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(54) **AGENTS LIANTS THERMODURCISSABLES**

(54) **THERMOSETTING BONDING AGENTS**

(57) Thermosetting bonding agents for products that contain cellulose contain tannin and a substance that releases formaldehyde when heated. The working materials produced with them display good strength and low swell values after storage in water.



## ABSTRACT

Thermosetting bonding agents for products that contain cellulose contain tannin and a substance that releases formaldehyde when heated. The working materials produced with them display good strength and low swell values after storage in water.

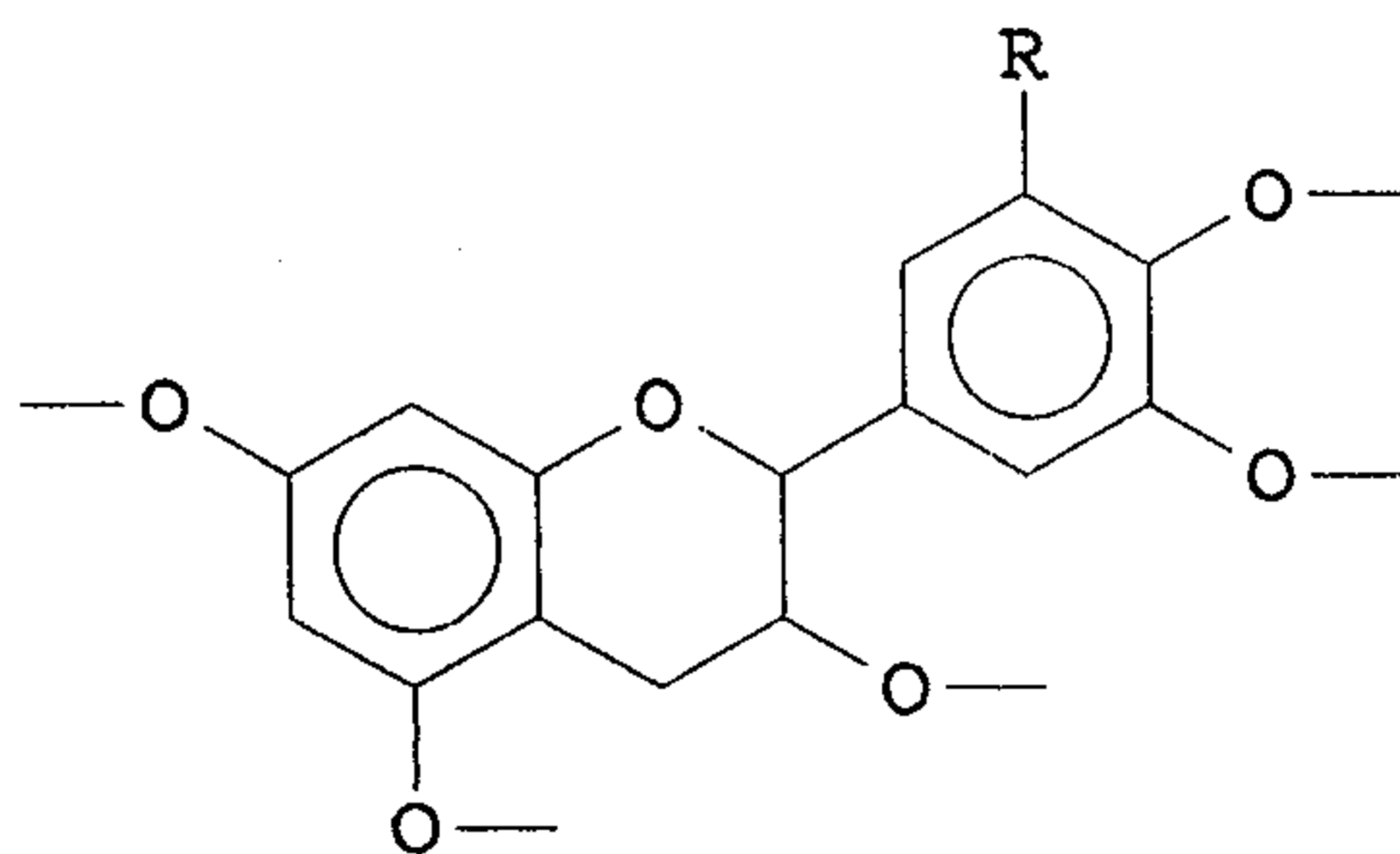
The present invention relates to bonding agents that can be hardened when heated, that are compatible with wood and other products that contain cellulose, and which are suitable, in particular, for manufacturing wood materials, such as, for example, chipboard.

