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(54) Title: ADHESIVE COMPOSITION

(57) Abstract: The use of TiO_2 as a filler in an adhesive composition gives many advantages, mainly due to the small particle size, e.g. 0.2-0.4μm. Advantages include long storage life and pot life and low viscosity. It can also be used at extreme pHs, e.g. in acid compositions (e.g. containing $AlCl_3$) or in contact with alkaline cement. The adhesive compositions may comprise one or more of PVAc, PVOH, styrene-butadiene latex and crosslinkers such as polyisocyanates and polyaziridines.

ADHESIVE COMPOSITION

The present invention relates to an adhesive composition, to the preparation of the composition, to uses of the composition, and to products of such use. It is particularly but not exclusively concerned with adhesive compositions for wood and wood-based materials. Exemplary compositions include wood glues, wood sealers, putties, wood surface reinforcing agents, and impregnants for paper or card.

The present compositions find particular, but not exclusive, use as adhesives and binding, coating and sealing materials. They may be used in producing 'modified woods'.

In another aspect the invention provides a new use for titanium dioxide (TiO_2).

Many adhesives currently available, particularly for use in woodworking, contain polyvinyl alcohol (PVOH) or a dispersion of another polymer such as polyvinyl acetate (PVAc) in polyvinyl alcohol (PVOH). The adhesives operate by forming a physical bond with the wood substrate. In this respect the -OH groups in the adhesive composition and the -OH groups from cellulose in the wood substrate together form strong hydrogen bonds.

WO 96/37551 and US 5880183 (YEO) disclose adhesives in the form of a pack containing components A and B. Component A contains: (Ai) a solution or dispersion comprising a polymer containing units having hydroxyl groups, and (Aii) a polymer derived from an optionally substituted styrene monomer, said polymer containing units having carboxyl groups. Component B comprises (Bi) a polyfunctional aziridine crosslinker capable of crosslinking with at least one carboxyl group and at least one hydroxyl group. Preferably the component A includes polymers containing acetate groups, e.g. polyvinyl acetate homopolymers or copolymers, (e.g. an ethylene vinyl acetate copolymer or terpolymer), preferably as a dispersion with polyvinyl alcohol. The composition may contain a filler, for improving water resistance. Talc, silica, kaolin and calcium carbonate are exemplified.

US-A-3,931,088 (assigned to Kuraray Co., Ltd.) discloses an adhesive composition comprising (1) an aqueous solution of polyvinyl alcohol and (2) a hydrophobic solution of a polyisocyanate compound. Preferred further ingredients include an aqueous emulsion of vinyl acetate polymer and/or an aqueous latex of butadiene polymer such as an aqueous latex of a copolymer of styrene and butadiene or an aqueous latex of a

copolymer of acrylonitrile and butadiene. It states that urea resins, melamine-urea co-condensation resins and phenol resins are predominately used as the adhesives for making plywood. These adhesives are widely used because of their low price and relatively good water-resistance; however it had been found that such adhesives tend to release formaldehyde, so alternatives were desired. It is disclosed that fillers may be used: "suitable fillers include organic substances such as wood powder and powder of walnut shell, etc., as well as inorganic substances, such as clay, kaolin and talc, etc." The effect of the filler is stated to be: "not only to prevent excessive penetration of adhesive into the wood, but also to impart better water resistance and initial adhesive strength by reacting with the isocyanate".

The article on "Fillers" in "Concise Encyclopaedia of Polymer Science and Engineering", ed. J. I. Kroschwitz, USA, 1990, states that "Fillers include calcium carbonate (the most widely used filler for plastics, caulks, sealants and coatings), kaolin, talc, alumina trihydrate and organic fillers (e.g. ground by-products and waste products based on wood, shells and rice."

Titanium dioxide is widely used as a white pigment, in paints and other compositions. However its use as a

filler for adhesive compositions appears to be completely unknown. I have made extensive searches, e.g. of the websites of the main suppliers of TiO_2 materials (www.titanium.dupont.com, and www.huntsman.com) and textbooks (e.g. the Concise Encyclopaedia referred to above) without finding any references to such uses. This may be at least partly due to the cost of TiO_2 materials: about 10 times that of the usual clay-type fillers. However I have now discovered that the use of titanium dioxide as a filler in adhesive compositions can give substantial and unexpected advantages.

