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DESCRIPTION

[0001] The present invention relates to a vinyl ester latex adhesive composition with improved stability and tensile adhesion at elevated temperatures, produced by the delayed addition of silane compounds. The present invention also relates to a process for producing such a vinyl ester latex adhesive and it's use as a D3 type wood adhesive in the furniture industry.

[0002] Adhesives are used in smaller amounts to assemble building materials in residential and industrial construction. However, significant amounts are used in non-structural applications such as doors, windows and frames. Adhesives can excellently transfer and radiate stresses, thereby increasing the strength and stiffness of the materials. Effective transfer of stress from one substance to another depends on the strength of the links between the substances.

[0003] Wood chemically can be considered to be a blend of primarily cellulose and lignin, which are the most abundant organic substances in the world. Cellulose is a polysaccaride and lignin is an amorphous polyphenolic substance which does not have a regular pattern in its structure. Lignin can be described as a mixture of heterogeneous substances and it improves the properties of wood such as stiffness and strength. Besides these primary substances other components are also present and each of these contribute to fiber properties which effect the properties of final wood based material.

[0004] Mechanical connections is probably the primary mechanism by which adhesives adhere to porous structures such as wood. The most durable structural bonds to wood are believed to develop not only when an adhesive penetrates deeply into the spaces of wood surface, but also when an adhesive diffuses into cell walls to make molecular level contact with the cellulosic molecules which are one of the primary substances in wooden materials. If the adhesive molecules penetrate deeply enough into cellulosic molecules and react with that substance, the strength of the bond can be expected to exceed the strength of the wood molecules itself. Functional monomers are used in order to increase the bonding capability of the adhesives with wood in such a way that the adhesive molecules penetrate deeply enough into the cellulosic molecules. One of these functional monomers are silane coupling agents that provide advantageous features, such as providing crosslinking with the substance, adhesive bonding, maximizing composite strength, increasing mechanical properties. Reactive groups of silane modified adhesives react with the hydroxyl groups of cellulose which make the penetration of adhesive molecules into wood molecules easier and this is believed to contribute to the bonding capability of adhesives. However, due to the high condensation activity of the silanol groups, these substances adversely effect the stability of the product.

[0005] In all applications of adhesives, improving the performance of a binder is of extensive interest. However most of the time a change in order to improve one property, results with an adverse effect in other properties of the adhesive composition. Therefore it is also very important not to adversely effect other properties while improving the desired property. As

mentioned before, this is a problem also for wood adhesives when silane is used for improving the performance of the adhesive because on the other hand silane decreases the stability of the product. Given this problem, it is an object of the present invention to provide a silane modified D3 type wood adhesive with improved stability.

[0006] When variety of adhesives, types of materials, thermal and humidity effects are considered, different methods have been developed in order to evaluate the quality of these products and wood adhesives are classified based on the results of these tests. EN 204 is the European standard for the classification of thermoplastic wood adhesives for non-structural applications. This standard gives a common classification with respect to the durability classes for wood adhesives so that specific properties are guaranteed by the adhesive manufacturer based on the type of wood adhesive. The durability classes are determined to be D1, D2, D3 and D4 by EN 204, each class explained as below:

D1: Interior, in which the moisture content of the wood does not exceed 15 %

D2: Interior with occasional short-term exposure to running or condensed water and/or to occasional high humidity provided the moisture content of the wood does not exceed 18%

D3: Interior with frequent short-term exposure to running or condensed water and/or to heavy exposure to high humidity. Exterior not exposed to weather.

D4: Interior with frequent long-term exposure to running or condensed water. Exterior exposed to weather but with protection by an adequate surface coating.

[0007] Based on EN 204, D3 type wood adhesives are for non-structural applications. These are suitable for interior use in which they are exposed to running or condensed water in a frequent short-term basis and/or heavily exposed to high humidity.

[0008] One of the application areas of D3 type wood adhesives is the lap joints which actually are simplest options for joining pieces to make a bigger structure. A notch cut out of one board and a notch cut out from another are overlapped and sticked together by applying a wood adhesive. For the D3 type wood adhesives of EN 204 Classification, tensile adhesion of lap joints at elevated temperatures is a desired property. However, in order to achieve this object and reach the desired tensile adhesion at high temperatures, a variety of functional monomers are added, which in return increase the cost of the product. As mentioned in EP 0035332 typical unsaturated organo-silicon monomers y-methacryloxypropyl trimethoxy silane, vinyl triethoxy silane and vinyl trimethoxy silane are rather expensive and it is disclosed that it's possible in emulsion polymerization to use only very low quantities, (from 0.1-1.0% by weight of unsaturated organo-silicon monomers), and be effective in promoting water resistant adhesion.

