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(54) **LIANT A BASE DE TANIN**
(54) **BONDING AGENT BASED ON TANNIN**

(57) The present invention relates to new bonding agents that harden at higher temperatures and are compatible with materials, such as wood, that contain cellulose, and are suitable for manufacturing wood materials such as chip boards. They consist of tannins and weakly acid reacting compounds.

Abstract

The present invention relates to new bonding agents that harden at higher temperatures and are compatible with materials, such as wood, that contain cellulose, and are suitable for manufacturing wood materials such as chip boards. They consist of tannins and weakly acid reacting compounds.

A Bonding Agent Based on Tannin

The present invention relates to new bonding agents that harden at higher temperatures and are compatible with materials, such as wood, that contain cellulose, and are suitable for manufacturing wood materials such as chip boards.

The use of tannins has been known throughout the course of the search for natural and in particular renewable raw materials for the manufacture of bonding agents for wood materials (J. Macromol. SCI.-Chem. A 16 (7), 1243-1250 (1981).

Despite good availability, the use of these tannins has not advanced since the tensile strength of wood materials bonded by tannins is unsatisfactory, particularly after moisture has had effect.

Although, in the past, the applicant developed a heat-hardened bonding agent containing tannin (DE 43 28 220.2), which hardens by the addition of an agent that liberates formaldehyde when heated, and results in wood materials of good strength and low swell values when stored in water, these good values were obtained solely with tannin from the pecan nut. In addition, in the event that agent that liberates formaldehyde is incorrectly metered, it is impossible to preclude formaldehyde separating off or being liberated after the pressing process.

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For this reason, it is the task of the present invention to make available agents that broaden the raw-material basis for bonding agents, which result in wood materials with enhanced mechanical properties, and at the same time display reduced or not separation of formaldehyde.

According to the present invention there is provided a thermohardening, tannin-based, formaldehyde-free bonding agent containing tannin of the polyflavonoid type and a hardening catalyst comprising a weakly acid reacting compound.

Weakly acid-reacting compounds are inorganic acids or, in an aqueous milieu, acid-reacting substances with a pka-value that is greater than 7.5.

Examples of such weakly acidic reagents are boric acid, aluminum trichloride, zinc dichloride, tin tetrachloride, or silicon dioxide.

As an example, after the addition of 6%-wt of the substances shown at room temperature, in each instance extracts of tannin from the pecan nut (Ph 9.55) will gel in the times shown below:

$AlCl_3$ (pka = 8.6), within 780 seconds

H_3Bo_3 (pka = 9.2), within 360 seconds

SiO_2 (pka = 10), within 49 seconds.

In the bonding agents according to the present invention, the preferred hardening catalyst is silicon dioxide, and

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this can be contained in a highly dispersed or crystalline form in a quantity of up to 10%-wt, preferably in a quantity of 1 to 6%-wt.

Examples of tannins of the polyflavonoid type are tannins from the pecan nut, the Pinus radiata (fir), Acacia mearnsii (mimosa), or Schinopsis balansae (quebracho), either alone or mixed with each other.

These bonding agents can be use to manufacture wood materials or working materials that are based on products that contain cellulose, when they are mixed with or sprayed onto products that contain cellulose, in particular wood chips, the mixture or the wetted products that contain cellulose are place in a mould, and processed therein at a temperature in the range from 150 to 210°C at a pressure that is within the range from 0.1 to 4MPa/mm^2.

Using such bonding agents, which are free of formaldehyde, it is possible to manufacture working materials whose tensile strength matches that of, for example, working materials bonded by phenolic resin, but whose resistance to moisture is higher, so that they are particularly suitable for use in an outside environment.

Of particular advantage is the fact that the tannins can also be used without any digesting treatment, as is frequently described in the literature.

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As an example, tannin from the pecan nut (Carya Illinoensis), a commercially available product that has long been used as a tanning agent, can be used.

