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(54) Titre : COLLE A PARQUET A UN COMPOSANT, MODIFIEE AU SILANE ET EXEMPTÉ D'EAU, DE SOLVANT ET DE PLASTIFIANT, ET UTILISATION DE CELLE-CI POUR COLLER DU PARQUET, DES REVETEMENTS DE SOL EN BOIS ET DES PANNEAUX A BASE DE BOIS, AVEC TOUTES SORTES DE SUPPORTS COURANTS EN AMENAGEMENT INTERIEUR, MEME PROBLEMATIQUES
(54) Title: WATER-, SOLVENT- AND PLASTICIZER-FREE, SILANE-MODIFIED, ONE-COMPONENT PARQUET ADHESIVE AND USE THEREOF FOR GLUING PARQUET, WOODEN FLOOR COVERINGS AND WOOD-BASED MATERIAL BOARDS TO ALL SUB-FLOORS WHICH ARE COMMON IN INTERIOR FITMENT, EVEN THOSE WHICH ARE PROBLEMATIC

(57) **Abrégé/Abstract:**

The present invention relates to a one-component, silane-modified, water-, solvent- and plasticizer-free parquet adhesive and also to its use for the bonding of parquet, wood floor coverings and wood-based material boards to all, including problem, substrates customary in interior fitment.



Abstract

The present invention relates to a one-component, silane-modified water-, solvent- and plasticizer-free parquet adhesive and also to the use thereof for gluing parquet, wooden floor coverings and wood-based material boards to all sub-floors which are common in interior fitment, even those which are problematic.

Water-, solvent- and plasticizer-free, silane-modified, one-component parquet adhesive and use thereof for gluing parquet, wooden floor coverings and wood-based material boards to all sub-floors which are common in interior fitment, even those which are problematic

The present invention relates to a one-component, silane-modified water-, solvent- and plasticizer-free parquet adhesive and also to the use thereof for gluing parquet, wooden floor coverings and wood-based material boards to all sub-floors which are common in interior fitment, even those which are problematic.

Parquet adhesives based on silane-modified, oligomeric compounds typically have the advantage of being processing- and application-friendly and also free of water, solvents and health-endangering substances, such as isocyanates, but have the disadvantage of being formulated with migratable components, such as plasticizers and/or non-reactive liquid extenders. The dissolving properties of these additives cause significant restrictions in the adhesion on sub-floors, such as mastic asphalt, which are susceptible thereto. In addition, in the case of correspondingly susceptible treatment agents for wooden floor surfaces such as acrylate- or polyurethane parquet water-based varnishes, they can cause solvation and dissolution in the joint region between two wooden floor elements. The parquet adhesive according to the invention overcomes these problems by means of its special composition described in patent claim 1, based on at least two silane-terminated, moisture-reactive polyalkylene oxide oligomers with at least two mineral components and also suitable hardening catalyst, drying agent and adhesion promoter. Preferably, in addition at least one UV light absorber, antioxidant and rheological additive are contained. The terminal silane groups of the at least two polyalkylene oxide oligomers

are bonded via alkyl groups to the oligomeric skeletal structure. The two polyalkylene oxide oligomers and the two mineral components are present in defined mixing ratios and are characterised with respect to type, structure, surface property and molecular weight or particle size. Drying agent and adhesion promoter contain moisture-reactive silane groups, preferably trimethoxysilane groups.

The parquet adhesive according to the invention is free of water, solvents, health-endangering substances, plasticizers and non-reactive liquid extenders. It has the application- and processing-friendly advantageous properties of conventional silane-modified parquet adhesives. In addition, it has excellent adhesion properties on all sub-floors which are common in interior fitment, even those which are problematic. Treatment agents for wooden floor surfaces are not solvated or attacked by it.

The present invention relates to a one-component, silane-modified, water-, solvent-, and plasticizer-free parquet adhesive and also to the use thereof for gluing parquet, wooden floor coverings and wood-based material boards to all sub-floors which are common in interior fitment, even those which are problematic.

In the case of gluing wooden floor coverings, in particular parquet, adhesives are in demand, which enable simple handling and processing, entail no health risks, are environmentally-friendly, ensure a frictional, strong connection between covering wood and sub-floor, adhere well equally to all sub-floors and cause no dimensional changes and/or damage to the wooden floor covering.

These requirements are fulfilled to a respectively different degree by the adhesives which are commonly used for gluing wooden floor elements,

in particular parquet. They are divided in detail into the following classes: dispersion adhesives, solvent adhesives, powder adhesives, methylene diisocyanate (MDI)-based two-component polyurethane adhesives, MDI-based one-component polyurethane adhesives, toluene diisocyanate (TDI)-based polyurethane adhesives and silane-modified polymeric adhesives (SMP-adhesives).

Dispersion adhesives based on vinyl acetate homopolymer dispersions have been used since the fifties for gluing parquet. They bond by evaporation of the water, the adhesion being based exclusively on physical interactions of the molecules (dipole-dipole-, van der Waals interactions). What is disadvantageous with these parquet adhesives which have been used to date is the high water content which can lead to significant swelling of the wood and consequently to dimensional changes in the parquet and other wooden floor coverings. Furthermore, the small amount of time which remains for laying the wooden floor covering element after application of the adhesive on the sub-floor (open time) and also the in part only moderate sub-floor adhesion are disadvantageous. The high glass transition temperature of the vinyl acetate homopolymers makes it necessary in addition to use coalescent agents in order to achieve filming of the dispersion at the processing temperature (room temperature). Coalescent agents are volatile organic compounds (VOCs) which, even after gluing of the parquet, are still discharged in the room air for a fairly long period of time and hence can represent environmental and health risks.

A further development of the dispersion parquet adhesives based on vinyl acetate homopolymer dispersions are the parquet adhesives based on vinyl acetate-ethylene copolymer dispersions. In the case of these similarly formulated adhesives, the lower glass transition temperature of the copolymer dispersions requires no coalescent agents. In addition,

also special dispersions based on styrene acrylic acid ester copolymers are used nowadays. These adhesives can be formulated likewise without coalescent agents because of the low glass transition temperature of the dispersions. However, the wood-swelling properties, the short open times (10 to 20 minutes) and the only moderately pronounced adhesion properties continue to be disadvantageous.

