

SPECIFICATION Bonding Agent

This invention relates to bonding agents containing polyphenolic material extracted from bark, and to the manufacture and uses of such bonding agents; particularly but not solely their use in composite bonded materials, examples of which are particle board, plywood and various fibre boards.

10 Bonding agents are employed in the art of composite bonded material manufacture to plywood and various fibre boards.

Bonding agents are employed in the art of composite bonded material manufacture to provide an adequate connection or adhesion between adjacent flakes, particles, fibres, veneers or the like for the transmission of forces. Common examples of such composite bonded materials are particle board and plywood as used in the constructions, materials handling, and furniture industries.

The bonding agents most commonly used at present are the synthetic resin adhesives phenol-formaldehyde, urea-formaldehyde and melamine reinforced urea-formaldehyde. Many materials used to produce these adhesives are petrochemicals or are derived therefrom.

In addition to providing a strong bond, it is often necessary that bonding agents be resistant to degradation by the elements in exterior exposure, and to high humidity and water generally. The bonding agents also need to be readily available at moderate cost.

With the objective of providing bonding agents at moderate cost from readily available renewable resources there has been some manufacture of extracts from the bark of trees for use in bonding agents, principally from Black Wattle (*Acacia Mearnsii*) the extract being known as "Mimosa tannin". The Black Wattle bark is extracted with hot water to produce an aqueous extract which is usually spray-dried for storage. It has also been contemplated that bark from other species could be used including *Pinus radiata*. As far as we are aware however extracts are not prepared commercially from *Pinus radiata* bark at the present time due to difficulties which are not encountered with Black Wattle bark extracts. The extracts derived from the bark of trees and shrubs consist substantially of polyphenolic compounds and are referred to hereinafter as bark extract(s).

The bark extract is co-reacted with aldehydic materials or aldehyde donor materials (paraformaldehyde being preferred) to produce resinous polymer substances which function as bonding agents or adhesives.

It has been found that in some respects bonding agents manufactured from bark extracts are inadequate for more critical bonding applications, such as where high bond strength is required and/or where extended resistance to degradation by the elements such as rain and sun is required. In an effort to overcome these inadequacies and to extend the uses of bark

65 extracts as bonding agents it has been proposed to modify the bark extracts by reacting them prior to use, in a heated vessel under acid conditions in the presence of a certain reactive compound or compounds. The reaction is intended to be performed under closely controlled conditions, the reaction product being cooled and stored for use. Such modification of bark extract is costly and therefore is of limited economic value. Also, bark extract has been found to exhibit a variation in properties depending upon the bark species from which it was derived and even depending upon the position of the bark on the tree and the tree age. The process of modification of bark extract at elevated temperature in the presence of one or more reactive compound is sensitive to variations in properties of the bark extract and the variations are difficult to control in a natural product. Also it is not always possible to use bark from a more desirable species when manufacturing bark extract and it usually becomes necessary to utilise bark from a species abundant in a particular region. For example, we have found that bark extract prepared from Black Wattle bark (i.e. *Mimosa* tannin) is remarkably similar to bark extract prepared from *Pinus radiata* bark when ¹³C Nuclear Magnetic Resonance spectra (¹³C NMR) of the two extracts are compared, yet in aqueous solution the viscosity of the two extracts at the same concentration is quite different; *Pinus radiata* extract being significantly higher in viscosity than *Mimosa* tannin extract. It has also been observed that the chemical reactivity of *Pinus radiata* bark extract is significantly greater than that of *Mimosa* tannin extract, making it very difficult to control reactions at elevated temperature to modify *Pinus radiata* bark extract as proposed by some experiments. If bark resources are to be used in New Zealand for example to prepare modified bark extract for use as bonding agents it is necessary to use extract prepared from the species abundant in this region which is *Pinus radiata*. Also, there is a need for a simple method for the modification of bark extracts generally, which provides improved bark extracts at lower costs, and at least minimises some of the foregoing disadvantages.

It is an object of this invention to provide bonding agents containing bark extract.

For the purpose of this invention bark extract is defined as polyphenolic substances extracted from the bark of trees and existing in either a liquid phase or as a dry powder. This liquid phase is commonly aqueous.

According to one aspect of this invention there is provided a bonding agent including bark extract (as defined herein) and at least one caustic free phenol-aldehyde condensation product which have been combined without the application of heat, said bonding agent having a pH between 4 and 7.