Thus in a first aspect the invention provides the use of a titanium dioxide (TiO_2) material as a filler in an adhesive composition. The adhesive composition generally comprises (a) a cross-linkable composition; and (b) a filler comprising titanium dioxide.

Generally the compositions of the invention employ synthetic adhesives such as hot melt, vinyl, rubber, urea, acrylic, polyethylene, epoxy and phenolic adhesives. Phenolic adhesives (including resorcinolic adhesives) are generally not preferred, as they tend to cure to highly coloured (usually deep red) products. Preferred adhesives are those taught in WO96/37551 (US 5880183) and US 3931088, which are incorporated herein by reference.

The cross-linkable composition may comprise one or more of the following components:

(a)(i) a polymer containing units having hydroxy groups;

(a)(ii) a polymer containing units having acetate groups;

(a)(iii) a polymer comprising styrene and/or butadiene and/or acrylonitrile derived units;

(a)(iv) a cross-linker suitable for linking groups on one or more other components of the composition and/or on the substrate (e.g. hydroxy groups on a carbohydrate-containing substrate such as paper or wood).

The cross-linkable composition may comprise urea resins, melamine-urea resins and phenol resin.

A component (a)(i) may comprise a solution of polyvinyl alcohol.

A component (a)(ii) may comprise a polyvinyl acetate homopolymer or copolymer, preferably an ethylene vinyl acetate copolymer or terpolymer.

A component (a)(iii) may be a latex. It may comprise a polymer derived from an optionally substituted styrene monomer. It may contain units having carboxy units. It may be an SBR latex. It may comprise a latex of an acrylonitrile/butadiene copolymer.

A compound (a)(iv) may comprise a polyisocyanate or a polyfunctional aziridine (e.g. as disclosed in WO 96/37551). This will generally be provided in a separate part of a two-part pack.

The composition may be an aqueous composition comprising a polyvinyl alcohol and an isocyanate, e.g. as disclosed in US 3931088.

The composition may be a pre-catalysed polyvinyl acetate (PVAc) composition, e.g. containing $AlCl_3$ catalyst.

In another aspect the invention provides an adhesive composition comprising (a) a cross-linkable composition and (b) a filler comprising titanium dioxide.

Titanium dioxide may be the only filler. More usually it will be used together with one or more other fillers which may be conventional fillers, generally of much larger particle size (e.g. kaolin, calcium carbonate). Usually titanium dioxide is a minor component of the total filler, e.g. 2-40% by weight, preferably 5-30%, more preferably 10-25%.

Titanium dioxide may be used as a filler in adhesive compositions which are intrinsically colourless or light coloured, so that there would be no reason to use it as a pigment. Indeed, compositions such as those taught in WO96/37551 and US 3931088 can be so pale (particularly

when admixed with TiO_2) that it is desirable to add pigments to darken and colour them so that they are less visible when used on wood. Of course different pigmentation may be appropriate for different woods.

The titanium dioxide preferably has particle sizes generally under 5μm, preferably under 2μm, and possibly even under 0.1μ, e.g. about 0.025μm. Material with particle sizes ranging from 0.2 to 0.4μm is widely available and generally suitable. (In comparison, materials conventionally used as fillers typically have particle sizes of 15-20μm.)

The titanium dioxide preferably constitutes 10-50% by weight of the solid content of the composition and/or at least 5% of total filler weight.

Use of titanium dioxide as a filler can offer one or more of the following advantages.

i) The small particle size tends to give a small rate of sedimentation and hence a relatively long storage life.

ii) The small particle size also leads to enhanced pot life or working life.

iii) Compositions can be of lower viscosity than corresponding compositions using only conventional fillers (due at least in part to particle size and/or smoothness). This can enable (a) use of thinner layers

of composition and hence economy; (b) better and more rapid spreading and penetration into gaps and pores. This can enhance anchoring, which may be particularly valuable with hardwoods which tend to be of low porosity. It can be very useful in the production of veneers, especially thin veneers (e.g. 0.25mm thick) where it can be used for reinforcing veneers to reduce susceptibility to splitting and/or for lamination of veneers.