[0009] In the prior art in general, silanes are often used as functional monomers which are added as adhesion promoters in order to reach the desired tensile adhesion. However, silanes in return decrease the stability of the product as also mentioned in US 2011/201727 B2 which

discloses silane modified additives in order to solve the storage stability of compositions both in aqueous and solid form even at high silane contents. It is stated that "In aqueous polymer compositions, organosilicon compounds tend to separate from the aqueous phase and undergo an uncontrolled self-condensation so that an increase in the viscosity or even gelling occur. However, even if polymer compositions containing organosilicon compounds are present in solid form, an uncontrolled self-condensation of the organosilicon compounds occurs in the presence of residual moisture or because of atmospheric humidity, so that corresponding polymer compositions can no longer be completely taken up in water. The problems described occur in particular in polymer compositions having high contents of organosilicon compounds." It is disclosed that phase separation or an uncontrolled condensation of the silane is absent owing to the presence of the amount of water soluble polymers and as a result of the mixing. So the presence of water soluble polymers and mixing are addressed as the solutions to the stability problem.

[0010] EP 0943634A1 discloses a silicone resin-containing emulsion composition obtained by emulsion polymerization of a mixture containing (A) a silanol group-bearing silicone resin and (B) a radical-polymerizable vinyl monomer. It is mentioned that silicone resins resulting from hydrolytic condensation of silane compounds are advantageous as a coating since they are able to form films having a high hardness and satisfactory weather resistance, water resistance, heat resistance and water repellency.The problem with silicone resin containing emulsion compositions is also mentioned, as the drawbacks of poor film-forming ability, alkali resistance, flexibility, and shelf stability due to the high condensation activity of silanol groups. However no intention to solve this by the delayed addition of silane compounds is disclosed.

[0011] WO 2013/057214 A1 discloses formulation of a non-structural thermoplastic wood adhesive with water resistance greater than 3 N/mm2, heat resistance greater than 7 N/mm2, creep resistance more than 21 days and shelf life more than 6 months. However the formulation of the wood adhesive includes a polyvinyl alcohol with a high degree of hydrolysis, prefarably modified with ethylene.These specific type of ethylene modified vinyl alcohol polymers increase the cost of the formulation but besides the cost, using an ethylene modified type of polyvinyl alcohol different than commonly used types bears practical problems such as storage in industrial scale productions: If a special type of polyvinyl alcohol is required in the production then there should be a dedicated storage tank for this type of polyvinyl alcohol however if the production capacity does not justify investing for a storage tank then it will be stored in barrels or IBCs and will be fed into the reactor by manual operations. This will bring safety, health and envrionment risks into the process, besides the quality risks of manual operations.

[0012] US Patent 3,932,335 discloses adhesive compositions based on vinyl ester polymer dispersions. For providing the desired shelf life stability of the product, water-miscible alcohol having 1-3 Carbon atoms selected from the group consisting of methanol, ethylene glycol, propylene glycol, ethanol, isopropanol and n-propanol. Methanol or ethylene glycol were added optionally as a blend with glyoxal, to the emulsion polymer. The stability that was achieved with these post additions was not enough as the results with very high viscosities in

ageing tests show.

[0013] EP 0561221 A1 discloses PvOH-stabilized aqueous emulsions containing a vinyl acetate-N-methylolacrylamide copolymer and tetramethylol glycoluril (TMGU) demonstrating an improved combination properties as an RF curable (bonding with radio frequency heating) Type-1 wood adhesive. It is mentioned that the Vac/NMA copolymer emulsions have low grit values and excellent viscosity stability and good catalyzed pot life. However, the stability of these products are again not adequate for all wood applications. When TMGU is used compatible with the teaching of the present invention a high amount of viscosity change generated during the ageing tests indicate the stability to be not as good.

[0014] EP 0686682 B1 relates to aqueous dispersion adhesives having pH value of from 2 to 6 that comprise homo- or copolymeric polyvinyl esters, polymeric protective colloids, water-soluble compounds which can be complexed with polymeric protective colloids, and at least partially masked polyaldehydes having at least 3 C atoms. However the pot life of these polymers are as short as to be mentioned in hours as disclosed in the examples.

[0015] EP 0 035 332 B1 discloses an aqueous emulsion polymer composition for use as a ceramic tile adhesive wherein the composition is prepared in the presence of at least one unsaturated organosilicon monomer such as y-methacryloxypropyl trimethoxy silane, vinyl triethoxy silane and vinyl trimethoxy silane. In example 1 of the disclosure 2 different emulsions are prepared and y-methacryloxypropyl trimethoxy silane is included in the 2nd emulsion feed. So the silane compound has been added into the polymerization medium after the addition of first main monomer emulsion comprising styrene, ethyl acrylate and acrylic acid is completed. However the effect of delayed addition is not mentioned and it is not clear if the solution is based on delayed addition of silane compound. Additionally the silane compound is present in an emulsion where vinyl acetate is not present and the resulting adhesive is used as a tile adhesive which is a different application.