It will be appreciated by those skilled in the art, that some heat may be generated during the process of combining the bark extract with the caustic free phenol-aldehyde condensation

product. Also it will be appreciated that heat may be present at some position adjacent to the process being carried out, while such heat may not relate in any way to the carrying out of the process. In such cases, it will be appreciated that the process will still take place without the application of heat in or as a constituent part of the process is concerned, although the temperature present at the time of the process being carried out might be slightly raised, or near ambient, rather than being precisely ambient.

The invention is described by way of example, with reference to the accompanying drawings, wherein:

Figure 1: is a graph illustrating the viscosity reducing effect of combining various proportions of bark extract with preferred condensation product in emulsion form.

Figure 2: is a graph illustrating the viscosity reducing effect of combining various proportions of bark extract with preferred condensation product in solution form.

While it has been proposed to modify bark extracts by reacting them at elevated temperature under acid conditions with one or more reactive compound such as those capable of reaction with aldehyde to form phenolic or amino resins such treatments significantly increase the cost of bark extracts and are difficult to control, especially when more reactive bark extract such as *Pinus radiata* bark extract is being so treated.

We have found that excellent modified bark extracts can be prepared while entirely avoiding the need to react the components at elevated temperatures for lengthy periods prior to use by selecting certain condensation products and combining these at or near ambient temperature.

Certain condensation products of a caustic free phenol aldehyde type are used in the present invention to modify bark extract at or near ambient temperature to produce improved bonding agents for use in the manufacture of improved composite bonded materials, examples of which are particle board and plywood. The modified bark extract is co-reacted *in situ* at elevated temperature usually in a press at the time of manufacture of the composite bonded product such as particle board or plywood for example to form a novel thermo-set resin bond which we have found to be at least equal to that produced by prior art bonding agents.

Preferred phenol-aldehyde condensation products of a caustic-free type employed in this invention are as follows:

(a) Condensation products produced by reaction including a phenol and an aldehyde or aldehyde donor at elevated temperature in the presence of an acid. These condensation products are well known in the art. Many acids are suitable including sulphuric acid, hydrochloric acid, oxalic acid for example.

(b) Condensation products produced by reaction including a phenol and an aldehyde or aldehyde donor at elevated temperature in the presence of one or more metal ion catalyst. Metal

ion catalysts which have been used include zinc, cadmium, manganese, copper, tin, magnesium, cobalt, lead, calcium, barium, nickel, iron and chromium. An example of these condensation products is disclosed in United States patent number 3,485,797.

(c) Condensation products produced by reaction including a phenol and an aldehyde or aldehyde donor at elevated temperature in the presence of catalysts consisting in salts of mono-carboxylic acids with metals selected from the Transition Elements with reference to the Periodic Table of The Elements, preferred salts being zinc acetate and manganese acetate. An example of these condensation products is disclosed in United Kingdom patent number 1,265,465.

(d) Condensation products produced by reaction substantially as in (a), (b) or (c), said condensation products being further modified by the addition of controlled amounts of acid after completion of the condensation reaction. A wide range of acids, both organic and inorganic may be employed including aryl sulphonic acids such as benzene sulphonic acid and toluene sulphonic acid, and the various inorganic acids such as phosphoric acid, sulphuric acid, and mixtures thereof. An example of these acid modified condensation products is disclosed in New Zealand patent number 175,042.

For use in this invention the condensation products, disclosed in groups (a), (b), (c) and (d) will be referred to hereinafter as preferred condensation products and are combined with bark extract which is preferably in aqueous solution. It is preferable that preferred condensation products be in solution, water solution, water miscible organic solvent solution, or in stable emulsion, and it is preferred that such solution (which includes emulsions) have a pH not substantially greater than pH 7, and more preferably a pH of less than pH 7. The selection of a particular solution will depend upon the particular preferred condensation products used since not all are water soluble for example. Any of the preferred condensation products (a), (b), (c) or (d) may be used in this invention either separately or a combination and such products will be referred to hereinafter as the preferred condensation products, this reference including mixtures thereof.

Hot water or hot water including one or more compounds to aid extraction is used to produce bark extract from comminuted bark. Commercially available Mimosa tannin bark extract is simply prepared from Black Wattle bark by extraction with hot water. Unfortunately this simple method does not produce a satisfactory yield of bark extract when *Pinus radiata* bark is extracted and a more costly method has to be resorted to.

Although no commercial production of *Pinus radiata* bark extract has yet resulted we have found that excellent bark extract can be prepared by using hot water to which is added a combination of sodium carbonate and sodium sulphite when extracting bark of this species. Bark

extracts are usually concentrated prior to use, and where transportation or storage is involved it is usual to spray dry bark extracts, the bark extracts being made into solution again from the powder prior to use, usually by mixing with water.