iv) In a system also including larger particles (e.g. of conventional filler such as clay, and/or of polymer), the small particles can occupy interstices between the larger particles, leading to a reduction in capillary size. This can improve properties of the crosslinked product, e.g. stiffness, strength, and water and heat resistance.

v) Titanium dioxide is stable over a wide pH range (greater than pH3-10). Thus it is compatible with many adhesive compositions, e.g. compositions containing ammonium chloride, like many urea-formaldehyde resins. (Calcium carbonate and clays tend not to be suitable for acidic compositions. Therefore flour is commonly used, but this is prone to sedimentation). It can be used in producing plywood coatings for concrete moulding panels, where resistance to cement alkalinity is desirable.

vi) The particles can be smoother than conventional filler particles (e.g. clays). This can give lower water-absorbing capacity and hence faster setting.

vii) The compositions containing titanium dioxide can easily be pigmented so as to match a particular substrate (e.g. wood type). This is particularly useful for pale woods with exposed glue lines, and veneer laminates.

viii) The particles of TiO_2 are hard (6-7 mohs). This leads to enhanced stiffness and strength of the set compositions and of substrates bonded with it.

There are three crystalline forms of titanium dioxide: anatase, brookite and rutile. Rutile is preferred. Anatase may be used.

In one preferred type of embodiment, urea-formaldehyde ("UF") resin is compounded with a filler comprising titanium dioxide to uplift its bonding strength and setting speed and to reduce formaldehyde levels to achieve environmental compliance, e.g. for use for making bamboo composite flooring and some indoor materials. Titanium dioxide is also suitable to mix into pre-catalyzed polyvinyl acetate ("PVAc") to serve a similar purpose. Pre-catalyzed PVAc dispersions containing $AlCl_3$ or other metal salts have been particularly problematic because their highly acidic

nature (e.g. pH 3-4) prevents the use of conventional fillers. Thus it has not been possible using conventional fillers to achieve high solid contents. By using a filler comprising TiO_2, one can easily reach solid contents of 60% or more. This can give advantageous properties such as water and heat resistance, stiffness, gap-filling ability, and faster setting.

Another type of embodiment employs an aqueous polymer isocyanate, as disclosed in US 3,931,088. For example, diphenyl methanediisocyanate (MDI) may be used with a butadiene latex.

Some embodiments of the inventions and comparative examples will now be described.

Test 1: Glue Film Darkening of Aqueous Polymer Isocyanate Compositions

Formulation A was prepared with the following composition and characteristics:

Formulation A:

Carboxylated SBR latex (solid content : 50%) - 30 p.b.w.

Polyvinyl Acetate Dispersion (s.c. 55%) - 20 p.b.w.

Polyvinyl Alcohol Solution (s.c. 8%-9%)

(BP-17, partially hydrolysed, from Chang

Chung Taiwan) - 50 p.b.w.

Ground Calcium Carbonate (particle size : 20 microns) - 25 p.b.w.

Sodium dodecyl benzene sulfonate (s.c. 50%) - 0.3 p.b.w.

Solid content : approx 44%.

Viscosity : 2,500 cps.

pH : approx. 7.5.

Formulation B was prepared by homogeneously mixing 15% by weight of formula A into measured MDI - Lupranate M20S (supplied by BASF).

Surface portions (10 x 10 cm) of specimens of American hard maple wood were spread at a loading of 180g/m_2.

Sample API-1 received formulation A.

Sample API-2 received formulation B.

The samples were exposed to normal room conditions for 7 days.

Glue film results:

API-1 - white cloudy and very low opacity, wood grain clearly visible.

API-2 - light amber colour, almost transparent, wood grain clearly visible.

Test 2

This was a repetition of Test 1, except that MDI was replaced by Suprasec / Rubinate 9236 (water emulsifiable) from Huntsman Polyurethane.

Results: Same as Test 1.

Test 3

This was a repetition of Test 1 using samples API3 and 4, except that the filler (25 pbw calcium carbonate in Test 1) was replaced by 20 pbw calcium carbonate and 5 pbw titanium dioxide.

After 7 days, the glue films were fully opaque ivory white, and the wood grain was entirely invisible.

The presence of TiO_2 led to faster setting speed, and the cured glue films were more 'stiff-tough' than corresponding films of Test 1.