[0016] EP 0 640 630 B1 (DE 4 329 090) discloses silicon modified aqueous plastic dispersions for the production of adhesive compositions with improved wet adhesion.The silicon modified plastic dispersions are prepared by a process in which the addition of the vinyl silane (suitable silanes are mentioned as vinyltrimethoxysilane, vinyltriethoxysilane, vinyltriacetoxysilane, vinyl tert-butoxydiethoxysilane, methylvinyldiethoxysilane) takes place during the entire feed time of the other monomers or in the initial phase of the polymerization between 0-40 % conversion of the total monomers. It is mentioned that if an influence on the particle formation is to be excluded, the addition of silane dissolved in a part of the monomers, should be made in 60-180 minutes, after 10 to 20 minutes of the start of polymerization. The timing of silane addition is important in this disclosure, too. However it is either fed in parallel with the entire monomer feed or only in the initial phase of the polymerization.

[0017] WO 2013/057214 A1 discloses a wood adhesive resistant to humidity produced by polymerization of vinyl acetate in the presence of a polymer of polyvinylalcohol (PVOH), adding a glutaldehyde based cross-linker and AlCl3 however does not use any silane.

[0018] US 2014/350172 A1 discloses vinyl ester-ethylene/acrylic multistage emulsions for use in paints and plasters, comprising vinyl silane which is added before all or most of the vinyl acetate has been added.

[0019] The object of the present invention is, to increase the stability of the wood adhesive product even though it contains a silane monomer by arranging the addition timing of said silane monomer so that it is added to the reaction medium, only after a certain amount of the monomer has already been fed into the reactor.

[0020] Said object is achieved by a vinyl ester latex adhesive composition comprising, based on the total amount of monomers,

1. a. from 50 to 99% by weight of vinyl esters of C2-C12-carboxylic acids and from 0,05 to 5% by weight of vinyl silanes capable of copolymerizing with the said vinyl esters, added after at least 50% of the vinyl esters of C2-C12-carboxylic acids has been fed into the reaction medium,
2. b. from 0,5% to 15% by weight of polyvinyl alcohol with a degree of hydrolysis of between 90% and 99%,
3. c. from 0,25% to 10% by weight of polyvinyl alcohol with a degree of hydrolysis of between 70 and 90%,
4. d. from 0,05% to 5% by weight of at least one crosslinking agent,
5. e. from 1% to 20% by weight of at least one Lewis acid metal salt,
6. f. optionally from 0,15% to 15% of a coalescing agent to reach the desired minimum film formation temperature. The amount of coalescing agent is determined based on the application, in order to adjust the minimum film formation temperature to the desired level for the intended application.

[0021] It has been surprisingly found out that, when polymerizable silane is added only through the end of the monomer feed, at least after 50%, preferably %70 or most preferably after 90% by weight of the total amount of vinyl esters of C2-C12 carboxylic acids has been fed into the reaction medium, the shelf life stability of the polymer is improved while also maintaining the heat resistance.

[0022] The resultant latex adhesive was tested according to EN 205 and found suitable to be classified as a D3 type wood adhesive according to EN 204. The resultant polymer was also tested according to EN-14257 (WATT 91, determination of tensile strength of lap joints at elevated temperature) and the tensile adhesion at elevated temperature was found to be above 7 N/mm2.

[0023] In a preferred embodiment of the present invention, vinyl esters of C2-C12-carboxylic acids are vinyl acetate, vinyl propionate, vinyl butyrate, vinyl laurate, vinyl 2-ethylhexanoate, 1-methylvinyl acetate and vinyl pivalate; particular preference is given to vinyl acetate.

[0024] In a further preferred embodiment of the present invention, vinyl silanes are added only after 70%, more preferably after 85% and most preferably after 90% addition of the vinyl esters of C2-C12-carboxylic acids to the reaction medium have already been completed. The vinyl silane feed continues until the end of vinyl esters of C2-C12 carboxylic acids addition. Ethylenically unsaturated silane compounds that can be used are vinyl tri(alkoxy)silanes, where the alkoxy groups may be methoxy, ethoxy, methoxyethylene, ethoxyethylene. Prefferred ethylenically unsaturated silane compound is vinyl trimethoxy silane.

[0025] In a different embodiment of the present invention vinyl silane addition is made by a so called shot addition in less than 5 minutes, where it is added at least after 50%, preferably %70 or more preferably after 90% by weight of the total amount of vinyl esters of C2-C12 carboxylic acids has been fed into the reaction medium.

[0026] Most of the time the reaction is not completely over right after the monomer addition. Therefore after monomer addition is completed -in the cooking stage of the process-the reactor contents are kept close to the reaction temperature for a period of time in order to let the unreacted monomers to polymerize by themselves. In a further embodiment of the present invention vinyl silane addition continues after the end of vinyl esters of C2-C12 carboxylic acids addition, in a part or throughout the entire period of the cooking stage.

