfer agent and multifunctional monomer are defined as modifiers. They are used to regulate the amount of each formed gel phase through a combination of polymer kinetic chain length reduction (chain transfer agent) and by induction of crosslinking reactions and formation of polymer network (multifunctional monomer). The amount of added modifier to the monomer mixture should be sufficient to provide a gel phase that is in the range of about 60% to about 95% by weight with respect to the polymer, preferably within the range of about 70% to about 90% by weight with respect to the polymer. The amount of said chain transfer agent needed for such gel phase is up to 0.2% by weight with respect to the polymerizable starting monomer(s) and for multifunctional monomer up to 0.2% by weight with respect to the polymerizable starting monomer(s).

Useful chain transfer agents for free radical polymerizations are e.g. halogen and sulfur containing organic compounds. Without any limitations, examples of such compounds may e.g. be carbon tetrabromide, carbon tetrachloride, dodecanethiol, iso-octylthioglycolate, butyl mercaptan, and tertiary-dodecyl mercaptan. Particularly useful chain transfer agents are long chain mercaptans, such as dodecanethiol. The amount of chain transfer agent suitable for the synthesis process with combination of multifunctional monomer for production of microsphere adhesive are calculated on a weight basis of the monomer(s) in the reaction mixture. The chain transfer agent is preferably added in amount up to 0.2% by weight with respect to the polymerizable monomer(s), more preferably in amount of about 0.05% to about 0.1% by weight with respect to the polymerizable monomer(s). These levels together with appropriate amount of multifunctional monomer are suitable for the synthesis of microsphere adhesive with gel phase amount ranging from about 60% to about 95% by weight with respect

to the polymer, more preferably in range of about 70% to about 85% by weight with respect to the polymer.

The addition of multifunctional monomer, which acts as a crosslinking agent, is necessary to obtain a desired amount of the insoluble gel phase. Examples of useful crosslinking agents include – without any limitations - multifunctional (meth)acrylate(s), e.g., butanediol diacrylate or hexanediol diacrylate, trimethylolpropane triacrylate, tripropyleneglycol dicrylate or other multifunctional crosslinkers such as divinylbenzene and mixtures thereof. When used in combination with chain transfer agent, crosslinker(s) is (are) added in amount of up to about 0.2% by weight with respect to the polymerizable monomer(s), preferably up to about 0.1% to about 0.15% by weight with respect to the polymerizable monomer(s), with the provision that the combination of crosslinking agent and modifier concentrations are chosen to obtain a microsphere with about 60% to about 95% of the insoluble gel phase, more preferably in range between about 70% and 85% by weight with respect to the polymer.

In present invention an one-step suspension polymerization synthesis is provided for preparing polymeric microspheres. The process comprises the following subsequent steps:

- a) stirring or agitating a reaction mixture comprising polymerizable monomer starting materials comprising:
 - (i.) at least one C₄-C₁₄ alkyl(meth)acrylate monomer and at least one C₄-C₁₄ alkyl(meth)acrylate comonomer;
 - (ii.) an initiator for the polymerizable monomer starting material in an amount between about 0.1% and about 2% by weight with respect to the polymerizable monomer(s) starting material;
 - (iii.) a polymeric stabilizer in an amount between about 0.01% and about 2% by weight respect to the polymerizable monomer(s) starting material, preferably about 0.01% to about 1% by weight respect to the polymerizable monomer(s) starting material;
 - (iv.) a surfactant in an amount of between about 0.1% to about 3% by weight respect to the polymerizable monomer(s) starting material, preferably about 1 to about 3% by weight respect to the polymerizable monomer(s) starting material;
 - (v.) a modifier, wherein the modifier can be one of the chain transfer agent and a multifunctional monomer or the like in an amount, which is needed to provide microspheres with a insoluble gel phase amount in the range of about 60% to

- about 95% by weight with respect to the polymer, preferably in the range of about 70% to about 85% by weight with respect to the polymer; and
- (vi.) water (with added viscosity modifier) intended to form an oil in water suspension.
- b) polymerizing the (meth)acrylate monomer(s) and comonomer(s), wherein the microspheres are provided.