It will be appreciated that the concentration of aqueous bark extracts may be varied, the limits of variability not being narrowly critical and depending upon the bark extract is derived and the purpose for which the bark extract is to be used. As stated hereinafter different species produce extracts at different viscosities at similar concentration, examples of which are Mimosa tannin bark extract at a concentration of 50% extract solids w/w and *Pinus radiata* bark extract at a concentration of 30% extract solids w/w having similar viscosities and Mimosa tannin bark extract at a concentration 30% extract solids W/W being very significantly lower in viscosity than *Pinus radiata* bark extract at a similar concentration.

By way of example we have produced many products experimentally according to this invention using *Pinus Radiata* bark extract at concentrations between 30% and 55% extracts solids by mass.

For the purpose of illustrating this invention examples where *Pinus radiata* bark extract at a concentration of neat 35% extract solids by mass will be shown, although bark extract derived from other species, including bark extracts which are commercially available at present such as Black Wattle (Mimosa tannin) bark extract may be used and aqueous bark extracts generally of other solids concentrations may also be used. Concerning the preferred condensation products described hereinbefore, we have found that these have typical concentrations of between 40% solids and 60% solids by mass, irrespective of whether in solution or emulsion form although some preferred condensation products in solution form are available up to near 80% solids by mass. Because the condensation products can be varied we refer to the solids in these and when describing combinations of bark extracts and preferred condensation products we refer to solids ratios by mass.

We have found that the preferred condensation products may be combined with bark extracts in any proportion, the two components being fully compatible provided certain precaution is taken as disclosed herein to react free formaldehyde where present prior to preparing the combination.

We have found that it is usually advantageous to use greater proportions of the preferred condensation products when bonding plywood for example and lesser proportions when bonding particle board, although this is a generalisation only and not intended to be limiting.

We have found that it is usual for the preferred condensation products to contain free formaldehyde which can react with bark extracts to the disadvantage of this invention and for this reason, in a preferred form of this invention addition of a compound capable of reaction with

free formaldehyde present in the preferred condensation products, or at least in some of them is made. The compound capable of reaction with free formaldehyde is added to the preferred condensation products, and sufficient time is allowed for the reaction to proceed prior to combination of the treated preferred condensation products and bark extracts, several days being sufficient time at ambient temperatures, the time required being reduced as temperature is elevated above ambient.

Examples of suitable compounds which may be added to preferred condensation products for the purpose of reaction with free formaldehyde include urea, thiourea and dicyanodiamide. Urea has been found satisfactory and is preferred because it is low in cost. Usually up to 10% urea by mass circulated on preferred condensation product solids is sufficient, with a typical range between 2% urea by mass and 6% by mass being found.

Examples of improved bonding agents, their preparation and use according to this invention will now be described, it being emphasised that these examples do not define the invention but simply fall within the range of improved bonding agents which may be manufactured within the scope thereof.

Also it is common to adjust the pH of adhesive systems containing an aldehydic or aldehyde donor material such as paraformaldehyde as a means of pot life control, and in addition we have found that the natural pH of bark extract is in the region of pH 4.5 which corresponds to a dip in the hydrolysis curve of paraformaldehyde. Accordingly the pH range giving the optimum performance of bonding agents of this invention has been found to be pH 4 to pH 7, and the pH may be adjusted to within this range by addition of suitable acid or alkali, for example acetic or sulphuric acid, and sodium hydroxide.

An example of improved bonding agents according to this invention may include the following proportions of solids by mass:

(1) Preferred condensation product (a condensation product selected from (a), (b), (c), (d) (as defined herein) or a mixture thereof)	up to 69%
(2) Urea (or other compound capable of reaction with free formaldehyde)	up to 7%
(3) Bark extract	22% to 94%
(4) Paraformaldehyde (or other aldehydic or aldehyde donor material)	0.5% to 12%

A further example of improved bonding agents according to this invention, more suited to the manufacture of particle board or fibre board may include the following proportions of solids by mass:

(1) Preferred condensation product (Condensation product	
--	--

- selected from (a), (b), (c), (d)
(as defined herein) or mixtures thereof) 5% to 25%
- 5 (2) Urea (or compound capable of reaction with free formaldehyde) 0.1% to 2%
- (3) Bark extract 74% to 94%
- (4) Paraformaldehyde (or other aldehydic or aldehyde donor material) 0.5% to 10%

A particular example of the preparation of a bonding agent according to this invention will now be described. This example, falling within the scope of the invention is not intended to be limiting, but is included by way of example only to illustrate the preparation of bonding agents according to this invention. This particular example includes the following proportions of solids by mass:

- 20 (1) Preferred condensation product (condensation product selected from (a), (b), (c), (d) (as defined herein) or mixtures thereof) near 8.7%
- 25 (2) Urea near 0.3%
- (3) Bark extract near 86%
- (4) Paraformaldehyde near 5%

In this example of the manufacture of an improved bonding agent containing bark extract an aqueous bark extract having for example 35% solids by mass is prepared. The exact percent solids is not very critical but needs to be reasonably well known so that the intended solids ratios can be achieved. A preferred condensation product is also required, which we have found may contain free formaldehyde capable of reaction with bark extract. Since the reaction of free formaldehyde with bark extract is undesirable in the present invention, since it may adversely reduce pot life of the bonding agent it is avoided by reaction of the free formaldehyde with a suitable compound such as urea, prior to introduction of the bark extract. In this example urea is used, which is added to the preferred condensation product at the rate of 3% by mass, calculated on the solids of the preferred condensation product. Consequently the percent solids of the preferred condensation product, which may vary as stated hereinbefore, also needs to be known for satisfactory formulation according to this invention. The percent solids by mass of the preferred condensation product could for example be near 44%. Urea is mixed well into the preferred condensation product usually at near ambient temperatures and allowed to react with free formaldehyde therein. Typical of chemical reactions, the rate of reaction between the free formaldehyde and urea is temperature dependent. While elevating the temperature may accelerate the reaction, it is a major advantage of this invention that the entire preparation of

improved bonding agents according thereto may be accomplished at or near ambient temperatures thus entirely avoiding the need for heated vessels and elaborate process control. We have found that it is usually convenient to mix the urea or other suitable material into the preferred condensation product several days prior to combining this combination with bark extract, in which case sufficient time is available for the desired reaction between free formaldehyde and urea to take place at ambient temperatures. The free formaldehyde and urea combine chemically to form an amino resin type product. Aqueous bark extract, 35% solids by mass in this example, is now added to the preferred condensation product with constant stirring. Infra-red spectra investigations indicate that there is a reaction, at least between some preferred condensation products and aqueous bark extract at and following the combination of the two according to the invention, probably by linking of some aliphatic side chains, the changes in the infra-red spectra being best discerned by differential recording of the spectra, it being appreciated that even after quite extensive cross-linking the spectra do not show a great amount of change. Notwithstanding any cross-linking which may take place at the time the preferred condensation product is combined with the bark extract, the most significant reactions to form the novel bonding agent of this invention take place *in situ* in a press or the like, at elevated temperature when for example composite products incorporating the bonding agent, such as particle board or plywood are manufactured. In the present example, the preferred condensation product which has been treated with urea, is combined with aqueous bark extract in the ratio of near 10:1 aqueous bark extract solids: preferred condensation product solids. To this combination, an aldehydic material or aldehyde donor material is added. In the present example 4% W/W paraformaldehyde solids is added to the total solids of the previously prepared combination and thoroughly mixed in. (4% W/W has been found to be near the lower limit a typical range being 4% to 10% W/W). The preparation, now including the preferred condensation product and urea reacted with any free formaldehyde therein, aqueous bark extract, and paraformaldehyde in this example may be applied to wood flakes and formed into particle board by conventional processes. The wood flakes with bonding agent according to this invention are pressed in a particle board press for example, typically at temperatures between 140°C and 200°C for a substantially predetermined time as known in the art, and the various components present in the bonding agent as disclosed herein co-react *in situ* during pressing to develop the desired novel bond.

A further particular example of the use of this invention for the manufacture of an exterior grade plywood with a strong bond will now be described. An example of improved bonding

agents according to this invention, more preferred for plywood manufacture may include the following solids proportions W/W:

- | | | |
|----|--|------------|
| 5 | (1) Preferred condensation product (condensation product selected from (a), (b), (c), (d) (as defined herein) or mixtures thereof) | 10% to 75% |
| 10 | (2) Urea (or other compound capable of reaction with free formaldehyde) | 0.5 to 5% |
| | (3) Bark extract | 24% to 82% |
| 15 | (4) Paraformaldehyde (or other aldehydic or aldehyde donor material) | 0.5% to 8% |

For plywood manufacture conventional extenders such as walnut shell flour, olive stone flour or wood flour for example are often used in the adhesive system, and any of these or other suitable extenders may be added to the bonding agents of this invention as desired.