[0027] After the cooking stage some unreacted monomers are still present. In order to prevent the final product to have a free monomer content, monomer reduction should be carried out so that all or most of the unreacted monomers left after the cooking stage are polymerized. Different methods can be used for monomer reduction. According to the present invention, in different embodiments the vinyl silanes may be added with different timings after at least 50% by weight of the total amount of vinyl esters of C2-C12 carboxylic acids has been fed into the reaction medium, but it cannot be added before 50%. Besides, in different embodiments of the present invention the vinyl silane addition may continue after the vinyl esters of C2-C12 carboxylic acids addition is completed, but it cannot continue when the monomer reduction stage is reached. Similarly the vinyl silane addition cannot be made after, neither the start nor the end of the monomer reduction stage.

[0028] As dispersants, it is possible to use all kinds of emulsifiers employed in emulsion polymerization. To stabilize the dispersion, it is possible to use either protective colloids or emulsifiers or combinations of both of these two substances. Suitable protective colloids are, polyvinyl alcohols, polyethylene glycol, polyvinylpyrrolidone, celluloses such as hydroxyethyl cellulose, hydroxypropylcellulose and carboxymethyl cellulose, starches and dextrins, cyclodextrins, homopolymers or copolymers of acrylamidopropanesulfonic acid.

[0029] Polyvinyl alcohols are obtained with the hydrolysis reaction of vinyl acetate monomer and are classified according to the hydrolysis level and their viscosities. Only one type of polyvinyl alcohol with a hydrolysis degree of between 70% and 99% may be used, in an amount of from 0,75% to 25% by weight based on the total amount of monomers. However it is

preferred to use a combination of at least 2 types of polyvinyl alcohols with differing hydrolysis degrees. When using a blend of 2 different types of polyvinyl alcohols the amount and hydrolysis degrees should be selected from the ranges specified as below:
Polyvinyl alcohols with the hydrolysis degree of 90% to 99% are used in an amount of from 0,5% to 15%, more preferably from 3% to 14% and the most preferably from 5% to 10% based on the total monomers.

[0030] Polyvinyl alcohols with the hydrolysis level of 70% to 89% are used in an amount of from 0,25% to 10%, more preferably from 0,5% to 5% and the most preferably from 0,6% to 3% based on the total monomers.

[0031] In a preferred embodiment of the present invention the ratio of the amount of PVOH with the higher degree of hydrolysis to the lower degree of hydrolysis is 10 to 15.

[0032] The selected PVOH compounds can be mixed before being transferred into the reaction medium or can be mixed in the reaction medium after being fed one after the other, in order to make the blend.

[0033] Suitable emulsifiers can be all commercial ionic and non-ionic emulsifiers. Particularly, preferred examples are; ethoxylated fatty alcohols and also alkali metal and ammonium salts of long-chain alkyl sulfates (C8-C12-alkyl radical), of sulfuric monoesters of ethoxylated alkanols and ethoxylated alkylphenols of alkyl acids and of alkylaryl sulfonic acids.

[0034] Acidic metal salt compounds or salts or acids of oxo anions are used so that they can form complexes or coordinate bonds with the protective colloids namely polyvinyl alcohol compounds. These are selected from the group of compounds comprising aluminium chloride, aluminium nitrate, titanium sulfate, zirconium oxychloride, phosphoric acid and boric acid. These acidic salts containing polyvalent cation complexable by polyvinyl alcohol are added at the end of the polymerization reaction.

[0035] Preferably $AlCl_3.6H_2O$ can be used as a Lewis acid metal salt from 1% to 20% based on the total amount of monomers.

[0036] Monomer units having a crosslinking reaction are preferably used in an amount of from 0,001% to 10% by weight, more preferably from 0,05% to 5% by weight and most preferably from 0,1% to 3% by weight based on the total amount of monomers. Examples are N-metylol acrylamide, N-methylolmethacrylamide, N-(alkoxymethyl)acrylamides or N-(alkoxymethyl)methacrylamides containing a C1-C6-alkyl radical, e.g. N-isobuthoxymethyl)acrylamide (IBMA), N-(isobutoxymethyl)methacrylamide (IBMMA), N-(n-butoxymethyl)acrylamide (NBMA), N-(n-butoxymethyl)methacrylamide (NBMMA); multiple ethylenically unsaturated comonomers such as ethylene glycol diacrylate, 1,3- butylene glycol diacrylate, 1,4-butylene glycol diacrylate, propylene glycol diacrylate, divinyl adipate, divinyl benzene, vinyl methacrylate, vinyl acrylate, allyl methacrylate, allyl acrylate, diallyl maleate, diallyl phthalate, diallyl fumarate, methylenebisacrylamide, cyclopentadienyl acrylate or triallyl

cyanurate. Particular preference is given to n-methylol acrylamide.