Conclusion: TiO_2 is able to elevate film strength, and also provide pigmentable environment for desired wood colours to reduce glue line visibility.

Test 4: Sedimentation

Specimens :

(I) Formulation A

(II) Formulation C - same as Formulation A, but reversing the levels of SBR latex and PVAc.

(III) Formulation D - same as Formulation A except fillers are fully employed TiO_2.

(IV) Formulation E - same as Formulation D, but reversing the levels of SBR latex and PVAc.

Testing Detail

All specimens placed in normal room conditions for 2 weeks.

Results: Specimen (I) - Slight sedimentation found.
Specimen (II) - Much more than specimen (I).
Specimen (III) & (IV) - No sedimentation found.

Test 5: Tests Complying with EN 204 Class D3

12 testpieces per test.

1. Test 5-1 - Formulation A-1

Carboxylated Styrene butadiene rubber latex (solid content 50%) - 35 p.b.w.

Polyvinyl acetate homopolymer dispersion (solid content 55%) - 41 p.b.w.

Ground calcium carbonate powder (20 micron/1,000 mesh) - 24 p.b.w.

Sodium dodecyl benzene sulfonate (neutralized) - 0.2 p.b.w.

Add Polyfunctional Aziridine crosslinker (CX-100 from Avecia) - 3 p.b.w.

Results : Average Lap Shear Strength.

Stage 1. After 7 days in normal room conditions - 12.4 N/mm^2

Stage 2. 4 days of 23°C cold water soaking - 3.6 N/mm^2

Stage 3. 7 days room conditions after stage 2 - 8.3 N/mm^2

2. Test 5-2 - Formulation A-2

Same as Formulation A-1 but fillers varied to ground calcium carbonate (20 pbw) & TiO_2 (4 pbw).

Results : Average Lap Shear Strength.

Stage 1. 13.6 N/mm^2

Stage 2. 4.2 N/mm^2

Stage 3. 8.8 N/mm^2

Setting speed and stiffness-toughness greater than for A-1 (withou TiO_2).

3. Test 5-3

Specimens : 2 pieces of American hard maple, surface measurement 6 x 6 cm.

Testing Details

(a) Specimen 3-3-1 coated with Formulation A-1 (crosslinked).

(b) Specimen 3-3-2 coated with Formulation A-2 (crosslinked).

7 days normal conditions and placed under direct sunlight for 6 hours/day consecutive for 7 days.

(a) Specimen 3-3-1 cloudy translucent off-white colour and light translucent amber colour after sunlight exposure.

(b) Specimen 3-3-2 white opaque colour even after sunlight exposure. No visible colour change.

Conclusion: Enhanced bonding strength and water resistance with the participation of TiO_2. Consistent colour before and after light exposure.

Glue film becomes pigmentable to desired colour, e.g. to match darker woods like rosewood and ebony to suppress visible glue lines.

4. Test 5-4: Setting Speeds

Formulations A-1 and A-2 were used as in test 5-1. They were used for bonding a maple wood veneer to medium density fibre board (MDF). The samples of veneer and MDF were of surface area 50x50cm. The veneer was of thickness 0.8mm (approximately). The MDF board was of thickness 15mm (approximately).

(1) Formulations A-1 and A-2 were applied to respective samples of the MDF board at approximately 180g/m^2. Immediately, samples of the veneers were laminated onto the MDF boards, and the laminates were pressed in a hot press

for 20 seconds at 112°C. They were then swiftly removed from the hot press.

Result: Both adhesives (A-1 and A-2) were fully set, and both veneers were successfully laminated on the MDF board.

(2) The procedure was repeated, except that the hot pressing time was reduced to 15 seconds.

Once again the formulation A-2 (including titanium dioxide) was fully set. It was difficult to separate the veneer from the MDF. When they were forced apart, there was obvious fibre tear.

However, the laminate employing formulation A-1 (without titanium dioxide) was not fully set. It was possible to lift up the veneer with little evidence of fibre tear.

Thus the inclusion of TiO_2 in the formulation led to faster setting speed. This could be used for substantial increase in productivity.

The easier setting of formulations embodying the invention can have other advantages too. Wood and other natural-type

and related materials (e.g. paper) tend to have a water content. This may be in equilibrium with atmospheric moisture. If the water content is reduced (e.g. by heating), and the material is subsequently returned to normal atmospheric conditions, it may tend to warp.