In the course of the search for natural and, in particular, for renewable resources for manufacturing bonding agents for wood materials, it has also been found that tannins can be used (J. Macromol. SCI.-Chem. A 16 (7), 1243-1250 (1981)).

Despite good availability, they have not been widely used because the tensile strength of wood materials that are bonded with tannin is not satisfactory, particularly after such products have been stored in water.

For this reason, it is an object of the present invention to describe a bonding agent that is based on tannin, with which wood materials having significantly improved mechanical properties can be manufactured.

It has been found that tannins that contain units of the general structure



wherein R represents hydrogen or a hydroxy group and the free bonds at the oxygen radicals are either saturated with hydrogen or are bonds to other molecular groups such as sugar radicals or radicals of other or identical polyvalent compounds with phenolic hydroxyl groups, display a bonding capability that is superior in comparison to other tannins if they are used together with a material that liberates formaldehyde when heated and are used as a bonding agent for products that contain cellulose. Tensile strength increases and achieves values as are found, for example, in the case of corresponding materials that are bonded with phenol resin. The reduction of transverse tensile strength after storage in water is clearly reduced, and swelling values in boiling water are similarly reduced.

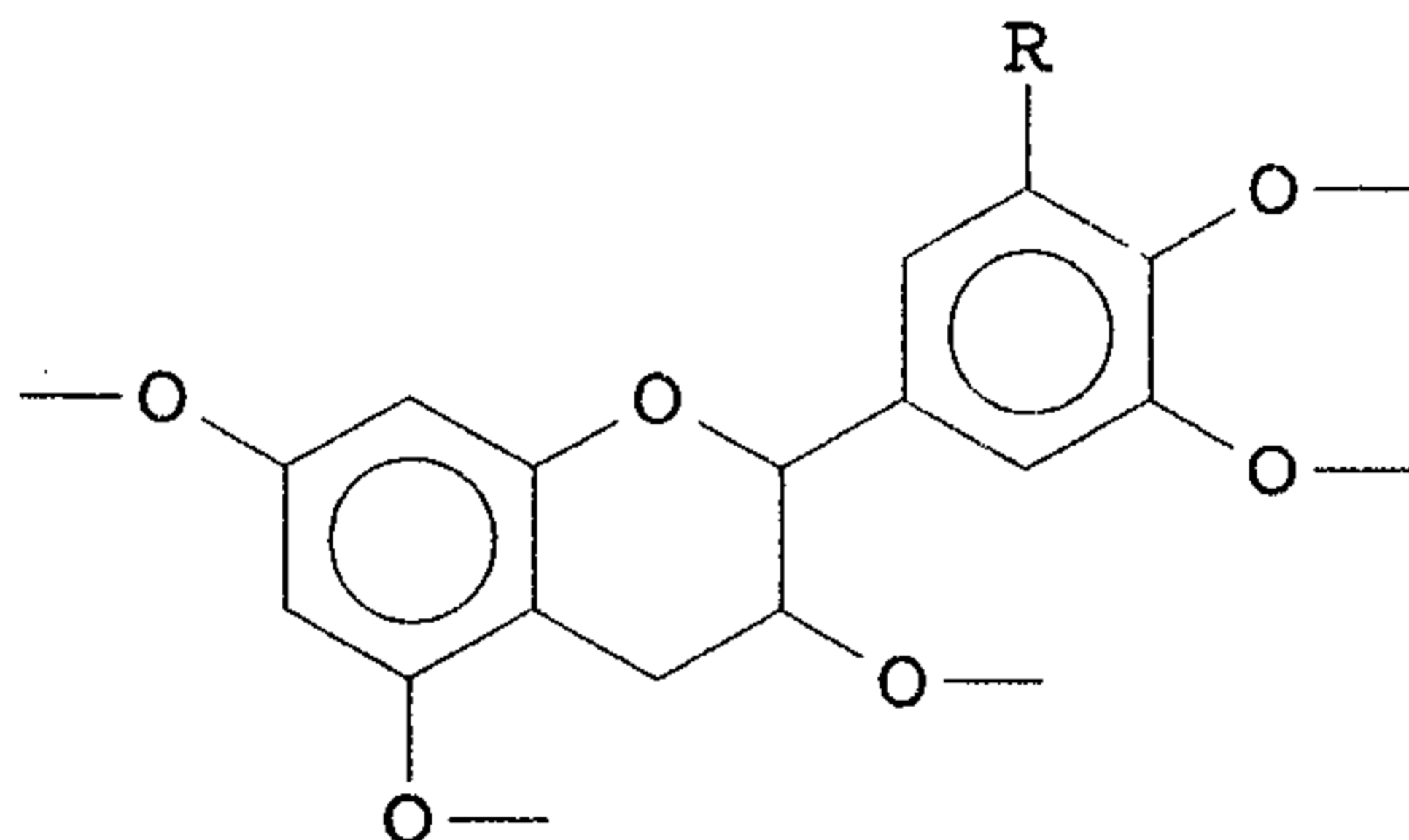
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In this regard, it is an added advantage that these tannins can be used without prior breakdown treatment as is known in the case of other tannins.

Suitable tannins are those from the group of procyanidines and prodelpinidines, in particular tannin from pine bark or from the pecan nut. Although mixtures of these tannins with, for example, minosa or quebracho tannin in the ratio of 2:5 to 5:2 have a longer hardening time, they cannot, however, be used. These tannins are commercially available products and up to now have been used mainly as tanning agents. Commercial quality is adequate for use as foreseen in the present invention.

Substances that liberate formaldehyde when heated are, for example, paraformaldehyde, trioxane and, in particular, hexamethylenetetramine (hexa).

- 5 In the simplest case, the thermosetting bonding agents according to the present invention are mixtures of tannin that contains structural units of the formula



- 10 and a substance that releases formaldehyde when heated, the proportion of material that releases formaldehyde, in particular hexamethylenetetramine, amounting to 3.0 to 9%-wt, relative to the tannin.

- 15 However, it is also within the scope of the present invention if, in addition to the special types of tannin and a substance that releases formaldehyde when heated, the bonding agent also contains up to 50%-wt of a novolak or up to 20%-wt of an isocyanate compound that is at least  
 20 difunctional, such as, for example, diisocyanatonaphthaline, 4,4',4''-triisocyanato-triphenylmethane, isophoron-, toluol- or hexamethylene- diisocyanate or diisocyanato-diphenylmethane (MDI), when, in practical use, the di- or  
 25 cellulose in parallel with the dry mixture of the tannin

that is used according to the present invention and the substance that releases formaldehyde when heated, before these are pressed to form the appropriate materials.

5 Suitable products that contain cellulose are, for example, wood chips, fibres based on cellulose, such as, for example, cotton or flax, or straw, from which chipboards, textile fleeces, or accoustic and thermal insulating panels are produced.

10

The materials are manufactured in such a way that the bonding agents according to the present invention are mixed with products that contain cellulose, the mixture is placed in a mould, and then hardened under pressure at a  
15 temperature that is above the decomposition temperature of the substance that releases the formaldehyde and below the decomposition temperature of the tannin, preferably at 150 to 210°C. Depending on the working material that is used and the thickness that is desired, the pressure will be in  
20 the range from 0.1 to 4 MPa/mm<sup>2</sup>. Because it is possible, for example, to manufacture three layered chipboards, with a pressure of 2 to 3.5 MPa/mm<sup>2</sup>.

Depending on the desired material and the desired strength,  
25 the quantity of bonding agent will in the range of 4 to 20%-wt, relative to the product that contains the cellulose. The bonding agent can be in the form of a solid mixture or as a solution of the components in water, alcohol, or water-alcohol mixtures.

30

Suitable solutions can be stored at room temperature for several weeks without any major increase in viscosity. In the case of aqueous solutions, it is recommended that a fungicide be added in order to prevent the formation of  
5 fungus.

The following examples illustrate the binding agent according to the present invention, as used to manufacture chipboards.

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#### Example

Woodchips are sprayed with a water-alcohol solution that contains bonding agent at the rate of 11%-wt of the wood,  
15 and these are then dried. Subsequently, they are formed in the usual manner (2.5 N/mm<sup>2</sup>; 195°C) to form panels measuring 400 x 350 x 12 mm, pressed, and hardened.

Density, transverse tensile strength of the panels, a. dry  
20 and b. after storage in water (2 hours in boiling water, subsequently dried for 16 hours at 105°C) as well as the swell thickness are determined after 2 hour storage in boiling water, with various mixture proportions of the bonding agent components, the quantity of bonding agent, and  
25 the press time.

#### Examples 1 - 5

In Example 1, the proportion of hexamethylenetetramine  
30 varies from 7.5 to 5.5% of the bonding agent. The

proportion of pecan nut tannin varies accordingly, from 92.5 to 94.5%.

In Example 2, the proportion of hexamethylenetetramine relative to the tannin, amounts to 6.4%, i.e., the proportion of pecan nut tannin is 93.6%. The press time is varied.

Example 3 shows values for a three-layer chipboard at 6.4% hexamethylenetetramine in the bonding agent, and with a bonding agent content of 10% in the inner layers, and 12% in the outer layers.

Examples 4 and 5 show values that are analogous to Examples 1 and 2 when mimosa (wattle) tannin is used.

The following tables show the values that were obtained:

## TABLES

| 5  |  | Example 1              |      |      | Example 4    |      |
|----|--|------------------------|------|------|--------------|------|
|    |  | Hexamethylenetetramine |      |      | (comparison) |      |
|    |  | 7.5%                   | 6.4% | 5.5% | 7.5%         | 6.5% |
| 10 | Press time<br>[sec/mm]   | 17.5                   | 17.5 | 17.5 | 17.5         | 17.5 |
|    | Density<br>[kg/m <sup>3</sup> ]                                      | 729                    | 730  | 736  | 731          | 711  |
| 15 | Transverse<br>tensile strength,<br>dry<br>[MPa]                      | 0.82                   | 0.81 | 0.79 | 0.45         | 0.43 |
| 20 | Transverse<br>tensile strength<br>after storage<br>in water<br>[MPa] | 0.25                   | 0.27 | 0.26 | 0.09         | 0.07 |
| 25 | Swelling<br>[%]  | 25.0                   | 23.9 | 22.1 | 32.1         | 31.5 |
| 30 | HCHO emission<br>[mg/100 g; WKI]                                     | 1.71                   | 1.45 | 0.84 | 2.01         | 1.87 |

|    | Example 2<br>(6.4% hexa)   |      |      | Example 5<br>(comparison)<br>(6.5% hexa) |      |      |
|----|--|------|------|--|------|------|
| 5  | Press time<br>[sec/mm]<br>12.5   | 17.5 | 12.5 | 8.5                                      | 30.0 | 17.5 |
| 10 | Density<br>[kg/m <sup>3</sup> ]<br>722                                       | 730  | 738  | 733                                      | 714  | 731  |
| 15 | Transverse<br>tensile strength,<br>dry<br>[MPa]<br>0.41                      | 0.81 | 0.75 | 0.67                                     | 0.5  | 0.45 |
| 20 | Transverse<br>tensile strength<br>after storage<br>in water<br>[MPa]<br>0.03 | 0.27 | 0.19 | 0.17                                     | 0.13 | 0.09 |
| 25 | Swelling<br>[%]<br>36.7  | 23.9 | 22.4 | 20.9                                     | 29.7 | 32.1 |
| 30 | HCHO emission<br>[mg/100 g; WKI]<br>1.28                                     | 1.45 | 1.32 | 1.1                                      | 1.64 | 2.01 |

## Example 3

|    |  |       |
|----|--|-------|
|    | Press time<br>[sec/mm]   | 12.5  |
| 5  | Bonding agent [%]<br>middle-/cover<br>layers                         | 10/12 |
| 10 | Moisture - chips<br>after coating [%]<br>middle-/cover<br>layer      | 28/26 |
| 15 | Density<br>[kg/m <sup>3</sup> ]                                      | 723   |
| 20 | Transverse<br>tensile strength,<br>dry<br>[MPa]                      | 0.83  |
| 25 | Transverse<br>tensile strength<br>after storage<br>in water<br>[MPa] | 0.27  |
| 30 | Swelling<br>[%]  | 22.1  |
|    | HCHO emission<br>[mg/100 g; WKI]                                     | 1.4   |

## Example 6

Single layer chipboards were produced and tested according to the general description for the examples (press time 15  
5 s/mm at 190°C, 2.5 N/mm<sup>2</sup>).

## Bonding agent:

|    |                        |                      |
|----|------------------------|----------------------|
|    | Tannin from pine bark  |                      |
| 10 | (37% aqueous solution) | 337 parts by weight  |
|    | Hexamethylenetetramine |                      |
|    | (40% aqueous solution) | 19.3 parts by weight |
|    | Zinc acetate           |                      |
|    | (25% aqueous solution) | 19.3 parts by weight |
| 15 | Water                  | 10 parts by weight   |

## Results:

|    |  |      |
|----|--|------|
|    | Density (kg/m <sup>3</sup> ):                                | 708  |
| 20 | Transverse tensile strength, dry (MPa):                      | 0.23 |
|    | Transverse tensile strength after storage<br>in water (MPa): | 0.1  |
|    | HCHO emission (mg/100 g):                                    | 0.1  |

## 25 Example 7

Three-layer chipboards were produced and tested according to the general description of the examples (press time 15 s/mm at 190°C; 2.5 N/mm<sup>2</sup>).

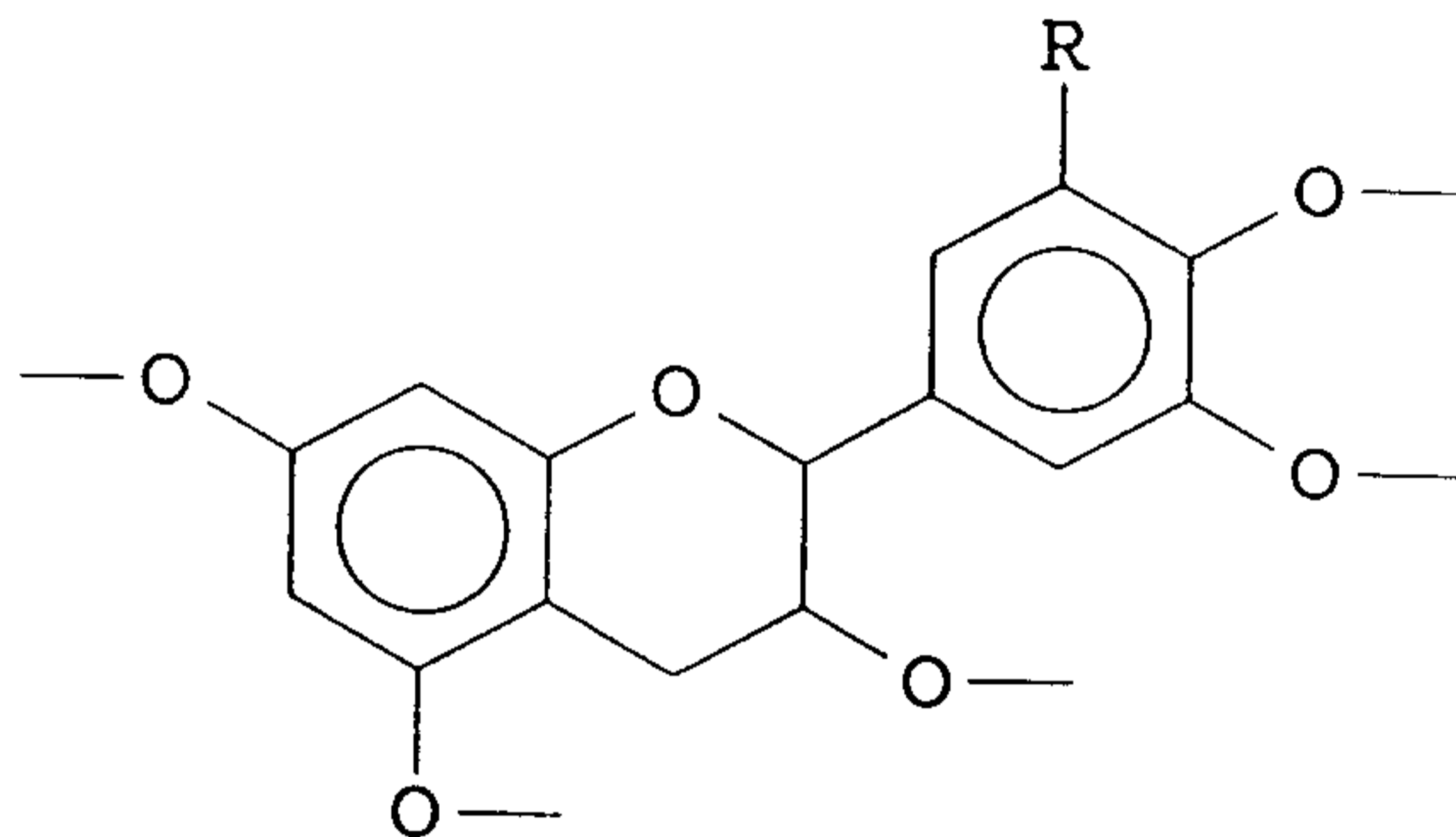
| Bonding agent:                                    | Core layers | Outer layers         |
|---|-------------|----------------------|
| Tannin from pine bark<br>5 (37% aqueous solution) | 327         | 327 parts by weight  |
| Hexamethylenetetramine<br>(40% aqueous solution)  | 19.5        | 19.5 parts by weight |
| Zinc acetate<br>(25% aqueous solution)            | 24.0        | 19.5 parts by weight |
| 10 Water  | 12          | -- parts by weight   |

## Results:

|  |      |
|--|------|
| Density (kg/m <sup>3</sup> ):                                | 723  |
| 15 Transverse tensile strength, dry (MPa):                   | 0.80 |
| Transverse tensile strength after storage<br>in water (MPa): | 0.29 |
| HCHO emission (mg/100 g):                                    | 0.16 |

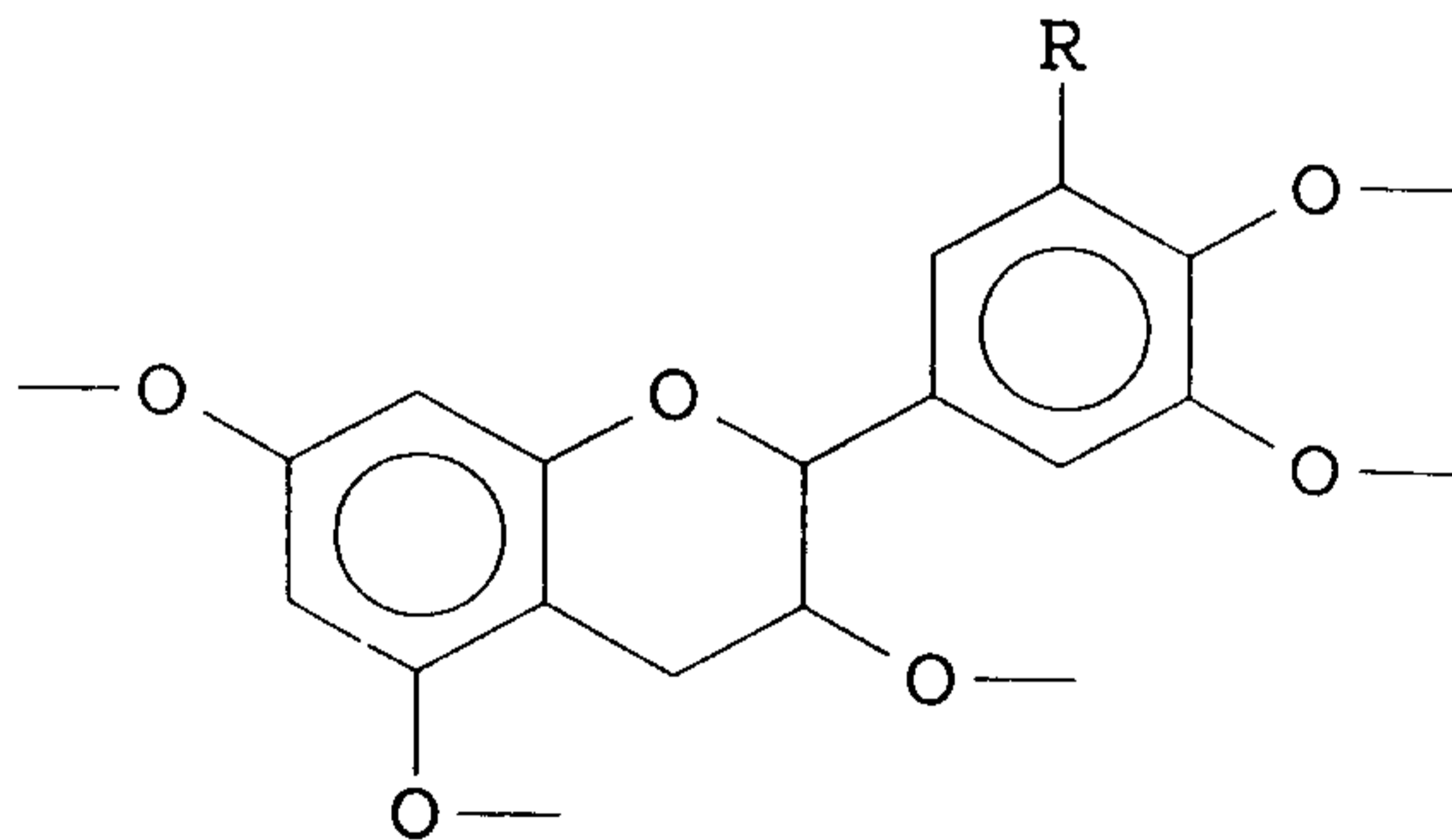
THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A thermosetting bonding agent for products containing cellulose based on tannin, said bonding agent containing tannin and a substance that releases formaldehyde when heated, the tanning containing units being of the general structure



wherein R stands for hydrogen or a hydroxyl group and the free bonds at the oxygen radicals are saturated with hydrogen.

2. A thermosetting bonding agent for products containing cellulose based on tannin, said bonding agent containing tannin and a substance that releases formaldehyde when heated, the tanning containing units being of the general structure



wherein R stands for hydrogen or a hydroxyl group and the free bonds at the oxygen radicals are bonds to other molecular groups.

3. The bonding agent as claimed in claim 1 or 2, wherein the tannin is from the pecan nut or from pine bark.

4. The bonding agent as claimed in claim 1, 2 or 3, wherein the substance that releases formaldehyde when heated is hexamethylenetetramine.

5. The bonding agent as claimed in claim 4, wherein the proportion of hexamethylenetetramine amounts to 3.0 to 9%-wt, relative to the tannin.

6. The bonding agent as claimed in any one of claims 1 through 5, containing up to 50%-wt of a novolak.

7. The bonding agent as claimed in any one of claims 1 through 6, containing up to 20%-wt of an isocyanate compound that is at least difunctional.

8. A method of manufacturing working materials, comprising mixing a bonding agent as defined in any one of claims 1 through 7 with product containing cellulose, placing the mixture in a mould, and processing the mixture in the mould at a temperature in the range from 150°C to 210°C and at a pressure in the range of 0.1 to 4 MPa/mm<sup>2</sup>.

9. The method as claimed in claim 8, wherein the bonding agent is mixed in the form of powder with the wood chips.

10. The method as claimed in claim 8, wherein the bonding agent is sprayed onto the wood chips in the form of a solution.