[0037] The polymerization reaction of the vinyl ester based emulsion polymer is preferably carried out in a temperature range of from 40°C to 100°C and is initiated by means of water-soluble free-radical initiators used for emulsion polymerization. These are the known organic and inorganic preoxides such as alkali metal peroxo-disulfates, hydrogene peroxide, tert-butyl hydrogene peroxide or organic azo compounds. These known compounds are preferably used in combination with reducing agents such as the sodium salt of hydroxymethanesulfinic acid, ascorbic acid, sodium sulphite, sodium bisulfite, sodium sulfoxylate derivatives. In addition, it is possible to use metal compounds in which the metal can be present in various oxidation states, e.g. iron(II)sulfate.

[0038] It may be necessary to add coalescing agents depending on the glass transition temperature of the polymer to reach the minimum film formation temperature of ≤ 0 °C.

[0039] Example to these coalescing agents are propylene glycol, polyethylene glycol, butyl carbitol acetate, mixtures of mono- and bi-carboxylic acid esters. According to technical practice, as the coalescent increases, the tensile adhesion strength of the polymer at elevated temperature (WATT 91) decreases. To be on the safe side, the coalescing agents were added in an amount of from 4% to 5% based on the total amount of monomers.

EXAMPLES

Inventive Example 1

[0040] 395 parts of deionized water, 39,50 parts of polyvinyl alcohol (30/92) (a/b; a is viscosity in mPa.s and b is the hydrolysis degree of the PVOH) and 3,10 parts of polyvinyl alcohol (4/88) were added to a 3-necked flask equipped with a stirrer, thermometer and reflux condenser. The flask was heated to 90°C and the polyvinyl alcohols were dissolved completely. The flask was then cooled down to 65°C and 3,7 parts of disodium ethoxylated alcohol (C10-12) half ester of sulfosuccinic acid was added. At 65°C, 52 parts of vinyl acetate, 0,026 parts of tert-butyl hydrogen peroxide dissolved in 0,63 parts of deionized water and 0,029 parts of sodium sulfoxylate, 0,029 parts of sodium bicarbonate dissolved in 0,68 parts of water were added to reactor. The reactor temperature was increased gradually from 65°C to 72°C. After the reaction temperature was stabilized, feeding of 461 parts of vinyl acetate started in parallel to 0,17 parts of tert-butyl hydrogene peroxide dissolved in 24,3 parts of water and 0,17 parts of sodium sulfoxylate and 0,17 parts of sodium bicarbonate dissolved in 24,3 parts of deionized water. After 15 minutes, feeding of 15,8 parts of N-methylol acrylamide (25%) started in parallel. After 90% of vinyl acetate has been fed (414,90 parts), feeding of 1 part of vinyl trimethoxysilane started and continued in parallel with the remaining 10% of the vinyl acetate feed (46,10 parts).

[0041] The feeding of vinyl acetate was 3 hours in total, in parallel with the t-BHP and sodium sulfoxylate, sodium bicarbonate solution. The feeding time of N-methylol acrylamide (as a 25% solution of water) was 2 hours. The reactor was heated to 90°C and kept close to this temperature for 15 minutes. Then the reactor temperature was decreased to 65°C and at this temperature 0,59 parts of t-BHP dissolved in 7,9 parts of deionized water was introduced. After that, 0,59 parts of sodium sulfoxylate dissolved in 7,9 parts of deionized water was added to the flask. The temperature was decreased to 40°C and at this temperature 21,7 parts of butyl carbitol acetate was added. Then, 37,28 parts of AlCl3.6H2O dissolved in 37,3 parts of water was introduced. The final latex polymer has a solid content of 49,8%, pH:2,5, viscosity: 7500 cps (6/20).

Inventive Example 2

[0042] 395 parts of deionized water, 39,50 parts of polyvinyl alcohol (30/92) and 3,10 parts of polyvinyl alcohol (4/88) were added to a 3-necked flask equipped with a stirrer, thermometer and reflux condenser. The flask was heated to 90°C and the polyvinyl alcohols were dissolved completely. The flask was then cooled down to 65°C and 3,7 parts of disodium ethoxylated alcohol (C10-12) half ester of sulfosuccinic acid was added. At 65°C, 52 parts of vinyl acetate, 0,026 parts of tert-butyl hydrogene peroxide dissolved in 0,63 parts of deionized water and 0,029 parts of sodium sulfoxylate, 0,029 parts of sodium bicarbonate dissolved in 0,68 parts of water were added to reactor. The reactor temperature was increased gradually from 65°C to 72°C. After the reaction temperature was stabilized, feeding of 461 parts of vinyl acetate was started in parallel to 0,17 parts of tert-butyl hydrogene peroxide dissolved in 24,3 parts of water and 0,17 parts of sodium sulfoxylate and 0,17 parts of sodium bicarbonate dissolved in 24,3 parts of deionized water. After 15 minutes, feeding of 15,8 parts of N-methylol acrylamide (as a 25% solution of water) started in parallel. After 90% of vinyl acetate has been fed (414,90 parts), feeding of 1 part of vinyl trimethoxysilane started and continued in parallel with the remaining 10% of the vinyl acetate (46,10 parts).

[0043] The feeding of vinyl acetate was 3 hours in total, in parallel with the t-BHP and Sodium sulfoxylate, sodium bicarbonate solution. The feeding of N-methylol acrylamide (25%) was 2 hours. The reactor was heated to 90°C and kept close to this temperature for 15 minutes. Then the reactor temperature was decreased to 65°C and at this temperature 0,59 parts of t-BHP dissolved in 7,9 parts of deionized water was introduced. After that, 0,59 parts of sodium sulfoxylate dissolved in 7,9 parts of deionized water was added to the flask. The temperature was decreased to 40°C and at this temperature 18,6 parts of butyl carbitol acetate and 5,15 parts of butyl diglycol were added. Then, 24,85 parts of AlCl3.6H2O dissolved in 24,9 parts of water was introduced. The final latex polymer has a solid content of 49,3%, pH:2,4, viscosity: 9800 cps (6/20).

Comparative example 1

[0044] 395 parts of deionized water, 39,50 parts of polyvinyl alcohol (30/92) and 3,10 parts of polyvinyl alcohol (4/88) were added to a 3-necked flask equipped with a stirrer, thermometer and reflux condenser. The flask was heated to 90°C and the polyvinyl alcohols were dissolved completely. The flask was then cooled down to 65°C and 3,7 parts of disodium ethoxylated alcohol (C10-12) half ester of sulfosuccinic acid was added. At 65°C, 52 parts of vinyl acetate, 0,026 parts of tert-butyl hydrogene peroxide dissolved in 0,63 parts of deionized water and 0,029 parts of sodium sulfoxylate, 0,029 parts of sodium bicarbonate dissolved in 0,68 parts of water were added to reactor. The reactor temperature was increased gradually from 65°C to 72°C. After the reaction temperature was stabilized, feeding of 461 parts of vinyl acetate and 1 part of vinyl trimethoxysilane were started in parallel to 0,17 parts of tert-butyl hydrogene peroxide dissolved in 24,3 parts of water and 0,17 parts of sodium sulfoxylate and 0,17 parts of sodium bicarbonate dissolved in 24,3 parts of deionized water. After 15 minutes, feeding of 15,8 parts of N-methylol acrylamide (25%) started in parallel.

[0045] The feeding of the vinyl acetate and vinyl trimethoxysilane were 3 hours in total, in parallel with the t-BHP and Sodium sulfoxylate, sodium bicarbonate solution. The feeding of N-methylol acrylamide (25%) was 2 hours. The reactor was heated to 90°C and kept close to this temperature for 15 minutes. Then the reactor temperature was decreased to 65°C and at this temperature 0,59 parts of t-BHP dissolved in 7,9 parts of deionized water was introduced. After that, 0,59 parts of sodium sulfoxylate dissolved in 7,9 parts of deionized water was added to the flask. The temperature was decreased to 40°C and at this temperature 21,7 parts of butyl carbitol acetate was added. Then, 37,28 parts of AlCl3.6H2O dissolved in 37,3 parts of water was introduced. The final latex polymer has a solid content of 49,8%, pH:2,5, viscosity: 7300 cps (6/20).

Comparative example 2

[0046] 395 parts of deionized water, 39,50 parts of polyvinyl alcohol (30/92) and 3,10 parts of polyvinyl alcohol (4/88) were added to a 3-necked flask equipped with a stirrer, thermometer and reflux condenser. The flask was heated to 90°C and the polyvinyl alcohols were dissolved completely. The flask was then cooled down to 65°C and 3,7 parts of disodium ethoxylated alcohol (C10-12) half ester of sulfosuccinic acid was added. At 65°C, 52 parts of vinyl acetate, 0,026 parts of tert-butyl hydrogene peroxide dissolved in 0,63 parts of deionized water and 0,029 parts of sodium sulfoxylate, 0,029 parts of sodium bicarbonate dissolved in 0,68 parts of water were added to reactor. The reactor temperature was increased gradually from 65°C to 72°C. After the reaction temperature was stabilized, feeding of 461 parts of vinyl acetate and 1 part of vinyl trimethoxysilane started in parallel to 0,17 parts of tert-butyl hydrogene peroxide dissolved in 24,3 parts of water and 0,17 parts of sodium sulfoxylate and 0,17 parts of sodium bicarbonate dissolved in 24,3 parts of deionized water. After 15 minutes, feeding of 15,8 parts of N-methylol acrylamide (as a 25% solution of water) started in parallel.

[0047] The feeding of the vinyl acetate and vinyl trimethoxysilane were 3 hours in total, in

parallel with the t-BHP and Sodium sulfoxylate, sodium bicarbonate solution. The feeding of N-methylol acrylamide (25%) was 2 hours. The reactor was heated to 90°C and kept around this temperature for 15 minutes. Then the reactor temperature was decreased to 65°C and at this temperature 0,59 parts of t-BHP dissolved in 7,9 parts of deionized water was introduced. After that 0,59 parts of sodium sulfoxylate dissolved in 7,9 parts of deionized water was added to the flask. The temperature was decreased to 40°C and at this temperature 18,6 parts of butyl carbitol acetate and 5,15 parts of butyl diglycol were added. Then, 24,85 parts of AlCl3.6H2O dissolved in 24,9 parts of water was introduced. The final latex polymer has a solid content of 49,8%, pH:2,5, viscosity: 7800 cps (6/20).

Application Tests of the Inventive and Comparative Examples

Evaluation of the water resistance

[0048] D3-1, D3-3 and D3-4 tests were done for the emulsion polymer latexes based on EN 204 and EN 205. The test specimen preparations were carried out according to EN 205 and the water resistance of the polymer latexes were classified based on EN 204.

[0049] The minimum required tensile adhesion strength values were given in Table 1:

Table 1. Evaluation of D3 type wood adhesives based on EN 204 according to their water resistance

EVALUATION OF D3 TYPE WOOD ADHESIVES BASED ON EN 204 ACCORDING TO THEIR WATER RESISTANCE		
D3-1	7 days at std. ambient cond.	> 10 N/mm^2
D3-3	7 days at std. ambient cond.,4 days in cold water	> 2 N/mm^2
D3-4	7 days at std. ambient cond.,4 days in cold water,7 days at ambient cond.	> 8 N/mm^2

[0050] In table 2, it can clearly be seen that, with the delayed addition of vinyl silanes to the reaction medium, the D3-3 test results were improved. As a result, all the adhesives produced in the examples are acceptable as D3 type wood adhesives according to EN 204.

Table 2. Evaluation of the inventive and comparative examples based on EN 204 according to their water resistance

Example #	D3-1	D3-3	D3-4
Inventive example 1	13,23 N/mm^2	2,79 N/mm^2	13,23 N/mm^2
Inventive example 2	13,3 N/mm^2	2,8 N/mm^2	13,3 N/mm^2

Example #	D3-1	D3-3	D3-4
Comparative example 1	13,1 N/mm^2	2,5 N/mm^2	13,1 N/mm^2
Comparative example 2	13,1 N/mm^2	2,6 N/mm^2	13,1 N/mm^2

Evaluation of tensile strength of wood glues at elevated temperature

[0051] The heat resistance of the polymer latexes were evaluated based on EN 14257:2006 (Table 3):

Tensile strength of lap joints at elevated temperature-EN 14257:2006	
Type of adhesive	vinylic mono component
Wood type	beech (Faqus Sylvatica)
Moisture content of wood	10±2%
Conditioning	23±2°C and 50±5% relative humidity
Surface treatment:before testing	sanding with abrasing paper grit size 100
Number of test specimen	10
Adhesive layer	thin
Gluing area	200 m2
Testing apparatus	Zwick Universal test machine
Testing speed	50 mm/min
Test temperature	23±2°C
Gluing temperature	20±2°C
Coveraqe	150±10 g/m2
Application of glue	both surfaces
Open assembly time	120±10 s
Closed assembly time	180±10 s
Pressure	0,7/0,8 N/mm2
Pressure time	120 min
Conditioning sequence	7 day in normal atmosphere (23°C and 50% r.h.), then 60±5 min.in oven at 80±2°C

[0052] When all the patent examples were exposed to tensile adhesion test at high temperatures (WATT91), the inventive example 1 and inventive example 2 had improved results.

Table 4. Evaluation of tensile strength of wood glues at elevated temperature

Example #	EN 14257 test result
Inventive example 1	7,9 N/mm2
Inventive example 2	7,7 N/mm2
Comparative example 1	6,9 N/mm2
Comparative example 2	6,8 N/mm2

[0053] According to these results it can clearly be seen that, when vinyl trimethoxy silane was added after 90% of the vinyl acetate has been fed, the tensile adhesion of the polymers at elevated temperature were improved; when it was introduced at the beginning of the feed, the heat resistance of the polymers were lower.

Stability tests of the polymer latexes

[0054] The stability of the emulsion polymers were evaluated at 40°C for 3 weeks and at 60°C for 3 days. Results are showing that, inventive example 1 and inventive example 2 are far better than the comparative examples (Table 5).

Table 5. Stability test results of the emulsion polymer latexes

Example Code	Initial viscosity	Viscosity after 3 days @60°C	Viscosity after 3 weeks @D40°C	Visocsity change @60°C	Visocsity change @40°C
Inventive example 1	7500 cps	8000 cps	8050 cps	6,6%	7,3%
Inventive example 2	9800 cps	9850 cps	9900 cps	0,5%	1,02%
Comparative example 1	7300 cps	12000 cps	12500 cps	64,38%	71,23%
Comparative example 2	7800 cps	13000 cps	14000 cps	66,6%	79,48%

[0055] As a result, the examples clearly show that, when vinyl trimethoxy silane was added after 90% of the monomer has been fed, the stability of the latexes were significantly improved in inventive example 1 and inventive example 2 as shown with the percantages of 7,3% and 1,02%, respectively.

REFERENCES CITED IN THE DESCRIPTION

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PATENTKRAV

1. Fremgangsmåde til fremstilling af en silan-modificeret vinylester-latex-klæber sammensætning ved fri radikal initieret vandig emulsion polymerisering af vinylester-monomerer under tilstedeværelse af i det mindste et dispergeringsmiddel og i det mindste en fri radikal initiator, som tilvejebringer en silan-modificeret vinylester-latex-klæber sammensætning, omfattende, baseret på de totale mængder af monomerer,

a. fra 50 til 99 vægt-% vinylestere af C2-C12-carboxylsyrer og fra 0,05 til 5% af vinylsilaner, som er i stand til at copolymerisere med de nævnte vinylestere,
b. fra 0,75 til 25 vægt-% af i det mindste en polyvinylalkohol med en grad af hydrolyse på imellem 70% og 99%,
c. fra 0,05 til 5 vægt-% af i det mindste et tværbindingsmiddel,
d. fra 1 til 20 vægt-% af i det mindste et Lewissyremetalsalt,
hvor vinyl-silan-monomeren tilføjes til reaktionsmediet efter at i det mindste 50 vægt-% af den totale mængde af vinylestere af C2-C12-carboxylsyrer er tilført reaktionsmediet og før monomer-reduktionstrinnet er nået.

2. Fremgangsmåde ifølge krav 1, hvor i det mindste 50% af vinylestere af C2-C12-carboxylsyrer er vinylacetatmonomer.

3. Fremgangsmåde ifølge krav 1 eller 2, hvor tilføjelse af vinyl-silanmonomer til reaktionsmediet starter efter at i det mindste 70 vægt-% af den totale mængde af vinylestermonomerer af C2-C12-carboxylsyrer er tilført reaktionsmediet og fortsætter indtil afslutningen af monomertilførsel.

4. Fremgangsmåde ifølge krav 1 eller 2, hvor vinyl-silan tilførsel til reaktionsmediet starter efter at i det mindste 50 vægt-% af den totale mængde af vinylestere af C2-C12-carboxylsyrer er tilført reaktionsmediet og fortsætter efter afslutningen af tilførsel af vinylestermonomer således, at tilførsel af vinyl-silan fortsætter i op til 15 minutter efter at alle vinylesterne af C2-C12-carboxylsyrer er tilført reaktionsmediet.

5. Fremgangsmåde ifølge krav 1 eller 2, hvor vinyl-silanmonomer tilføres efter at 90 vægt-% af vinylesterne af C2-C12-carboxylsyrer er blevet tilført reaktionsmediet og før monomerreduktionstrinnet er nået.

6. Fremgangsmåde ifølge krav 1 eller 2, hvor vinyl-silanet tilføres polymerisationsmediet således, at alt vinyl-silanet polymeriseres efter at mere end halvdelen af vinylesterne af C2-C12-carboxylsyrer er blevet polymeriserede.

7. Fremgangsmåde ifølge ethvert af kravene 1, 2, 5 eller 6, hvor tilførslen af vinyl-silan til polymerisationsmediet foretages som en skudtilførsel, således at alt vinyl-silanet tilføres på mindre end 5 minutter.

8. Fremgangsmåde ifølge ethvert af kravene 1 til 7, hvor vinylsilanmonomeren er vinyltrimethoxysilan.

9. Fremgangsmåde ifølge ethvert af kravene 1 til 8, hvor polyvinylalkoholen er en blanding af, baseret på den totale mængde af monomeren,

a. fra 0,05 til 15 vægt-% polyvinylalkohol med en grad af hydrolyse på imellem 90 og 99%,
b. fra 0,25 til 10 vægt-% polyvinylalkohol med en grad af hydrolyse på imellem 70 og 89%.

10. Fremgangsmåde ifølge krav 9, hvor forholdet imellem mængden af polyvinylalkohol med den højere grad af hydrolyse og den lavere grad af hydrolyse er 10 til 15 gange.

11. Fremgangsmåde ifølge ethvert af kravene 1 til 10, hvor forholdet imellem tværbindingsmiddelmængde og vinylsilanmængde er 2 til 5 gange.

12. Fremgangsmåde ifølge ethvert af kravene 1 til 11, hvor et koaleserende middel fra 0,15 til 15% tilføres den silanmodificerede vinylester-latex-sammensætning med henblik på at justere den minimale filmdannelsestemperatur.

13. Silan-modificeret vinylester-latex-klæber sammensætning, som kan opnås ved fremgangsmåden ifølge ethvert af kravene 1 til 12.

14. Anvendelse af den silan-modificerede vinylester-latex-klæber sammensætning som angivet i krav 13 som en D2 type træklæber.