At the end of the sixties, solvent-synthetic resin parquet adhesives were introduced. These adhesives are based on solutions of vinyl acetate homopolymers in a solvent mixture which can comprise methanol, ethanol, methyl acetate, ethyl acetate and acetone. They bond very rapidly by evaporation of the solvent. What is advantageous with these parquet adhesives used to date are the wood-swelling properties which are reduced by approx. 50 to 70% in comparison with dispersion parquet adhesives. However, the high content of solvents, the emission of which means a burden to the processor and to the environment, is disadvantageous and consequently use in interiors is limited. The products are generally characterised as readily-inflammable and health-damaging or irritant. In addition, the open times of these parquet adhesives are particularly short (5 to 10 minutes) and hence disadvantageous for the processing process. The adhesion properties are better than those of dispersion adhesives.

An advantageous further development of these parquet adhesives, with respect to solvent emissions, is found in a patent of Stauf Klebstoffwerk GmbH (US 7,420,009 B2: LOW EMISSION ADHESIVE COMPOSITION BASED ON A SOLVENT).

Another further development of the dispersion parquet adhesives is pulverulent adhesive formulations. These are based on re-emulsifiable dispersion powders – generally vinyl acetate-ethylene copolymers. They

contain a mineral component which can comprise calcium sulphate hemihydrate, Portland cement or aluminate cement. These adhesives concern 2-component systems which consist of powder and a further component. The second component which is mixed with the powder component is water or a polymer dispersion. The advantage of this class of parquet adhesives is the chemical water bonding of the mineral component. The disadvantageous wood swelling of the dispersion adhesives is reduced consequently to approximately the level of solvent parquet adhesives. The limited pot life between mixing the components and the end of the processing in which the chemical reaction takes place which increasingly effects a viscosity increase is disadvantageous. The laying time (open time) between the application of the adhesive and laying of the wooden floor element is just as short as in the case of dispersion parquet adhesives. In addition, the difficulties which are basically inherent to all two-component systems and reside in the additional mixing complexity, in the danger of non-homogeneous mixing and in inadequate adjustment of the mixing ratio by the user are disadvantageous. The adhesion properties correspond to those of the dispersion parquet adhesives.

In the nineties, reaction adhesives based on polyurethane for gluing parquet were introduced. At first these were 2-component systems which consist of a resin component and an isocyanate hardener. The binding agent in the resin component is a hydroxy-functional polyol; the formulated resin component contains in addition water scavengers, mineral fillers, catalysts and additives. The isocyanate hardener component generally consists of commercial, oligomeric methylene diphenyldiisocyanate (MDI, often also termed polymer MDI). In the case of these adhesives, the wood-swelling effect which is again reduced in comparison with powder parquet adhesives and hence no longer relevant in practice and also the longer open times of approx. 30 to 60

minutes are advantageous. Furthermore, the strengths and adhesion properties which ensure an extremely frictional connection of the covering wood to all sub-floors which are common in interior fitment, even those which are problematic, are advantageous. However, the danger to health and environment which is based on the isocyanate content and is expressed inter alia in the hazardous material labelling according to the German Ordinance on Hazardous Substances or the international GHS system is disadvantageous. Accordingly, these adhesives are classed as health-damaging, irritant and sensitising. Furthermore, the problems which are basically inherent to all two-component systems, as were described already in the case of powder adhesives, are disadvantageous.

Shortly after the two-component polyurethane adhesives, reactive one-component polyurethane parquet adhesives were developed. The basis of these adhesives is isocyanate group-containing, moisture-reactive prepolymers based on methylene diphenyldiisocyanate (MDI) which often also comprise oligomeric and monomeric MDI. Further components of these adhesives are mineral fillers, catalysts and additives. In comparison with two-component polyurethane adhesives, the again extended open times are advantageous and facilitate handling and processing of the adhesives together with the one-component aspect. The wood-swelling effect corresponds to that of two-component polyurethane adhesives and is correspondingly unproblematic. The adhesion properties correspond to those of the solvent parquet adhesives and ensure good adhesion on common sub-floors. However, what is disadvantageous in one-component polyurethane adhesives is furthermore the danger to health and environment, which corresponds to that of two-component polyurethane parquet adhesives, and is based on a residual content of monomeric and oligomeric MDI in the prepolymers.

At the end of the nineties, one-component reaction adhesives based on toluene diisocyanate oligomers (TDI adhesives) for gluing wooden floor coverings were introduced. In comparison with the established MDI-based polyurethane adhesives, the advantage of these adhesives is that they are not classed as health-damaging, irritant or sensitising and they do not require a specific labelling according to the German Ordinance on Hazardous Substances and the international GHS labelling system. This property can be attributed to their extremely low residual content of monomeric TDI. With respect to the open time and wood-swelling properties, they are similar to the MDI-based polyurethane adhesives. However, in comparison with these, the only moderately pronounced adhesion properties are disadvantageous. Although the adhesion with these adhesives, in addition to physical interactions, is based also on formation of covalent chemical bonds, it is no better than in the case of the dispersion- and powder parquet adhesives.

The newest development is parquet adhesives based on silane-modified, oligomeric compounds, so-called SMP adhesives (now and then also termed hybrid adhesives). These adhesives are characterised by oligomeric organic compounds (frequently also termed prepolymers) which carry moisture-reactive silane groups, generally dimethoxymethyl- or trimethoxysilane groups. After contact with moisture from the sub-floor, the covering wood or the air, the moisture-reactive silane groups crosslink by means of hydrolysis and subsequent condensation to form a three-dimensional siloxane network, the adhesive matrix.

Further components of these adhesives are liquid extenders, plasticizers, mineral fillers, water scavengers, adhesion promoters,

catalysts and further additives. For the gluing of parquet, silane-modified adhesives generally have the following advantages:

- one-component aspect
- free of water and solvents
- sufficiently long open times
- no relevant wood-swelling effect in practice
- not classed as environment- or health-endangering and therefore need no labelling according to the German Ordinance on Hazardous Substances and the international GHS labelling system.