The fact that an adhesive formulation embodying the present invention may be set under milder conditions (e.g. lower temperature and/or lower heating time) means that its loss of water may be reduced, and the tendency to warp may thus be reduced.

CLAIMS:

1. An adhesive composition comprising (a) a synthetic adhesive selected from hot melt, vinyl, rubber, urea, acrylic, polyethylene and epoxy adhesives; and (b) a filler comprising titanium dioxide.

2. An adhesive composition according to claim 1 wherein the adhesive (a) comprises one or more of the following components:

(a)(i) a polymer containing units having hydroxy groups;

(a)(ii) a polymer containing units having acetate groups;

(a)(iii) a polymer comprising styrene and/or butadiene and/or acrylonitrile derived units;

(a)(iv) a cross-linker suitable for linking groups on one or more other components of the composition and/or on the substrate.

3. An adhesive composition according to claim 2 including a component (a)(i) comprising a solution of polyvinyl alcohol.

4. An adhesive composition according to claim 2 or 3 including a component (a)(ii) comprising a polyvinyl acetate homopolymer or copolymer.

5. An adhesive composition according to claim 2, 3 or 4 including a component (a) (ii) which comprises an ethylene vinyl acetate copolymer or terpolymer.

6. An adhesive composition according to claim 2, 3, 4 or 5 including a component (a)(iii) comprising a polymer derived from an optionally substituted styrene monomer.

7. An adhesive composition according to any of claims 2-6 including a compound (a)(iv) comprising a polyisocyanate or a polyfunctional aziridine.

8. An adhesive composition according to any preceding claim wherein the adhesive comprises one or more of urea resins and melamine-urea resins.

9. An adhesive composition according to any preceding claim wherein the titanium dioxide has particle sizes generally under 5μm.

10. An adhesive composition according to any preceding claim wherein the titanium dioxide has particle sizes generally under 2μm.

11. An adhesive composition according to any preceding claim wherein the titanium dioxide constitutes 10-50% by weight of the solid content of the composition and/or at least 5% of total filler weight.

12. An adhesive composition according to any preceding claim which includes a pigment for darkening the colour of the composition.

13. Use of titanium dioxide as a filler in an adhesive composition.

14. Use according to claim 13 wherein the adhesive composition is according to any of claim 1-12.

15. A substrate to which an adhesive composition according to any of claims 1-12 has been applied.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]: C09J 11/04, 109/06, 109/08, 113/02, 125/10, 129/04, 131/04, 163/00, 175/02,

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09J 11/04, 109/06,109/08, 113/02, 125/10, 129/04, 131/04, 163/00, 175/02

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT; JAPIO; Espace@net; IPC (above) and Keywords

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Accession No. 86-128626/20, Class A35 G03 (A18 A28), JP 61-066776 (NOK CORP. KK), 5 April 1986 See abstract	1-2, 4-15
X	CA 2357762 A (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN DE et al), 13 July 2000 Whole document	1-6, 9-11 & 13-15
X	US 6512039 A (MOWREY), 28 January 2003 Whole document	1-2, 4-8 & 11-15
X	EP 278642 A (LORD CORPORATION), 11 August 1993 Whole document	1-7, 11 & 13-15

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 May 2004	19 MAY 2004
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized officer **ALBERT S. J. YONG** Telephone No : (02) 6283 2160

INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2004/ 011569 A (STUMPHAUZER W. et al), 5 February 2004 Pages 3-14	1-3, 5-6, 9-11 & 13-15
X	Patent Abstracts of Japan JP 09-152616 A (SUMITOMO BAKELITE Co. Ltd.), 10 June 1997 See abstract & JP 09-152616 (whole document)	1-2, 8 & 9-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/SG2004/000059

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
JP	61066776		NONE				
WO	0040629	AU	20996/00	BR	9916667	CA	2357762
		CZ	20012247	DE	19959916	EP	1157053
		HU	0105161	PL	348505	US	6727305
		US	2004077761	ZA	200105362		
US	6512039	WO	03044115				
EP	0278642	AU	11431/88	JP	63196677	US	4855001
WO	04011569		NONE				
JP	09152616		NONE				

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX