AUSTRALIA 675575
Patents Act 1990

PATENT REQUEST: STANDARD PATENT/PATENT OF ADDITION

We, being the person(s) identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

[71] Applicant: **RÜTGERS AKTIENGESELLSCHAFT (formerly RÜTGERSWERKE AKTIENGESELLSCHAFT)**

Address: **MAINZER LANDSTRASSE 217, D-60326 FRANKFURT/MAIN, GERMANY**

[70] Nominated Person: **BAKELITE AG**

Address: **GENNAER STRASSE 2-4, D-58642 ISERLOHN-LETMATHE**

[54] Invention Title: TANNIN-BASED BONDING AGENTS ~~A METHOD OF PRODUCING A WOOD-DERIVED MATERIAL~~

[72] Names of actual inventors: **ANTONIO PIZZI, WILLI ROLL and BERTHOLD DOMBO**

[74] Address for service in Australia: c/o WATERMARK PATENT & TRADEMARK ATTORNEYS, of 290 Burwood Road, Hawthorn, Victoria 3122, Australia.

Attorney Code: **WM**

BASIC CONVENTION APPLICATION(S) DETAILS

[31] Application Number	[33] Country	Country Code	[32] Date of Application
P43 34 962.5	GERMANY	DE	13 OCTOBER 1993
P44 06 825.5	GERMANY	DE	2 MARCH 1994

Basic Applicant(s): Rütgerswerke Aktiengesellschaft

Drawing number recommended to accompany the abstract .....

RÜTGERS AKTIENGESELLSCHAFT
By our Patent Attorneys
WATERMARK PATENT & TRADEMARK ATTORNEYS

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Louis C. Gebhardt
Registered Patent Attorney

25 January 1996.

P/00/008b 12/11/91
Section 29 (1)
Regulation 3.1 (2)

AUSTRALIA

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NOTICE OF ENTITLEMENT

(To be filed before acceptance)

We, **RÜTGERS AKTIENGESELLSCHAFT** (formerly **RÜTGERSWERKE AKTIENGESELLSCHAFT)** of Mainzer Landstrasse 217, D-60326 Frankfurt/Main, Germany, being the applicant in respect of Application No. 74324/94 state the following:-

Person nominated for the grant of the patent has entitlement from the actual inventors by mesne assignment.

The person nominated for the grant of the patent has entitlement from the applicant of the basic applications listed on the patent request form by assignment.

The basic applications listed on the request form are the first applications made in a Convention country in respect of the invention.

RÜTGERS AKTIENGESELLSCHAFT

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

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Louis C. Gebhardt
Registered Patent Attorney

25th January, 1996

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(Date)

AU9474324

(12) PATENT ABRIDGMENT (11) Document No. AU-B-74324/94
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 675575

(Modified Examination)

(54) Title
TANNIN-BASED BONDING AGENTS

International Patent Classification(s)
(51)[5] **C09J 199/00**

(21) Application No. : **74324/94** (22) Application Date : **30.09.94**

(30) Priority Data

(31) Number	(32) Date	(33) Country
4334962	13.10.93	DE GERMANY
4406825	02.03.94	DE GERMANY

(43) Publication Date : **04.05.95**

(44) Publication Date of Accepted Application : **06.02.97**

(71) Applicant(s)
RUTGERS AKTIENGESELLSCHAFT

(72) Inventor(s)
ANTONIO PIZZI; WILLI ROLL; BERTHOLD DOMBO

(74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122

(57) Claim

1. A thermosetting, formaldehyde-free bonding agent with a tannin base, characterized in that it contains tannin of the polyflavonoid type, and a compound with a weak acid reaction as a curing catalyst.

8. A thermosetting bonding agent in accordance with any one of claims 1 to 7, characterized in that said bonding agent contains tannins of the pecan nut, Pinus radiata, Acacia mearnsii (mimosa), or Schinopsis balansae (quebracho), singly or a mixture.

P/00/011 20/5/91
Regulation 3.2(2)

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ORIGINAL

COMPLETE SPECIFICATION

STANDARD PATENT

Application Number:

Lodged:

Invention Title: TANNIN-BASED BONDING AGENTS
~~BINDERS BASED ON TANNIN~~

The following statement is a full description of this invention, including the best method of performing it known to us :-

TANNIN-BASED BONDING AGENTS

The invention relates to new bonding agents that will cure at higher temperatures, are compatible with materials containing cellulose, such as wood, and are suitable for the production of wood-derived products such as particle boards.

In the context of the search for natural - and especially renewable - raw materials for the production of bonding agents for wood-derived materials, the use of tannins is known in the art (J. Macromol. SCI.-Chem. A 16 (7), 1243-1250 (1981)).

In spite of their good availability, however, the use of tannins has not become generally established, because the tensile strength of tannin-bonded wood derived materials, particularly after they have been subjected to moisture, is not satisfactory.

The applicant has previously developed a thermosetting, tannin-based bonding agent (NZ 264187) which cures after the addition of an agent that splits off formaldehyde when heated, and which results in wood-derived materials that have good tensile strength and low swelling values when stored in water; however, these good values are only achieved when tannin from the pecan nut is used. Moreover, if the proportioning of the formaldehyde-separating agent is done incorrectly, the possibility of formaldehyde separation or release after pressing cannot be entirely excluded.

It is therefore the aim of the present invention to make available an agent which will widen the raw-materials base for bonding agents, will lead to wood-derived materials with improved mechanical properties, and will at the same time reduce or eliminate formaldehyde separation.

According to the present invention there is provided a thermosetting, formaldehyde-free bonding agent with a tannin base, characterized in that it contains tannin of the polyflavonoid type and a compound with a weak acid reaction as a curing catalyst.

The solution lies in:

a bonding agent consisting of a tannin of the polyflavonoid type and a compound with a weak acid reaction which serves as a curing-catalyst, in accordance with claims 1 to 8;

the use of this bonding agent for the production of wood-derived materials or materials based on cellulose-containing products ("cellulosic products") in accordance with claim 9;

and a method of producing these materials in accordance with claim 10.

Compounds with a weak acid reaction are: inorganic acids, or substances with an acid reaction in an aqueous medium, with a pK_a value of more than 7.5.

Examples of such compounds with a weak acid reaction are: boric acid, aluminium trichloride, zinc dichloride, tin tetrachloride, and silicon dioxide.

Thus, extracts of e.g. pecan-nut tannin (pH 9.55) jell at ambient temperature, after the addition of
6% by weight of $AlCl_3$ (pK_a = 8.6), within 780 seconds;
" " " " H_3BO_3 (pK_a = 9.2), within 360 seconds;
" " " " SiO_2 (pK_a = 10), within 49 seconds.

The preferred curing-catalyst in the bonding agent according to the invention is silicon dioxide, which can be present in a microdispersed or crystalline form at a concentration of up to 10% by weight, and preferably 1 to 6% by weight.

Examples of tannins of the polyflavonoid type are: tannins from the pecan nut, *Pinus radiata* (a pine), *Acacia mearnsii* (a mimosa), or *Schinopsis balansae* (a quebracho) – used alone or in combination with one another.

These bonding agents can be used for the production of wood-derived materials or other materials based on cellulosic products, as follows: the bonding agents are mixed with cellulosic products or sprayed onto cellulosic products, particularly wood chips; and then the mixture or the wetted cellulosic products are put into a forming-mould where they are treated at a temperature of 150 to 210°C and a pressure of 0.1 to 4 MPa/mm^2.

By means of such formaldehyde-free bonding agents, materials can be produced whose tensile strength corresponds to that of materials bonded with e.g. phenolic resin, but whose moisture resistance is greater, thus making them particularly suitable for use outdoors.

Of particular advantage is the fact that the tannins can also be used without a breakdown treatment such as has been frequently described in the literature.

For example, it is possible to use the commercially available tannin from the pecan nut (*Carya illinoensis*), which has long been in use, mainly as a tanning agent.

It has been found that for the production of the bonding agent according to the invention, the pH value can be adjusted to different values. Curing can be achieved both in the acid range (pH < 2) and in the alkaline range (pH > 7,5). The setting of the pH value affects how much of the compound with a weak acid reaction, particularly SiO_2, has to be used as a curing catalyst in the bonding agent in order to obtain optimal curing.

If, for example, 6% by weight of SiO_2 is added to a pecan-nut tannin solution with a pH of 8.2, particle boards produced using this mixture attain a tensile-strength maximum value of 0.55 MPa after a relatively long pressing time of 7.5 minutes. If, on the other hand, the same amount of SiO_2 is added but the pH is 10.2, particle-board production is no longer possible, because such bonding agents cure too rapidly, and at a low temperature. This means that the higher the pH, the less SiO_2 (curing-catalyst) has to be added to reactive tannins. This effect is so marked that a V 20 particle board (DIN) produced with a pecan-nut tannin at a pH of 10.2 but with only 0.1 to 0.2 % by weight of SiO_2 added, has 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 particle boards still have a tensile strength of 0.41 MPa, i.e. they are still satisfactory for V 20 boards.

The situation is different when less-reactive tannins are used. For example particle boards in which tannin from mimosa bark (*Acacia mearnsii*) is used as the sole bonding agent have only about 39% the strength of a pecan-nut tannin board. However, the addition of approx. 3% SiO_2 by weight gives sufficient strength to satisfy the requirements to be met by V 20 boards.

Tannins from pine bark (*Pinus radiata*) are very sluggish in reaction when used on their own, but if they are mixed with pecan-nut tannin then they too are sufficiently reactive for use as a bonding agent for cellulosic products in the presence of the SiO_2 curing-catalyst according to the invention. The addition of just 10% pecan-nut tannin by weight is sufficient for industrial use.

However, mixtures in which the ratio of pecan-nut tannin to pine tannin is from 30:70 to 50:50 are particular suitable, and enable pressing times of 10 sec/mm to be achieved.

With a mixing ratio of from 30:70 to 35:75 parts by weight of pecan-nut tannin to pine-tannin, satisfactory results are also achieved in the production of V 100 boards. Shorter pressing times can however be achieved with mixing ratios of between 35:75 and 40:60. Similar results were achieved with the very sluggishly reacting tannin of the quebracho.

Overall the tests carried out with the bonding agent according to the invention showed that considerably lower bonding-agent concentrations can be used compared with urea-formaldehyde bonding agents, and that pressing times are considerably reduced by the use of higher concentrations of bonding agent.

For the production of bonded cellulosic products, the tannins or mixture of tannins are brought to the desired pH, and are mixed with the compound having a weak acid reaction

– particularly SiO_2 in crystalline or microdispersed form – and with the cellulosic products; and then these are pressed to produce the desired materials.

Usually 10% by weight, and especially 1 to 6% by weight, of the compound with a weak acid reaction is used for bonding agents based on less-reactive tannins and for the achievement of short pressing times. The addition of more than 10% by weight of the curing-catalyst has been found to be pointless, because no further improvement is obtained.

Suitable products containing cellulose are, for example, wood veneers, wood chips, cellulose-based fibres or even straw; from which particle boards, plywood, or sound-absorbing or heat-insulating boards are produced.

The production of the materials is performed as follows: the bonding agent according to the invention is mixed with cellulosic products, the mixture is put into a forming-mould, and is cured under pressure at a temperature below the decomposition temperature of the tannin, preferably 150 to 210°C. The pressure used is from 0.1 to 4 MPa/mm^2, depending on the material used and the desired density.

For example, it is even possible to produce three-layer particle boards, using a pressure of 2 to 3.5 MPa/mm^2.

The amount of bonding agent used, relative to the amount of cellulosic product, lies in the range from 4 to 20% by weight, depending on the desired material and the desired strength of the latter. The bonding agent can be used as a solution of its components in water, alcohol, or an alcohol-water mixture.

The following tables show the use of the bonding agent of the invention for the production of particle boards, using microdispersed SiO_2 (Aerosil® 200) as the curing accelerator.

Wood chips are sprayed with an aqueous-alcoholic solution containing 11% of bonding agent by weight relative to the weight of the wood chips used. The chips are dried, and then moulded, ssed, and cured in a manner known in the art (2.5 N.mm^{-4}, 195°C) to produce boards of 400 x 350 x 12 mm.

TABLES

Table 1

Effect of the amount of SiO_2 added, on pecan-nut tannin used as bonding agent for particle boards 12 mm thick, at a pH of 8.2 and with a pressing time of 7.5 minutes.

% SiO_2	Transverse tensile strength (dry) (MPa)	Density (g/cm^3)	Moisture (%)
0	0.230	0.706	13
3	0.329	0.702	14
6	0.547	0.702	15
9	0.356	0.703	14
18	0.343	0.700	22

Table 2

Effect of the amount of SiO_2 added, on mimosa tannin used as bonding agent for particle boards 12 mm thick, at a pH of approx. 10 and with a pressing time of 7.5 minutes.

% SiO_2	Transverse tensile strength (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

Effect of the mixing ratio of pecan-nut tannin to pine tannin on the properties of particle boards 12 mm thick, with a pH of 10.2 and a pressing time of 7.5 minutes.

Pecan-nut tannin (%)	Pine tannin (%)	Transverse tensile strength (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	0.150	0.704	22
0	100	0.185	0.698	17

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A thermosetting, formaldehyde-free bonding agent with a tannin base, characterized in that it contains tannin of the polyflavonoid type, and a compound with a weak acid reaction as a curing catalyst.

2. A bonding agent in accordance with claim 1, characterized in that it contains SiO_2 as the curing catalyst.

3. A bonding agent in accordance with claim 1, characterised in that it contains boric acid as the curing catalyst.

4. A bonding agent in accordance with any one of claims 1 to 3, characterized in that the amount of curing catalyst that it contains is up to 10% by weight.

5. A bonding agent in accordance with any one of claims 1 to 3, characterized in that the amount of curing catalyst that it contains is from 1 to 6% by weight.

6. A bonding agent in accordance with claim 2, characterized in that it has a pH of 0 to 2.

7. A bonding agent in accordance with claim 2, characterized in that it has a pH of 7.5 to 14.

8. A thermosetting bonding agent in accordance with any one of claims 1 to 7, characterized in that said bonding agent contains tannins of the pecan nut, Pinus radiata, Acacia mearnsii (mimosa), or Schinopsis balansae (quebracho), singly or a mixture.

9. The use of thermosetting formaldehyde-free bonding agents in accordance with any one of claims 1 to 8 for the production of wood-derived materials or materials based on products containing cellulose.

10. A method of producing a wood-derived material, characterized in that a bonding agent according to any one of claims 1 to 8 is mixed with a cellulose-containing product and the mixture is introduced into a forming-mould where it is treated at a temperature of from 150 to 210°C and a pressure of from 0.1 to 4 MPa/mm^2

11. A bonding agent according to claim 1 substantially as herein described or exemplified.

12. A method according to claim 10 substantially as herein described or exemplified.

DATED this 11th day of January, 1996

RUTGERSWERKE AKTIENGESELLSCHAFT

WATERMARK PATENT & TRADEMARK ATTORNEYS
290 BURWOOD ROAD
HAWTHORN VICTORIA 3122
AUSTRALIA

LPS/MED/SH DOC 6 AU7432494.WPC

A b s t r a c t

The invention relates to new binders which are hardenable at higher temperatures and compatible with cellulose-containing materials, e.g. wood, and are suitable for the preparation of derived timber products such as particle board. They consist of tannins and compounds with weakly acid reactivity.