The pseudo-plastic rheology of SMP parquet adhesives is furthermore advantageous. In practice, this means that the adhesives do not flow and can be applied well with a toothed spatula. Drawn tracks of adhesive remain stable in shape and hence offer an important precondition of being able to bridge fairly small cavities between wooden floor covering and sub-floor.

Silane-modified parquet adhesives typically comprise plasticizers and/or non-reactive liquid extenders which reduce the viscosity of the adhesive and ensure necessary processing properties. Unfortunately they are also responsible for a series of technical application problems and restrictions. The dissolving properties of these migratable liquids cause in particular solvation of mastic asphalt as sub-floor and also solvation of dispersion primers used typically as primer and based on vinyl acetate-ethylene-, styrene-acrylate- or acrylic acid ester copolymers. Therefore in the case of silane-modified parquet adhesives, problems with adhesion on this type of sub-floors must basically be taken into account – a circumstance which has to date militated against greater acceptance and use of these parquet adhesives. Furthermore, because of the migration of liquid components for correspondingly

susceptible coatings and/or treatments of the covering wood, such as parquet water-based varnishes, the danger of solvation or dissolution exists, which can lead, in particular in the joint region, close to the adhesive, between two parquet elements, to unattractive impairments to the appearance.

Cyclohexane dicarboxylic acid derivatives as plasticizer for silane-modified adhesives and sealants are disclosed in detail in the patent document WO 2010/063740 A1.

Starting from this state of the art, it is the object of the present invention to make available a parquet adhesive which has all or several of the following advantages: it should be easy to apply, ensure a sufficiently long open time, have no relevant wood-swelling effect, not endanger health and environment, be free of water, solvents, plasticizers and non-reactive liquid extenders, have good adhesion properties on all sub-floors which are common, even solvatable, in interior fitment and not solvate treatment agents for wooden floor surfaces. A further object of the invention is to make available the use of the parquet adhesive according to the invention for gluing parquet, wooden floor coverings and wood-based material boards with the objectives indicated for the parquet adhesive.

This object is achieved by the one-component, silane-modified, water-, solvent- and plasticizer-free parquet adhesive according to claim 1, and also use thereof according to claim 12. Advantageous developments of the parquet adhesive according to the invention and of the use according to the invention are indicated in the respective dependent claims.

The parquet adhesive according to the invention is a silane-modified parquet adhesive with significantly improved adhesion properties and low dissolution capacity relative to substrates. It has the technical processing and application advantages of the silane-modified adhesives corresponding to the state of the art without including their migratable non-reactive components and having the adhesion and solvation problems associated therewith. All the liquids contained in the adhesive according to the invention comprise terminal silane groups and are bonded covalently in the polysiloxane network. The possibility of completely dispensing with non-reactive liquids and the advantageous properties, associated therewith, of the parquet adhesive according to the invention can essentially be attributed to a suitable combination of respectively at least two selected basic polymers having at least two special mineral components. The basic polymers are characterised with respect to structure and molecular weight and the mineral components with respect to type, surface quality and particle size. In addition, also the selection of a suitable hardening catalyst, drying agent and adhesion promoter are responsible for the advantageous adhesive properties.

According to the invention, the one-component, silane-modified, water-, solvent- and plasticizer-free parquet adhesive which comprises no non-reactive liquid extenders and is suitable for gluing parquet, wooden floor coverings and wood-based material boards to all sub-floors which are common in interior fitment, even those which are solvatable and problematic, comprises the following materials or consists of them:

- a) 12 to 36 per cent, by mass of a moisture-reactive, silane-terminated polyalkylene oxide binding agent with an average molecular weight of 6,000 to 20,000 g/mol,

the silane functions being bonded via alkyl groups to the oligomeric skeletal structure,

- b) 2 to 18 per cent by mass of a moisture-reactive, silane-terminated polyalkylene oxide binding agent with an average molecular weight of 300 to 3,000 g/mol,
the silane functions being bonded via alkyl groups to the oligomeric skeletal structure,
- c) 30 to 60 per cent by mass of a surface-hydrophobised marble powder with an average particle diameter of 0.8 μm to 4.0 μm ,
- d) 2 to 10 per cent by mass of a surface-hydrophobised chalk powder with an average particle diameter of 0.2 to 0.7 μm ,
- e) 0.1 to 1.0 per cent by mass of a hardening catalyst,
- f) 0.2 to 3 per cent by mass of a moisture-reactive, silane-modified drying agent,
- g) 0.2 to 3 per cent by mass of a moisture-reactive, silane-modified adhesion promoter,
the percentage data relating to the mass of the ready-to-use parquet adhesive and the sum of the components a) to g) being 46.5% to 100%.

In particular, the parquet adhesive can have the following proportions of components:

- a) 23 to 33 per cent by mass of a moisture-reactive, silane-terminated polyalkylene oxide binding agent with an average molecular weight of 7,000 to 13,000 g/mol,
the silane functions being bonded via alkyl groups to the oligomeric skeletal structure,
- b) 7 to 13 per cent by mass of a moisture-reactive, silane-terminated polyalkylene oxide binding agent with an average molecular weight of 700 to 1,300 g/mol,
the silane functions being bonded via alkyl groups to the oligomeric skeletal structure,
- c) 48 to 60 per cent by mass of a surface-hydrophobised marble powder with an average particle diameter of 1.0 μm to 3.0 μm ,
- d) 3 to 7 per cent by mass of a surface-hydrophobised chalk powder with an average particle diameter of 0.3 to 0.6 μm ,
- e) 0.15 to 0.29 per cent by mass of a hardening catalyst,
- f) 0.5 to 1.5 per cent by mass of a moisture-reactive, silane-modified drying agent,
- g) 0.5 to 1.5 per cent by mass of a moisture-reactive, silane-modified adhesion promoter,
the percentage data relating to the mass of the ready-to-use parquet adhesive and the sum of the components a) to g) being 82.15% to 100%.

A preferred embodiment provides that the mass ratio of component a) to component b) is 1 : 1 to 8 : 1 and the mass ratio of component c) to

component d) is 5 : 1 to 20 : 1. In particular, it is advantageous if the mass ratio of component a) to component b) is 2 : 1 to 4 : 1 and the mass ratio of component c) to component d) is 8 : 1 to 18 : 1.

As binding agent and basic polymer, the parquet adhesive according to the invention comprises 12 to 36 per cent by mass, preferably 23 to 33 per cent by mass, very particularly preferred 28 per cent by mass of a moisture-reactive, silane-terminated polyalkylene oxide, the silane functions of which are bonded via alkyl groups to the oligomeric skeletal structure. Preferably, the oligomeric skeletal structure is a polypropylene oxide and the silane functions are dimethoxymethylsilane groups. The average molecular weight of the oligomer is between 6,000 and 20,000 g/mol, preferably between 7,000 and 13,000 g/mol, very particular preferred are 10,000 g/mol.

As binding agent and reactive diluent, the parquet adhesive according to the invention comprises 2 to 18 per cent by mass, preferably 7 to 13 per cent by mass, very particularly preferred 10 per cent by mass of a moisture-reactive, silane-terminated polyalkylene oxide, the silane functions of which are bonded via alkyl groups to the oligomeric skeletal structure. Preferably, the oligomeric skeletal structure is a polypropylene oxide and the silane functions are dimethoxymethylsilane groups. The average molecular weight of the oligomer is between 300 and 3,000 g/mol, preferably between 700 and 1,300 g/mol, very particularly preferred are 1,000 g/mol.

At least one mineral component is a marble powder with an average particle size of 0.8 to 4.0 μm , preferably 1.0 to 3.0 μm , very particularly preferred 2.0 μm . The marble powder is contained at 30 to 60 per cent by mass, preferably 48 to 60 per cent by mass, very particularly

preferred 55 per cent by mass in the parquet adhesive according to the invention.

At least one further mineral component is a chalk powder with an average particle size of 0.2 to 0.7 μm , preferably 0.3 to 0.6 μm , very particularly preferred 0.4 μm . The chalk powder is contained in the parquet adhesive according to the invention at 2 to 10 per cent by mass, preferably 3 to 7 per cent by mass, very particularly preferred at 4 per cent by mass.

Substitution of chalk and/or marble by precipitated calcium carbonate powders is not possible since these have smaller particle sizes than those required according to the invention. Likewise, the substitution of the chalk and/or the marble by other calcium carbonate stone, such as limestone, does not lead to the advantages according to the invention.

The surfaces of the chalk- and marble particles are hydrophobised, the hydrophobising being effected either by treatment with one or more fatty acids and/or its salt/their salts, preferably by treatment with stearic acid and/or stearate or via silanisation, preferably by conversion with a reactive silane, very particularly preferred by conversion with aminosilane.

In order to accelerate the hardening process, the parquet adhesive according to the invention comprises 0.1 to 1.0 per cent by mass, preferably 0.15 to 0.29 per cent by mass, very particularly preferred 0.29 per cent by mass of a hardening catalyst. Organo-transition metal compounds are preferred hardening catalysts; dibutyltin diacetylacetonate is very particularly preferred.

As water scavenger, the parquet adhesive according to the invention comprises 0.2 to 3 per cent by mass, preferably 0.5 to 1.5 per cent by mass, very particularly preferred 0.8 per cent by mass of a moisture-reactive, silane-modified drying agent. Trimethoxysilane-terminated alkenes are preferably used; vinyl trimethoxysilane is very particularly preferred.

In order to improve the adhesion properties, the parquet adhesive according to the invention comprises 0.2 to 3 per cent by mass, preferably 0.5 to 1.5 per cent by mass, very particularly preferred 1.0 per cent by mass of a moisture-reactive, silane-modified adhesion promoter. Trimethoxysilane-terminated aminoalkyl compounds are preferably used; 3-aminopropyltrimethoxysilane is very particularly preferred.

In order to improve storage life, the parquet adhesive according to the invention can comprise in addition antioxidants and/or UV light absorbers (photostabilisers) of together up to 3 per cent by mass, preferably 0.2 to 1 per cent by mass, very particularly preferred 0.21 per cent by mass.

As antioxidant, preferably sterically hindered phenols are used, preferably 3,5-bis(1,1-dimethylethyl)-4-hydroxybenzylpropanoic acid-C7-C9-isoalkylester.

As UV light absorber, preferably sterically hindered amines are used, preferably bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate or methyl-1,2,2,6,6-pentamethyl-4-piperidylsebacate; a mixture of these sebacates is very particularly preferred.

As rheological additive, the parquet adhesive according to the invention can comprise in addition up to 3 per cent by mass, preferably 0.3 to 1.3 per cent by mass, very particular preferred 0.7 per cent by mass of a wax, preferably a polyamide wax.

The individual components of the adhesive composition according to the invention can be contained respectively as pure materials or, provided that the criteria applying to the respective component, such as total proportion, mass ratio, molecular weight, structure, chemistry, particle size and/or surface quality remain fulfilled, as a mixture of similar materials.

In order to improve or adjust appearance, rheology and/or stability, the parquet adhesive according to the invention can comprise further additives, such as pigments, colourants, organic/inorganic fillers, resins, waxes or preservatives.

The use of plasticizers and non-reactive liquid extenders is dispensed with completely because of their migratability and dissolving properties. The composition according to the invention of the parquet adhesive has the effect that this does not have a disadvantageous effect, rather the advantageous properties of silane-modified parquet adhesives are retained. In addition, the adhesion properties are significantly improved and the undesired solvation of substrate surfaces is avoided.

The parquet adhesive according to the invention has a series of technical processing and application advantages which no other parquet adhesive combines together in this combination:

- one-component aspect

- free of plasticizers and non-reactive liquid components and also of water and solvents
- sufficiently long open time
- no relevant wood-swelling effect in practice
- free of environment- and health-endangering substances
- labelling-free according to the current GHS labelling system and the German Ordinance on Hazardous Substances
- pronounced pseudo-plastic rheology with suitable processing viscosity
- easy applicability by means of toothed spatula and structure-retaining adhesive tracks
- excellent adhesion properties on all moist and dry sub-floors which are common in interior fitment, even those which are problematic
- no solvation or attack of treatment agents for wooden floor surfaces, in particular parquet water-based varnishes
- very extensive field of application
- easy and reliable handling and application

The parquet adhesive according to the invention is one-component and free of water, solvents, plasticizers, non-reactive liquid extenders and other migratable components.

The open time is in the range of 60 to 100 minutes (DIN EN 14293:2006-10), as a result of which a comparatively long processing time is ensured.

Because of the absence thereof of water and solvents, no relevant wood-swelling effect of the adhesive is present in practice.

The absence of solvents and completely dispensing with the addition of plasticizers, isocyanates and other potentially health-endangering substances causes the health- and environment-compatibility of the parquet adhesive according to the invention. This can be observed in the fact that the adhesive does not require to be labelled according to the current German Ordinance on Hazardous Substances and the international GHS hazardous material labelling system.

The pronounced pseudo-plastic rheology and viscosity between 60,000 and 120,000 mPa·s (test conditions according to DIN EN ISO 2555:2000-01, 20 revolutions per minute) ensure, together with the one-component aspect, simple processing of the adhesive according to the invention. The adhesive can be applied easily with a toothed spatula and allows adhesive tracks, which are stable in shape, up to a height of 10 mm.

The parquet adhesive according to the invention has excellent adhesion properties on all sub-floors which are common in interior fitment, such as mastic asphalt, concrete, cement, cement screed, cement liquid screed, cement mortar, cement-bonded wood fibre, ceramic, natural stone, calcium sulphate screed, calcium sulphate liquid screed, magnesite screed, wood, wood-based material, plywood, cork, gypsum, gypsum fibre, gypsum plasterboard, hardboard, knifing filler, primers, textile fibrous material, natural and synthetic polymeric material or a combination of these sub-floors. The adhesion is also ensured on sub-floors comprising up to 8 per cent by mass of water, such as e.g. moist concrete or cement screed.

Commercially available parquet, wooden floor coverings and/or wood-based material boards which consist entirely or partially of European deciduous and/or coniferous types of timber, non-European types of

timber or a combination of these types of timber are glued reliably and frictionally to the sub-floor.

Treatment agents for wooden floor surfaces, in particular parquet water-based varnishes, are not solvated or attacked by the parquet adhesive according to the invention.

The very wide field of use, simple handling and the advantageous processing properties of the parquet adhesive according to the invention ensure simple and reliable application. The user requires no technical constructional and/or chemical expert- or previous knowledge. Hence, the parquet adhesive according to the invention is even suitable for application by laypersons.

In Table 1, an embodiment of the parquet adhesive according to the invention having a particularly preferred composition is given.

In Table 4 and 5, the compositions of the commercially available parquet adhesives SMP-920 and SMP-930 (Stauf Klebstoffwerk GmbH) are summarised. In comparative tests, they serve as reference for the adhesive according to the invention.

In the composition thereof, the two commercially available parquet adhesives differ from the parquet adhesive according to the invention essentially by a different composition of basic polymer and mineral components and also the proportion thereof of plasticizer. Surface-hydrophobised marble powder – indispensable mineral main component of the adhesive according to the invention – is not contained in the commercially available adhesives. Conversely, both commercially available adhesives comprise limestone powder and partially also precipitated calcium carbonates and silicic acid which do not occur in

the parquet adhesive according to the invention. Also the average particle diameters and the distribution profiles thereof differ between adhesive according to the invention and the commercially available formulations. Thus, for example particle sizes of mineral components of $> 4 \mu\text{m}$ are not contained in the parquet adhesive according to the invention.

A further difference is the plasticizer content which, in the case of SMP-930, is 15 per cent by mass and, in the case of SMP-920, is 20 per cent by mass of the ready-to-use adhesive mixture. In contrast, no plasticizer is contained in the parquet adhesive according to the invention. SMP-920 consists of up to 20 per cent by mass of diisononylphthalate. SMP-930 comprises 11 per cent by mass of bis(2-propylheptylphthalate) and 4 per cent by mass of phenolalkylsulphonic acid as plasticizer. Against the background of a reproduction-damaging effect of the phthalates and undesired plasticizer effects, SMP-930 should be regarded as of higher quality in comparison with SMP-920.

With the parquet adhesive according to the invention, described in Table 1, the strength of the adhesive adhesion on different sub-floors was determined and compared with the commercially available, silane-modified parquet adhesives (SMP-920 and SMP-930, Stauf Klebstoffwerk GmbH).

As sub-floor, a wood-based material board coated with mastic asphalt, a fibre-reinforced cement board primed with VDP160 (dispersion primer based on styrene-acrylate, Stauf Klebstoffwerk GmbH) and an uncoated concrete slab (strength class C 20/25 according to DIN EN 206-1:2001-07) was selected. The shear strength which was determined according to DIN EN 14293:2006-10 (storage type A, 40°C) served as measuring parameter. The procedure in the test was such that the sub-floors to be

coated were initially coated with mastic asphalt (layer thickness 25 mm) or VDP160 (layer thickness 0.2 mm) and subsequently left to dry for 24 hours in a standard atmosphere (23°C, 50% relative air humidity). The concrete slab was likewise stored simultaneously for 24 hours in a standard atmosphere. Subsequently, the sub-floors were coated uniformly with a 0.85 mm thick adhesive layer and the slats of beech were pressed into the adhesive layer. After storage for seven days in a climatic chamber at 20°C and 50% relative air humidity, the temperature was increased to 50°C and conditioned for a further 7 days at 50% relative air humidity. Subsequently, the test pieces were conditioned for 24 hours in a standard atmosphere. The shear testing was now effected according to DIN EN 14293:2006-10, the measuring values displayed in Table 2 resulting.

The results show that the parquet adhesive according to the invention on the concrete sub-floor, which is unproblematic from a technical adhesion point of view, has a shear strength which is higher by 24% in comparison with SMP-930 and, in comparison with SMP-920, even a shear strength higher by 36%. On sub-floors which can be solvated by plasticizer and liquid-extender and therefore rather problematic, this difference is displaced further in favour of the adhesive according to the invention. Thus, it has a shear strength increased by 1,818% on mastic asphalt in comparison with SMP-930, which increases even to 2,538% in comparison with SMP-920. With the dispersion primer VDP160, similarly significant results are achieved. The parquet adhesive according to the invention on this sub-floor has a shear strength increased by 765%, in comparison with SNP-930, and a shear strength increased by 1,084% in comparison with SNP-920.

It is evident from these data that the parquet adhesive according to the invention, in contrast to the commercially available, silane-modified

parquet adhesives, has a comparatively high shear strength of greater than or equal to 2.0 N/mm^2 and ensures this even on problematic sub-floors. The adhesion properties of the parquet adhesive according to the invention can therefore be classed as significantly better than the commercially available, silane-modified parquet adhesives.

In the following experiment, the solvating and softening effect of the parquet adhesive according to the invention on parquet water-based varnishes was investigated and compared with the commercially available, silane-modified parquet adhesives (SMP-920 and SMP-930, Stauf Klebstoffwerk GmbH) with plasticizer proportions of 20 (SMP-920) and 15 per cent by mass (SMP-930). Commercially available, one-component systems based on polyurethane-/acrylate dispersion (Aqua-Seal® EcoGold W3, Berger-Seidle Siegeltechnik GmbH and LOBADUR® WS Global, Loba GmbH & Co. KG) with comparatively less resistance relative to plasticizers and liquid extenders were selected as parquet water-based varnish.

For the investigation, the corresponding adhesive was applied over the whole surface on the rear-side of a multilayer parquet element having the dimensions length = 600 mm, width = 75 mm, thickness = 11 mm. The rear-side of the multilayer parquet elements all had 5 cm rectangular incisions of a width of 2 mm and a depth of 6 mm, the incisions being oriented parallel to the narrow edge of the parquet elements. One parquet slat had in total 11 incisions.

For application of the adhesive, these were filled with adhesive and a smooth spatula was drawn over the entire rear-side of the parquet element such that only adhesive remained in the incisions. After a hardening time of 7 days at 20° and 50% relative air humidity, the rear-

side of the parquet elements was sanded so that the wood surface was rough again. In the region of the incisions, the adhesive remained.

The surface was now varnished over the whole area with water-based varnish. 3 layers of varnish with an application quantity of respectively 110 g/m² were applied, an intermediate sanding being effected after the first and second application respectively. After placing in a climatic chamber and 3 days drying at 20°C and 50% relative air humidity, the test pieces were conditioned further at 50°C and 50% relative air humidity. After a storage duration of 3, 20 and 45 days, the test pieces were tempered respectively within 3 hours down to 20°C and removed from the climatic chamber.

As test substance, the gap filling composition powder Pafuki of Berger-Seidle Siegeltechnik GmbH, Grünstadt was scattered onto the surface of the parquet elements and blown off again after an effective time of 10 seconds. The discolouration of the varnished surface was then assessed visually according to a five-stage, semi-quantitative classification system, there being meant 1 = no discolouration, 2 = minimal discolouration, 3 = slight discolouration, 4 = significant discolouration and 5 = pronounced discolouration. In the region of the incisions in which the varnishes were applied on the adhesives, and also the edges thereof, permanent discolourations which were strongly pronounced to a different degree could be detected. These can be attributed to the solvation and softening of the water-based varnishes as a result of the effect of migratable solvating adhesive components (softener and/or liquid-extender).

In order to be able to assess whether the discolourations remaining after blowing-off of the test substance (dry cleaning) are able to be washed off, the test piece surfaces were washed off (wet cleaning) with

surfactant-containing water after the first assessment of discolouration, dried and subsequently subjected to renewed assessment.

The results of these experiments are listed in Table 3. They indicate that the adhesive according to the invention, in contrast to commercially available SMP adhesives, has at no time a solvating or softening effect on the investigated polyurethane-acrylate water-based varnishes. Since the investigated one-component, water-based varnishes belong to water-based varnishes which are less resistant to plasticizers and liquid-extendors, no solvating or softening effect by the parquet adhesive according to the invention should be anticipated also with other, more highly resistant, e.g. two-component, water-based varnishes.

The open time of the adhesive according to the invention (composition according to Table 1) was determined according to DIN EN 14293:2006-10. It was 75 minutes, i.e. within this time period after application of the adhesive, parquet coverings can still be pressed into the adhesive layer and glued to the sub-floor. Also lifting of already laid coverings and new alignment thereof can be readily implemented within this time period.

The viscosity according to DIN EN ISO 2555:2000-01 was determined with the parquet adhesive according to the invention which is described in Table 1. A viscosity of $91,200 \pm 6,300$ mPa·s was measured ($n = 5$, 20 revolutions per minute). The viscosity is hence in the range of 60,000 to 120,000 mPa·s, which ensures easy applicability and adhesive tracks, which are stable in shape, up to a height of 10 mm. In combination with the one-component aspect and the open time, easy handling and processing of the parquet adhesive according to the invention results therefrom.

Raw material	Chemistry	Function	Manufacturer	Proportion [%]
SAX 260	Dimethoxymethylsilane-terminated polypropylene oxide oligomer, MW: approx. 10,000 g/mol	Binding agent, basic polymer	Kaneka	28.0
SAT 010	Dimethoxymethylsilane-terminated polypropylene oxide oligomer, MW: approx. 1,000 g/mol	Binding agent, reactive diluent	Kaneka	10.0
Omyabond 302	Chalk powder, surface-hydrophobised with stearic acid, average particle diameter: 0.4 µm	Mineral component	Omya	4.0
Omyabond 520 FL	Marble powder, surface-hydrophobised with stearic acid, average particle diameter: 2.0 µm	Mineral component	Omya	55.0
Metatin K 740	Dibutyltin diacetylacetonate	Catalyst	Acima	0.29
Geniosil XL 10	Vinyl trimethoxysilane	Drying agent	Wacker Chemie	0.80
Geniosil GF 96	3-aminopropyltrimethoxysilane	Adhesion promoter	Wacker Chemie	1.0
Tinuvin 765	Mixture of bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate and methyl-1,2,2,6,6-pentamethyl-4-piperidylsebacate	UV light absorber	Ciba	0.06
Irganox 1135	3,5-bis(1,1-dimethylethyl)-4-hydroxybenzylpropanoic acid-C7-C9-isoalkylester	Antioxidant	Ciba	0.15
Disparlon 6100	Polyamide wax	Rheological additive	Kusumoto	0.70

Table 1: By way of example, particularly preferred composition of the parquet adhesive according to the invention (proportions in per cent by mass).