It has been found that the Ph can be adjusted to various values in order harden the bonding agents according to the present invention. Hardening will take place both in the acid range
(Ph< 2) and in the alkaline range (Ph > 7.5). Adjustment of the Ph value also affects how much of the weakly acid reacting compound, in particular SiO_2 will have to be used as hardening catalyst in the bonding agent in order to achieve optimal hardening.

If, for example, 6%-wt SiO_2 is added to a pecan-nut tanning solution with a Ph value of 8.2, chip board panels manufactured with this mixture will display a maximum tensile strength of 0.55 MPa after a relatively long pressing time of 7.5 minutes. In contrast to this, if the same quantity of SiO_2 is added at a Ph value of 10.2, it is impossible to manufacture chip board, for such bonding agents harden too rapidly even at low temperatures. This means that the higher the Ph value is adjusted, the smaller the amount of SiO_2 that has to be added to the reactive tannins as hardening catalyst. This is so pronounced that a V 20 chip board panel (DIN), manufactured with pecan-nut tannin at a Ph value of 10.2, although with only 0.1 to 0.2%-wt SiO_2, displays a tensile strength of 0.71 Mpa after a pressing time of 7.5 minutes. In this case, even if the pressing time is reduced to 2 minutes (10 sec/mm), the

panels still display a tensile strength of 0.41 MPa, a value that is still satisfactory for V 20 panels.

This is different if tannins that are not so reactive are used. As an example, chip-board panels in which tannin from Mimosa bark (Acacia mearnsii) is used as the sole bonding agent, have a strength of only about 39 per cent of the tensile strength of a pecan-nut tannin panel. However, a strength that satisfies the demands imposed on V 20 panels can be achieved by the addition of approximately 3%-wt SiO_2.

Tannins from fir bark (Pinus radiata) are not very reactive on their own, but if they are mixed with pecan-nut tannin they become reactive enough in the presence of the SiO_2 hardening catalyst according to the present invention that they can be used as a bonding agent for products that contain cellulose. Even the addition of 10%-wt pecan-nut tannin is sufficient for an industrial application.

However, mixtures in which the proportion by weight of pecan-nut tannin to fir tannin is 30 : 70 to 50 : 50 are suitable, and pressing times of 10 sec/mm can be achieved with such mixtures.

At a mixing ratio of 30 : 70 to 35 : 75 parts by weight of pecan-nut tannin to fir tannin, it is possible to achieve satisfactory results when V 100 panels are manufactured. Shorter pressing times can, however, be achieved at mixing ratios between 35 : 75 to 40 : 60. Similar results were

achieved with quebracho tannin, which is of very low reactivity.

All in all, test with the bonding agents according to the present invention showed that, compared to urea-formaldehyde bonding agents, work can be done with much lower concentrations of bonding agent, and that pressing times are much shorter when higher concentrations of bonding agent are used.

In order to manufacture bonded products that contain cellulose, the tannins or the tannin mixtures are adjusted to the desired pH value, mixed with the products that contain cellulose and with the SiO_2, which can be either in crystalline or highly dispersed form, before said products are pressed to form the particular working material.

Usually, up to 10%-wt, in particular 1 to 6%-wt of the weakly acid reacting compound is used for bonding agents that are based on less reactive tannins, and in order to achieve shorter pressing times. Larger additions of hardening catalyst than 10%-wt have not been found to be useful, since no greater improvement can be achieved by so doing.

Appropriate products that contain cellulose are, for example, wood veneer, wood chips, cellulose-based fibres or straw, from which chip-board panels, plywood, or acoustic and thermal insulating panels are manufactured.

The working materials are produced such that the bonding agents according to the present invention are mixed with products that contain cellulose, the mixture is placed in a mould, and hardened under pressure at a temperature that is below the breakdown temperature of the tannin, preferably at 150 to 210°C. The pressure that is used is in the range from 0.1 to 4 MPa/mm^2.