The present invention provides a microsphere pressure sensitive adhesive comprising a high amount of insoluble gel fraction. The high amount of gel is needed to ensure appropriate cohesion of the microspheres. Due to high content of gel phase, the obtained microspheres retain the shape and are not deformed or ruptured when peeling the backing from the substrate. Regarding the adhesion properties of such adhesive, the following conclusions may be adopted. The microsphere adhesives synthesized by utilization of a chain transfer agent and multifunctional monomer (crosslinking agent) combination excel in a high degree of tackiness, while the peel values are reduced (approximately by a half) when compared with microsphere adhesives obtained by synthesis without adding modifiers. Consequently, such adhesives are suitable for coating various low grammage and easily deformable transparent papers. This kind of backing material can be easily deformed when peeling off the backing from the substrate, and they become useless for further usage.

The proposed invention deals with solid polymeric microspheres, which may be used in manufacturing of repositionable products such as labels, note papers, tapes and like. When using such a product it is normally desired that the backing material coated with microsphere adhesive may adhere to a wide variety of surfaces and can be completely removed from the surface without leaving any adhesive residue on the surface.

The microspheres may be applied to the backing material via transfer coating process, or directly to the backing. The term "solid" means that microspheres contain no interior voids or internal cavities having a diameter greater than 10% of the microsphere diameter although some number of the void microspheres may be detected in the overall product.

The basic monomers used for production of pressure sensitive adhesives in this invention are alkyl acrylate or (meth)acrylate monomers of which, the alkyl groups have from 4 to about 14

carbon atoms. Such acrylates are oleophilic, water emulsifiable, have restricted water solubility, and as homopolymers having glass transition temperatures below about -20°C . Quite non-limiting examples of such monomers may represent e.g. isooctyl acrylate, 4-methyl-2-pentyl acrylate, 2-methylbutyl acrylate, isoamyl acrylate, sec-butyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isodecyl methacrylate, isononyl acrylate, isodecyl acrylate, and the like, singly or in mixtures. Preferred acrylates include 2-ethylhexyl acrylate, isooctyl acrylate, isononyl acrylate, isoamyl acrylate, isodecyl acrylate, n-butyl acrylate, sec-butyl acrylate, and mixtures thereof.

Appropriate comonomers include nonpolar monomers. Non-limiting examples of such comonomers are ethyl acrylate, methyl acrylate, butyl acrylate, t-butyl acrylate, 4-methyl-2-pentyl acrylate, 2-methylbutyl acrylate, isoamyl acrylate, sec-butyl acrylate, n-isodecyl methacrylate, t-butyl methacrylate, isobornyl acrylate, octyl acrylamide, methylmethacrylate, isononyl acrylate, isodecyl acrylate, styrene and the like, as well as combinations thereof. The relative amount of added comonomer with respect to the weight of alkyl (meth)acrylate monomer and the comonomer may range from about 99/1 to about 50/50, preferably from about 85/15 to about 71/29.

Modifiers are used in order to regulate the adhesive properties of the adhesive. Various modifiers may be used for modification of microsphere adhesives, but in this invention a combination of two types of modifiers are used in the polymerization process. Such commonly used modifiers are e.g. chain transfer agents, which are added in order to control the molecular weight of the polymer and hence the subsequent adhesion properties. Due to the fact, that cohesion of the microspheres is a function of polymer molecules entanglements, the cohesion of the microspheres is substantially reduced by means of increasing chain transfer agent concentrations. Microspheres with low cohesion exhibit cohesion failure when peeling the backing and are therefore unacceptable for production of removable products.