Adhesive	Tension shear strength $\pm$ SD on mastic asphalt
Adhesive according to the invention (composition according to Table 1)	2.11 ± 0.22 N/mm ² (n = 7)
SMP-930	0.11 ± 0.07 N/mm ² (n = 6)
SMP-920	0.08 ± 0.06 N/mm ² (n = 6)

Adhesive	Tension shear strength $\pm$ SD on primer VDP160
Adhesive according to the invention (composition according to Table 1)	2.25 ± 0.26 N/mm ² (n = 7)
SMP-930	0.26 ± 0.08 N/mm ² (n = 6)
SMP-920	0.19 ± 0.09 N/mm ² (n = 6)

Adhesive	Tension shear strength $\pm$ SD on concrete slab
Adhesive according to the invention (composition according to Table 1)	2.30 ± 0.20 N/mm ² (n = 7)
SMP-930	1.85 ± 0.17 N/mm ² (n = 7)
SMP-920	1.69 ± 0.21 N/mm ² (n = 6)

Table 2: Results of the tension shear strength test according to DIN EN 14293:2006-10 (storage type A) on parquet adhesive according to the invention, SMP-930 and SMP-920 on various sub-floors. Measuring values $\pm$ standard deviation (SD) and also number of respective measurements (n).

	After 3 days		After 20 days		After 45 days	
	Dry cleaning	Wet cleaning	Dry cleaning	Wet cleaning	Dry cleaning	Wet cleaning
Water-based varnish Aqua-Seal® EcoGold W3						
SMP-930	5	5	5	5	5	5
SMP-920	5	5	5	5	5	5
Adhesive according to the invention	1	1	1	1	1	1
Water-based varnish LOBADUR® Global						
SMP-930	5	4	5	4	5	4
SMP-920	5	5	5	5	5	5
Adhesive according to the invention	1	1	1	1	1	1
Legend						
Pronounced discolouration	= 5					
Significant discolouration	= 4					
Slight discolouration	= 3					
Minimal discolouration	= 2					
No discolouration	= 1					

Table 3: Results relating to the solvating and softening effect of different parquet adhesives, (parquet adhesive according to the invention according to Table 1, SMP-920 and SMP-930) on two one-component parquet water-based varnishes (LOBADUR WS Global and Aqua-Seal EcoGold W3) after 3, 20 and 45 days of duration of the effect. Assessment of the discolouration according to 5-stage assessment system (5 = poorest, 1 = best result) of respectively 11 individual samples after blowing-off (dry cleaning) and wiping-off (wet cleaning) of the sample surface.

Raw material	Chemistry	Function	Manufacturer	Proportion [%]
S 203 H	Dimethoxymethylsilane-terminated polypropylene oxide oligomer; MW: approx. 12,000 g/mol	Binding agent, basic polymer	Kaneka	11
S 303 H	Dimethoxymethylsilane-terminated polypropylene oxide oligomer; MW: approx. 18,000 g/mol	Binding agent, basic polymer	Kaneka	6
Silquest A-171	Vinyl trimethoxysilane	Drying agent	Momentive	0.7
Silquest A-1637	4-amino-3,3-dimethylbutyltrimethoxysilane	Adhesion promoter	Momentive	0.7
TIB KAT 223	Diocetyl tin-bis(2,4-pentanedionate)	Catalyst	TIB Chemicals	0.34
Irganox 1726	4,6-bis(dodecylthiomethyl)-o-cresol	Antioxidant	Ciba	0.1
DINP	diisononylphthalate	Plasticizer	BASF	20
Crayvallac SLX	Polyamide wax	Rheological additive	Cray Valley	0.4
Omya BLP 3	Limestone powder, surface-hydrophobised with stearic acid, average particle diameter: 5.7 µm	Mineral component	Omya	19.5
Calcilit 6 HS	Limestone powder, surface-hydrophobised with stearic acid, average particle diameter: 7 µm	Mineral component	Alpha-Calcit	8.66
MS 70 F	Limestone powder, average particle diameter: 4.5 µm	Mineral component	Schön und Hippelein	15
Calcifin 20 H	Limestone powder, surface-hydrophobised with stearic acid, average particle diameter: 4.4 µm	Mineral component	Alpha-Calcit	16
HDK H 18	Highly dispersed silicic acid, surface-silanised	Mineral component	Wacker	1.6

Table 4: Composition of the commercially available parquet adhesive SMP-920 (Stauf Klebstoffwerk GmbH; proportions in per cent by mass).

Raw material	Chemistry	Function	Manufacturer	Proportion [%]
S 203 H	Dimethoxymethylsilane-terminated polypropylene oxide oligomer; MW: approx. 12,000 g/mol	Binding agent, basic polymer	Kaneka	3
S 303 H	Dimethoxymethylsilane-terminated polypropylene oxide oligomer; MW: approx. 18,000 g/mol	Binding agent, basic polymer	Kaneka	16
Dynasylan VTMO	Vinyl trimethoxysilane	Drying agent	Degussa	0.8
KBM 603	N-2-(aminoethyl)-3-aminopropyltrimethoxysilane	Adhesion promoter	Shin-Etsu	0.8
Neostann U 220 H	Dibutyltin diacetylacetonate	Catalyst	Nitto Kasei	0.32
Irganox 1726	4,6-bis(dodecylthiomethyl)-o-cresol	Antioxidant	Ciba	0.1
Palatinol 10-P	bis(2-propylheptylphthalate)	Plasticizer	BASF	11
Mesamoll	Phenolalkylsulphonic acid ester	Plasticizer	Bayer	4
Thixatrol MAX	Polyamide wax	Rheological additive	elementis	0.5
Omyacarb 10 BG	Limestone powder, average particle diameter: 7 µm	Mineral component	Omya	19.5
Calcifin 20 H	Limestone powder, surface-hydrophobised with stearic acid, average particle diameter 4.4 µm	Mineral component	Alpha-Calcit	41.58
Socal 312	Precipitated calcium carbonate, coated, average particle diameter: 0.07 µm	Mineral component	Solvay	2.4