Thus, for example, it is also possible to manufacture a three-ply chip-board panel at a pressure of 2 to 3.5 MPa/mm^2.

Depending on the working substance and strength that are desired, the quantity of bonding agent will be in the range from 4 to 20%-wt, relative to the product that contains the cellulose. The bonding agent can be in the form of a solution of the components in water, alcohol, or in an alcohol/water mixture.

The tables that follow show the bonding agents according to the present invention when used to manufacture chip-board panels, using highly dispersed SiO_2 (Aerosil®) as a hardening accelerator. Wood chips are sprayed with an alcohol/water solution that contains 11%-wt bonding agent, relative to the weight of the wood chips that are used, and then dried. Subsequently, they are formed into panels in the manner known per se (2.5 N/mm^2; 195°C) measuring 400 x 350 x 12 mm, pressed, and hardened.

T A B L E S

Table 1

The effect of the quantity of SiO_2 that is added on pecan-nut tannin as a bonding agent for chip-board panels 12 mm thick, at a Ph of 8.2 and after a pressing time of 7.5 minutes.

	Transverse Tensile Strength		
% SiO_2	(Dry) [MPa]	Density [g/cm^3]	Moisture [%]
0	0.230	0.706	13
3	0.329	0.792	14
6	0.547	0.702	15
9	0.356	0.703	14
18	0.343	0.700	22

Table 2

The effect of the quantity of SiO_2 that is added on mimosa tannin as a bonding agent for chip-board panels, 12 mm thick, at a pH value of approximately 10, and after a pressing time of 7.5 minutes.

	Transverse Tensile Strength		
% SiO_2	(Dry) [MPa]	Density [g/cm^3]	Moisture [%]
0	0.160	0.699	20
3	0.475	0.698	18
6	0.449	0.699	20
9	0.385	0.701	21

Table 3

The effect of the mixing proportions of pecan-nut tannin and fir tannin at a pH of 1.02 and after a pressing time of 7.5 minutes on the properties of chip-board panels, 12 mm thick.

Transverse Tensile Strength

Pecan-nut Tannin [%]	Fir Tannin [%]	(Dry) [MPa]	Density [g/cm^3]	Moisture [%]
100	0	0.710	0.705	21
50	50	0.530	0.704	22
40	60	0.555	0.705	22
30	70	0.590	0.699	22
20	80	0.535	0.704	22
10	90	0.450	0.704	22
0	100	0.185	0.698	17

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A thermohardening, tannin-based, formaldehyde-free bonding agent containing tannin of the polyflavonoid type and a hardening catalyst comprising a weakly acid reacting compound, said bonding agent containing tannins from the pecan nut, Pinus radiata, Acacia mearnsii (mimosa), or Schinopsis balansae (Quebracho), either alone or in mixture.

2. The bonding agent as claimed in Claim 1, wherein the hardening catalyst comprises SiO_2.

3. The bonding agent as claimed in Claim 1, wherein the hardening catalyst comprises boric acid.

4. The bonding agent as claimed in Claim 1, containing hardening catalyst in a quantity of up to 10% by weight of said bonding agent.

5. The bonding agent as claimed in Claim 1, containing hardening catalyst in a quantity from 1 to 6% by weight of said bonding agent.

6. The bonding agent as claimed in Claim 2, having a pH value from 0 to 2.

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7. The bonding agent as claimed in Claim 2, having a pH value from 7.5 to 14.

8. The use of thermohardening bonding agents as claimed in any one of Claims 1 to 7, for the manufacture of wood materials or working materials based on products that contain cellulose.

9. A method of manufacturing a working material, comprising mixing a bonding agent as defined in any one of Claims 1 to 7 with products that contain cellulose, placing the resulting mixture in a mould, and processing said mixture therein at a temperature in the range from 150 to 210°C and at a pressure in the range from 0.1 to 4 MPa/mm^2.