Each degree of polymer entanglements in the synthesized microspheres can be evaluated by using a Soxhlet extraction process with tetrahydrofuran, by which adequate information about the amount of insoluble gel phase is retrieved. The cohesion of the microspheres can be improved by crosslinking reaction. By introduction of crosslinking agent in the monomer mixture, crosslinking occurs and a polymer networks within microspheres are formed. This process may serve to increase cohesion of the microspheres and for this very reason a

combination of chain transfer agent and crosslinking agent is reasonable. With chain transfer agent the sol and gel phase molecular weight may be determined, whereas by adding a crosslinking agent crosslinking reactions are induced, which then has an impact on the cohesion of microspheres.

Many sulfur and halogen-containing organic compounds may be used as chain transfer agents in free radical polymerizations. Examples of such agents, however without any limitations, are e.g. carbon tetrabromide, carbon tetrachloride, dodecanethiol, iso-octylthioglycolate, butyl mercaptan, and tertiary-dodecyl mercaptan. In this invention it is very useful to employ long chain mercaptans such as dodecanethiol collectively with other modifiers, especially crosslinking agent (multifunctional monomer). The amount of chain transfer agent suitable for these microsphere polymerizations is calculated on the basis of weight with respect to the content of monomer and comonomer. The chain transfer agent is preferably added in an amount up to about 0.2% by weight with respect to the polymerizable monomer(s), more preferably in the range of about 0.07% to about 0.1% by weight with respect to the polymerizable monomer(s). These ranges of chain transfer agent (including a predetermined amount of crosslinking multifunctional) are adequate to provide a gel phase amount in the microsphere in the range of about 70% to about 85% by weight with respect to the polymer.

The second added modifier (together with the chain transfer agent) is a crosslinking agent. Such agents basically multifunctional monomers having at least two polymerizable carbon-carbon double bonds. Examples of appropriate multifunctional monomers – without any limitations – include multifunctional (meth)acrylate (e.g., butanediol diacrylate, trimethylolpropane triacrylate, tripropyleneglycol dicrylate or hexanediol diacrylate) or other multifunctional crosslinkers such as divinylbenzene and mixtures thereof. Crosslinkers are added in amount up to 0.4% by weight with respect to the polymerizable monomer(s), preferably up to about 0.15% by weight with respect to the polymerizable monomer(s). The ratio between the chain transfer agent and the multifunctional monomer should normally lie in the range of about 0.2/1 to about 1/3, preferably in the range of about 1/1.2 to about 1/1.3, and most preferably about 1/1.25. Using the defined chain transfer agent and multifunctional monomer ratio, the microsphere adhesives with the amount of insoluble gel fraction in range of about 70% to about 85% by weight with respect to the polymer are synthesized.

Microspheres according to the invention are prepared by means of one-step suspension polymerization process, wherein such process is described in detail below. The suspension polymerization is a process, where the monomer(s) is/are dispersed within an usual aqueous continuous phase. A thickening agent is often added into said aqueous phase for the purposes of increasing viscosity of the continuous phase. The monomer(s) is/are usually water insoluble, and the polymerization occurs within the dispersed monomer droplets. In order to ensure a successful polymerization, oil soluble free radical initiators are added into the monomer mixture. Commonly used initiators are those, which are normally used in free radical polymerization processes and are either thermally or photo activated. Thermally-activated initiators are usually azo compounds, hydroperoxides, peroxides or the like. Photoinitiators include benzophenone, benzoin ethyl ether and 2,2-dimethoxy-2-phenyl acetophenone. The amount of initiator should be sufficient to obtain each desired monomer conversion in a predetermined time of polymerization and temperature range. The specific nature of the product, in which microsphere adhesives are used, dictate a high monomer conversion (more than 99.9%). The initiator is typically present in amount, which may range from about 0.1% to about 2% by weight with respect to the polymerizable monomer(s).

The initiation of the suspension polymerization may be accomplished either by heat or by radiation. Heat initiation is normally used for thermal decomposition of the initiator and by this process free radicals are produced which are needed for starting the polymerization reactions. The temperature, at which the thermal decomposition occurs, depends on each initiator as used. Polymerization of monomers is an exothermic reaction. The maximum temperature of the polymerization is selected by taking into account each intended use of the produced microspheres. In free radical polymerization processes the molecular weight of the polymer as well as the number average degree of polymerization is inversely proportional to the rate of polymerization at given monomer concentration and temperature. It also follows that the number average degree of polymerization varies inversely with the square root of the rate of initiation. Since the rate of initiation depends on temperature, the number average degree of polymerization and hence the molecular weight of the polymer are both increased, when the temperature is decreased. By regulating the temperature of the polymerization, kinetics of the polymerization may be altered and by that different microsphere with different adhesive properties can be synthesized.

A polymeric stabilizer is considered as an important parameter, when bearing in mind efficiency i.e. a yield of the suspension polymerization. The main function of the stabilizer is to stabilize the synthesized microsphere suspension and thus, to prevent agglomeration within a suspension polymerization process. The presence of the stabilizer also permits use of relatively small amounts of needed surfactants. The amount of polymeric stabilizer may range in an amount of about 0.01% to about 2% by weight with respect to the polymerizable monomer(s) starting material, preferably about 0.01% to about 1% by weight with respect to the polymerizable monomer(s) starting material.

The surfactants used for polymerization reactions are divided into three different types, namely into anionic, cationic and non-ionic surfactants. Usually a combination of an anionic and a non-ionic surfactant is used in a suspension polymerization process. Anionic surfactants may e.g. include –without any limitations - alkyl aryl sulfonates (e.g. sodium dodecyl benzene and sodium decylbenzene), sodium and ammonium lauryl sulfate. Such non-limiting examples of nonionic surfactants are ethoxylated oleoyl alcohol and polyoxyethylene octylphenyl ether. Another useful property of the surfactants is lowering of the surface tension of the suspension. To this aim it is also possible to coat the adhesive onto release liner (siliconized paper) without addition of any extra surface tension additives. A surfactant is typically added in the reaction mixture in an amount ranging between 1% and 6% by weight with respect to the polymerizable monomer(s) starting material, preferably no greater than 5% by weight with respect to the polymerizable monomer(s) starting material.

The dissolved oxygen in the reaction mixture may inhibit the polymerization reaction and for this very reason deoxygenation is often desirable. This may be accomplished by introduction of an inert gas (typically nitrogen) into the reaction vessel, which then expels the dissolved oxygen. Stirring of the reaction mixture as such is an important process parameter and depends on monomers and initiators. A pre-dispersion of monomer(s) (prior to the polymerization reaction) is commonly performed in order to obtain an average monomer droplet size between 1 and 200 μm , preferably between 10 and 50 μm . The average monomer droplet sizes depend on the type of each used stirrer, but also on stirring rate. The particles also tend to decrease in their diameter with increased time of stirring. It should also be mentioned, that nitrogen purging and stirring are maintained thorough the whole polymerization process.

The process of suspension polymerization as such includes different stages. At the beginning, continuous water phase with the dissolved surfactants is added into reaction vessel. Nitrogen purging is started. In the next step monomers with dissolved initiator and mixed with modifiers are added to the reaction vessel. After a predetermined time of mixing, heating of the polymerization mixture is started. The initiation starts the polymerization process and because of the exothermic reaction, the reaction vessel is cooled. After the exothermic polymerization peak, the reaction mixture is further heated in order to achieve almost 100% monomer conversion, upon which the suspension is then cooled to room temperature.

The produced microsphere suspension may contain 20 to 50% by weight of non volatile solids. Depending from the stability of the suspension, such dispersion of solid microspheres may be separated into two phases. One phase is microsphere free (primarily aqueous phase) and the other one is a microsphere rich phase (although it is still an aqueous suspension). The microspheres suspension presented in this invention is considered as a very stable one, since no phase separation can be observed even after a prolonged standing. The suspension of microspheres can be coated immediately after the polymerization process, since the used surfactant also improves wettability by lowering the surface tension of the adhesive suspension. It can also be diluted with deionised water although a certain amount of surfactants must be added in order to prevent coagulation of the suspension.

Such obtained adhesive can be combined with various rheology modifiers or latex adhesives. Latex adhesives (adhesives produced via emulsion polymerization) are usually added to improve anchorage of the adhesive to the backing material. The adhesive properties may be altered by addition of various tackifiers (hydrogenated rosin esters) and/or plasticizers but optimal removability of the adhesive is achieved without addition of any tackifiers or/and plasticizers. They usually have a great impact on removability due to their unsaturated nature (crosslinking upon exposure to direct sunlight) despite the fact, that various types of tackifiers are considered as completely hydrogenated.

Suspensions of microspheres are normally coated onto release liner using conventional coating methods, dried and then transferred to the backing material. However, adding of a viscosity modifier for the purposes of increasing of suspension viscosity may be required in certain coating systems (e.g., gravure coating system). Normally dried adhesive coating weight ranges between 5 and 12 g/m². Appropriate backing materials, which may be coated

with the presented microsphere suspension, are – without any limitations – e.g. paper, plastic film (polyethylene, polypropylene, polyvinylchloride), cellulose acetate, ethyl cellulose, synthetic or natural materials (woven or nonwoven), metallized polymeric film, metallic film or the like. Due to their specific adhesive properties, these are especially useful for the purposes of coating of various low grammage papers and materials. The structure of such microsphere adhesive coating provides application to clean, dry and smooth or slightly rough surfaces, long term removability and repositionability as long as the adhesive does not pick up too much dust. Minimal application temperature is -5°C and the service temperature should normally lie within the range between -5°C and 50°C at approx. 55% relative humidity.

The aspects of the present invention will be now illustrated on the basis of several examples, which should however not be understood as a limitation of the scope of the invention anyway.

EXAMPLES

Test methods

Determination of gel phase

The gel fraction is defined as the ratio between the weight of a dry extracted gel and the weight of the original sample. The amount of such formed gel is determined by a Soxhlet extraction with tetrahydrofuran under reflux during 24 h. [see e.g. F. Alarcia, J. C. de la Cal, J. M. Asua, *Chem. Eng. J.* **2006**, 122(3), 117]. The adhesive suspension (approximately 3g) is poured into a filter cartridge (weight W_1) and dried in a vacuum oven at 95°C for 2 h. Each sample with dried adhesive (weight W_2) is then placed into the main chamber of the Soxhlet extractor and after 24 h performing of the extraction process (by using 200g of tetrahydrofuran) the filter is removed and dried in the first step within a vacuum oven at the room temperature for 24 h and in the second step at 100°C for 1h. The cartridge with gel phase is then weighed again (weight W_3). Two samples per adhesive are used for determination of gel phase. The amount of gel (which corresponds to the non-soluble portion) is calculated using following equation:

$$\text{gel content} = \frac{W_3 - W_1}{W_2 - W_1} \quad (1)$$

The measured amount of the gel phase corresponds to both crosslinked polymer and entangled high molecular weight polymer chains.

The sol phase was further determined by measuring of polymer relative molecular weight. The number average molecular weight ($\overline{M}_n$) of the sol phase is determined by gel permeation chromatography (GPC) using polystyrene standards. The samples were dissolved in the THF (1 % w/v solution), which was also used as a carrier solvent at the rate of 1 ml min⁻¹. To this aim, the PLgel mixed-bed 5 μ m (300 x 7,5 mm) column and Perkin Elmer series 200 pump in combination with Waters Associated Differential Refractometer were used.

Preparation of samples

Each of the synthesized adhesives suspensions was coated by means of transfer coating process on the pilot coater using a Mayer bar. As a release liner, a siliconized glassine paper with silicone coating weight of 1.1 g/m² was used. Coating weight of the dry adhesive was approximately 13 g/m², and was regulated by means of the pressure of said Mayer bar and also the speed of the release liner. After the coating, the adhesive was dried by using the infrared (IR) drying technique. The drying oven was namely equipped with two medium wave IR heating sources (3 kW power output each). The speed of the belt was controlled in order to achieve the desired moisture ratio in the adhesive coating. After drying the adhesive was laminated with the paper substrate.

Peel adhesion

Peel adhesion is defined as a force, which is required to remove a pressure sensitive coated material, which has been applied to a standard test plate under certain conditions from the plate at certain angle and speed. The test plates usually consist of glass or materials on the basis of polyethylene or metals. Adhesion is measured 20 minutes and 24 hours after application, the latter being considered as the ultimate adhesion.

Such used sample strips were 25 mm wide and at least 175 mm long. A strip of coated material was applied onto a glass plate, by which a standard Finat roller has been used for applying the strip onto the glass plate. The speed of roller should be approximately 10 mm per second. The peel adhesion is measured 20 minutes after the application. The plate is fixed in a tensile tester machine at 180° angle. The free end of the coated strip is clamped to the

adhesion tester load cell and the speed of moving the test plate from the loading cell is set at the constant rate of 300 mm/min. Upon that the test is carried out, wherein at least five readings at 10 mm intervals are recorded. The peel adhesion is expressed as the average result concerning six strips per sample, in units Newtons per 25 mm width. The test was carried out according to Finat test method (FTM 1) [see e.g. "*Finat Technical Handbook*", 6th ed., FINAT, The Hague, 2001].

Tack

The tack was measured according to ASTM D2979-95 test method using a Polyken Probe Tack Tester. This test method is applicable to those adhesives which form a bond of measurable strength rapidly upon contact with another surface and which can be removed from that surface cleanly, that is, without leaving of any eye-visible residue. For such adhesives, said tack may be measured as the force, which is required to separate an adhesive and the adherend at the interface shortly after they have been brought into contact due to a pre-defined load during a pre-determined duration as well as at a pre-determined temperature. The surface of the probe comes into contact with the adhesive, dwells for one second and is pulled away. The tack is then expressed as the average of ten measurements in units of gram.

Definitions

$\overline{M}_n$	number molecular weight distribution
T_g	glass transition temperature

Example 1

A 500 ml, five necked reactor equipped with a thermometer, mechanical stirrer, nitrogen inlet, condenser and ReactIR analyzing system probe was charged with a 244g of deionzed water, 8.4g of a 1.6% solid solution of Carbopol EDT 2691 (trade name for 100% solid, hydrophobically-modified, crosslinked polyacrylate powder commercially available from B.F. Goodrich Company) and was neutralized to a pH of 7.0 with ammonium hydroxide. To the prepared continuous phase solution then 4.0g of Hydropalat 88 solution (trade name for 50% solid solution of modified ester of sulfocarboxylic acid commercially available from Cognis

Company) and 3.2g of a 38% solid solution of Rhodasurf ON-870 (trade name for 100% solid, ethoxylated oleyl alcohol commercially available from Rhodia Inc.) was added. In such a monomer mixture then 120g of 2-ethylhexyl acrylate and 20g of ethyl acrylate (both are commercially available from BASF Company), and 0.56g of Luperox A75 (trade name for dibenzoylperoxide, 73-77% water damped powder, commercially available from Arkema Inc.) were added.

The used stirrer in the performed experiments was the so-called Rushton turbine and the stirring speed was set to 850 revolutions per minute. Nitrogen purging was maintained thorough the entire polymerization process. In the first stage the reaction mixture was mixed for 10 minutes, upon which the reaction mixture was heated to 60°C. During the exothermic reaction, the reaction mixture was cooled, so that the maximum peak temperature has never exceed 90°C. After the exothermic part of the polymerization reaction the batch was maintained at 75°C for 4 hours. Thereupon the suspension was cooled down to the room temperature.

In the synthesized adhesive dispersion 7.6g of a 28% solid solution of Acrysol ASE-60 (trade name for 28% solid solution of anionic thickener and suspension stabilizer – crosslinked acrylic emulsion copolymer commercially available from Room and Hass Company) and was neutralized to a pH of 7.0 by means of the ammonium hydroxide. The adhesive was then prepared for coating application as described above.

Examples 2 – 6

Several experiments were performed in accordance with the process, which is described in the Example 1, in which various amounts of 1-dodecanthiol (98% chain transfer agent commercially available from Aldrich) and butandiol diacrylate (multifunctional crosslinking monomer commercially available from BASF) were added. Relevant formulations concerning these experiments 1 to 6 i.e. Examples 1 to 6, incl. corresponding adhesive properties (T_g , particle size, gel phase and molecular weight) and adhesion properties are shown in Table 1 and 2.

Table 1

Example	1-dodecathiol (wt. %)	butandiol diacrylate (wt. %)	T _g (°C)	average particle size (μm)
1	0	0	-55.23	22.3
2	0.05	0.05	-57.39	21.2
3	0.05	0.01	-58.71	24.5
4	0.05	0.1	-56.53	25.3
5	0.07	0.09	-58.52	22.3
6	0.1	0.125	-57.62	23.0

Table 2

Example	gel phase amount (wt. %)	sol phase relative $\overline{M}_n$	peel strenght (N/25mm)	tack (g)
1	83.6	100448	2.97	149
2	71.6	85476	1.64	162
3	25.9	33739	1.27	155
4	79.1	13808	1.15	157
5	74.0	14810	0.99	165
6	73.6	16396	1.02	179

Various modifications and alternations of this invention will become apparent to those skilled in the art without departing from the scope and principles of this invention, and it should be understood that this invention should not be unduly limited to the illustrative embodiments set forth herein above. All publications and patents are incorporated herein by reference to the same extent as if each individual publication or patent was specifically and individually indicated to be incorporated by reference.

PATENT CLAIMS

1. A suspension based adhesive comprising:

- a plurality of polymeric, elastomeric microspheres, wherein the microspheres are the reaction product of polymerizable starting materials comprising at least one C₄-C₁₄ alky (meth)acrylate monomer and at least one C₄-C₁₄ alky (meth)acrylate comonomer;
- an initiator for the polymerizable monomer starting material in amount between 0.1 to 2% by weight with respect to the polymerizable monomer(s) starting material;
- a polymeric stabilizer in amount between about 0.01% and about 2% by weight with respect to the polymerizable monomer(s) starting material;
- a combination of anionic and non-ionic surfactants in amount between 0.1% and 3% by weight with respect to the polymerizable monomer(s) starting material, preferably from about 1% to about 3% by weight with respect to the polymerizable monomer(s) starting material; and
- a modifier, preferably one of the chain transfer agents or a multifunctional monomer or the like, in such amount, which is needed to provide the microspheres with a insoluble gel phase amount within the range between 60% and 95% by weight with respect to the polymer, preferably in the range between 70% and 85% by weight with respect to the polymer.

2. Adhesive according to Claim 1, wherein the stabilizer is present in amount of about 0.01% to about 1% by weight with respect to the polymerizable monomer(s) starting material.

3. Adhesive according to Claim 1, wherein the combination for surfactants are present in the amount of about 0.1% to about 3% by weight with respect to the polymerizable monomer(s) starting material, preferably about 1% to about 3% by weight with respect to the polymerizable monomer(s) starting material.

4. Adhesive according to Claim 1, wherein the chain transfer agent is used in combination with a multifunctional monomer.

5. Adhesive according to Claim 4, wherein said chain transfer agent is selected from the group consisting of carbon tetrabromide, carbon tetrachloride, dodecanethiol, iso-octylthioglycolate, butyl mercaptan, and tertiary-dodecyl mercaptan.
6. Adhesive according to Claim 4 and/or 5, wherein said chain transfer agent is present in amount up to 0.2% by weight with respect to the polymerizable monomer(s) starting material.
7. Adhesive according to Claim 1 wherein the multifunctional monomer is used in combination with a chain transfer agent.
8. Adhesive according to Claim 7, wherein said multifunctional monomer is selected from group consisting of multifunctional (meth)acrylate (e.g., butanediol diacrylate, trimethylolpropane triacrylate, tripropyleneglycol dicrylate or hexanediol diacrylate) or other multifunctional crosslinkers such as divinylbenzene and mixtures thereof.
9. Adhesive according to Claim 7 and/or 8, wherein said multifunctional monomer(s) is (are) present in an amount up to 0.4% by weight with respect to the polymerizable monomer(s) starting material, preferably up to about 0.15% by weight with respect to the polymerizable monomer(s) starting material.
10. Adhesive according to Claim 1 wherein the ratio between the chain transfer agent and the multifunctional monomer is chosen up to 1/3, preferably within the range of 1/1.2 to 1/1.3, and most preferably 1/1.25.
11. One-step suspension polymerization process for preparing microsphere adhesive according to Claim 1, comprising the steps of:
 - i) stirring of a mixture comprising polymerizable monomer starting materials, namely
 - at least one C₄-C₁₄ alkyl(meth)acrylate monomer and at least one C₄-C₁₄ alkyl(meth)acrylate comonomer;
 - an initiator for the polymerizable monomer starting material in an amount between 0.1% and 2% by weight with respect to the polymerizable monomers;

- a polymeric stabilizer in amount between about 0.01% and about 2% by weight with respect to the polymerizable monomer(s) starting material, preferably from about 0.01% to about 1% by weight with respect to the polymerizable monomer(s) starting material;
- a surfactant in amount between 0.1% and 3% by weight with respect to the polymerizable monomer(s) starting material, preferably from about 1% to about 3% by weight with respect to the polymerizable monomer(s) starting material;
- a modifier, preferably one of the chain transfer agents and a multifunctional monomer or the like, which is available in a sufficient amount to provide microspheres with a insoluble gel phase amount in the range between 60% and 95% by weight with respect to the polymer, preferably in the range between 70% and 85% by weight with respect to the polymer; and
- a water (with added viscosity modifier) to form a oil in water suspension; as well as

ii) polymerizing the (meth)acrylate monomer(s) and comonomer(s).

12. Process according to Claim 11, wherein the chain transfer agent is used in combination with a multifunctional monomer(s).

13. Process according to Claim 11, wherein the chain transfer agent is selected from the group consisting of carbon tetrabromide, carbon tetrachloride, dodecanethiol, iso-octylthioglycolate, butyl mercaptan, and tertiary-dodecyl mercaptan and is present in an amount up to 0.2% by weight with respect to the polymerizable monomer(s) starting material.

14. Process according to Claim 11 wherein the multifunctional monomer(s) is (are) selected from group consisting of multifunctional (meth)acrylate (e.g., butanediol diacrylate, trimethylolpropane triacrylate, tripropyleneglycol dicrylate or hexanediol diacrylate) or other multifunctional crosslinkers such as divinylbenzene and mixtures thereof.

15. Process according to Claim 14, wherein said multifunctional monomer(s) is (are) present in an amount up to 0.4% by weight with respect to the polymerizable monomer(s) starting material, preferably up to about 0.15% by weight with respect to the polymerizable monomer(s) starting material.

16. An adhesive article comprising a backing and a coating the microsphere adhesive comprising the claim 1 coated on at least a portion of at least on surface of the backing.

17. Use of the adhesive according to Claim s 1 to 10 for coating of articles consisting of materials, selected from the group, which includes paper, plastic films on the basis of polyethylene, polypropylene or polyvinylchloride, cellulose acetate, ethyl cellulose, synthetic or natural woven or nonwoven materials as well as metallized polymeric layers and metallic layers.

INTERNATIONAL SEARCH REPORT

International application No

PCT/SI2007/000034

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08F220/18 C09J133/00

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)

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/36041 A (3M INNOVATIVE PROPERTIES CO [US]) 22 June 2000 (2000-06-22) page 3, line 22 - line 30 page 4, line 21 - line 24 page 5, line 1 - line 5 page 8, line 5 page 9, line 13 page 9, line 28 page 10, line 17 - line 229 page 11, line 28 -----	1-17

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/SI2007/000034

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