Table 5: Composition of the commercially available parquet adhesive SMP-930 (Stauf Klebstoffwerk GmbH; proportions in per cent by mass)

Patent Claims

1. Water-, solvent- and plasticizer-free, one-component parquet adhesive which is based on silane-terminated polyalkylene oxide oligomers, characterised in that it comprises no non-reactive liquid extenders and comprises the following materials or consists of them:
 - a) 12 to 36 per cent by mass of a moisture-reactive, silane-terminated polyalkylene oxide binding agent with an average molecular weight of 6,000 to 20,000 g/mol, the silane functions being bonded via alkyl groups to the oligomeric skeletal structure,
 - b) 2 to 18 per cent by mass of a moisture-reactive, silane-terminated polyalkylene oxide binding agent with an average molecular weight of 300 to 3,000 g/mol, the silane functions being bonded via alkyl groups to the oligomeric skeletal structure,
 - c) 30 to 60 per cent by mass of a surface-hydrophobised marble powder with an average particle diameter of 0.8 μm to 4.0 μm ,
 - d) 2 to 10 per cent by mass of a surface-hydrophobised chalk powder with an average particle diameter of 0.2 to 0.7 μm ,
 - e) 0.1 to 1.0 per cent by mass of a hardening catalyst,

- f) 0.2 to 3 per cent by mass of a moisture-reactive, silane-modified drying agent, and also
- g) 0.2 to 3 per cent by mass of a moisture-reactive, silane-modified adhesion promoter,

the percentage data relating to the mass of the ready-to-use parquet adhesive and the sum of the components a) to g) being 46.5% to 100%.

- 2. Water-, solvent- and plasticizer-free, one-component parquet adhesive according to claim 1, characterised in that it comprises no non-reactive liquid extenders and comprises the following materials or consists of them:

- a) 23 to 33 per cent by mass of a moisture-reactive, silane-terminated polyalkylene oxide binding agent with an average molecular weight of 7,000 to 13,000 g/mol, the silane functions being bonded via alkyl groups to the oligomeric skeletal structure,
- b) 7 to 13 per cent by mass of a moisture-reactive, silane-terminated polyalkylene oxide binding agent with an average molecular weight of 700 to 1,300 g/mol, the silane functions being bonded via alkyl groups to the oligomeric skeletal structure,
- c) 48 to 60 per cent by mass of a surface-hydrophobised marble powder with an average particle diameter of 1.0 μm to 3.0 μm ,

- d) 3 to 7 per cent by mass of a surface-hydrophobised chalk powder with an average particle diameter of 0.3 to 0.6 μm ,
- e) 0.15 to 0.29 per cent by mass of a hardening catalyst,
- f) 0.5 to 1.5 per cent by mass of a moisture-reactive, silane-modified drying agent, and also
- g) 0.5 to 1.5 per cent by mass of a moisture-reactive, silane-modified adhesion promoter,

the percentage data relating to the mass of the ready-to-use parquet adhesive and the sum of the components a) to g) being 82.15% to 100%.

- 3. Water-, solvent- and plasticizer-free, one-component parquet adhesive according to one of the preceding claims, characterised in that the mass ratio of component a) to component b) is 2 : 1 to 4 : 1 and the mass ratio of component c) to component d) is 8 : 1 to 18 : 1.
- 4. Water-, solvent- and plasticizer-free, one-component parquet adhesive according to one of the preceding claims, characterised in that the terminal silane groups of the silane-terminated polyalkylene oxide binding agent according to a) are dimethoxymethylsilane groups, the polymeric skeletal structure is polypropylene oxide and the average molecular weight is 10,000 g/mol.
- 5. Water-, solvent- and plasticizer-free, one-component parquet adhesive according to one of the claims 1 to 3, characterised in

that the terminal silane groups of the silane-terminated polyalkylene oxide binding agent according to b) are dimethoxymethylsilane groups, the polymeric skeletal structure is polypropylene oxide and the average molecular weight is 1,000 g/mol.

6. Water-, solvent- and plasticizer-free, one-component parquet adhesive according to one of the preceding claims, characterised in that the marble powder according to c) has an average particle size of 2.0 μm , and the chalk powder according to d) has an average particle size of 0.4 μm .
7. Water-, solvent- and plasticizer-free, one-component parquet adhesive according to one of the preceding claims, characterised in that the viscosity of the ready-to-use adhesive, measured according to DIN EN ISO 2555:2000-01 (20 revolutions per minute), is $91,200 \pm 6,300 \text{ mPa}\cdot\text{s}$.
8. Water-, solvent- and plasticizer-free, one-component parquet adhesive according to one of the preceding claims, characterised in that the shear strength on mastic asphalt, measured according to DIN EN 14293:2006-10 (storage type A), is $2.11 \pm 0.22 \text{ N/mm}^2$.
9. Use of the water-, solvent- and plasticizer-free, one-component parquet adhesive based on silane-terminated polyalkylene oxide oligomers according to one of the preceding claims for gluing parquet, wooden floor coverings and/or wood-based material boards to a sub-floor.
10. Use of the water-, solvent- and plasticizer-free, one-component parquet adhesive according to the preceding claim, characterised

in that the sub-floor is dry or moist and consists of mastic asphalt, concrete, cement, cement screed, cement liquid screed, cement mortar, cement-bonded wood fibre, ceramic, natural stone, calcium sulphate screed, calcium sulphate liquid screed, magnesite screed, wood, wood-based material, plywood, cork, gypsum, gypsum fibre, gypsum plasterboard, hardboard, knifing filler, textile fibrous material, polymeric material, primer and/or a combination of these sub-floors and the glued parquet, the wooden floor coverings and/or wood-based material boards are treated or untreated with treatment agents for wooden floor surfaces and consist totally or partially of European deciduous and/or coniferous types of timber, non-European types of timber or a combination of these types of timber.