A bonding agent having a composition within the range stated for this example may contain the following solids proportions W/W.

- | | | |
|----|---|-----|
| 30 | (1) A preferred condensation product selected from group (d) herein | 28% |
| | (2) Urea | 2% |
| | (3) Bark extract | 65% |
| | (4) Paraformaldehyde | 5% |

As in the previous examples, the urea is mixed with the preferred condensation product and is allowed to react with any free formaldehyde present, sufficient time such as several days at ambient temperatures being allowed for the reaction to advance sufficiently. Bark extract in aqueous solution and the urea treated preferred condensation product are then combined with constant stirring. Paraformaldehyde is then added to the combination and mixed thoroughly in. Extenders such as olive stone flour may be added if desired. An example of a preferred condensation product selected from group (d) is sold commercially as Cortech Resin or Phenoset Emulsions by Revertex N.Z. Limited, a company specialising in the manufacture and supply of condensation products and resins generally. This preferred condensation product is supplied in one form by the manufacturers as an aqueous emulsion. Such aqueous emulsions may be prepared as known in the art, and to advantage may if desired, be stabilised by using a protective colloid such as hydroxyethyl cellulose during their manufacture, the protective colloid usually being added to the water before the resin is added. It is possible in fact, to produce a preferred condensation product of group (d) by taking a preferred condensation product of group (b) or group (c) for example, preparing an aqueous emulsion therefrom which may be protected by a

protective colloid such as hydroxyethyl cellulose, and then adding controlled amounts of toluene sulphonic acid or other suitable acid, thereby preparing a preferred condensation product of group (d) *in situ* in the aqueous emulsion. Urea is then added to the aqueous emulsion in accordance with the invention as usual, and then the bark extract is added. An improved bonding agent according to this invention and containing a combination of bark extract and preferred condensation product of group (d) may also be prepared by simply taking a preferred condensation product of group (b) or group (c) for example, and combining this directly with bark extract, and then adding controlled amounts of toluene sulphonic acid or other suitable acid, the acid reacting principally with the group (b) or group (c) preferred condensation product, thus converting it *in situ* with the combination to a group (d) preferred condensation product. Some care is necessary however if this method of preparation is used because we suspect that formaldehyde is released during reaction between the preferred condensation product of group (b) or group (c) and the toluene sulphonic acid or other suitable acid and this free formaldehyde can react with the bark extract leading to a shortened pot life of the bonding agent. The addition of urea or other suitable compound as disclosed hereinbefore to react with free formaldehyde is recommended to control this potential problem. The bonding agents, prepared as described herein, and optionally with the addition of an extender such as olive stone flour or other suitable extender of desired may be applied to veneers by conventional means in the manufacture of plywood. Experience has shown that typical application rates are between 150 grams and 200 grams of wet bonding agent per square metre per glue-line. Also, it is quite common in the art to introduce a cold pressing step in plywood manufacture, between assembly of the veneers and cure of the glue-lines by hot pressing, an initial bond being developed in the cold pressing with the veneer assemblies. We have found that bonding agents prepared according to this invention are suitable for use with processes including the cold pressing step. We have found that plywood manufactured by conventional methods, but employing bonding agents prepared according to this invention, and tested according to New Zealand Standard 3614:1973 have bonds at least equal to those obtained when conventional bonding agents are used. We have observed that during preparation of improved bonding agents according to this invention a useful reduction in viscosity usually takes place at the time bark extract and preferred condensation products are combined. This viscosity reduction effect is illustrated in Graph 1 which is a generalisation based upon observations made during the preparation of a number of improved bonding agents according to this invention, wherein the preferred condensation products were used in the form of

an aqueous emulsion. For the purpose of constructing Graph 1 viscosities of various preferred condensation product and bark extract were determined at 20°C using a Brookfield RVF 100 instrument on the 50 revolutions per minute setting. Graph 1 shows the viscosity reduction effect resulting from various combinations of *Pinus radiata* bark extract in aqueous solution and preferred condensation product in aqueous emulsion. *Pinus radiata* bark extract in aqueous solution is prone to relatively high viscosities as explained hereinbefore and the viscosity reduction effect may be employed to enable bonding agents with a higher percent solids W/W to be prepared while still keeping viscosity reasonably low. The viscosity reduction effect is particularly useful when preparing improved bonding agents from *Pinus radiata* bark extract.

By way of further explanation and illustration the viscosity reducing effect which results when bark extract and preferred condensation product are combined, wherein the preferred condensation product is in the form of a solution not an emulsion, is shown in Graph 2. Graph 2 is also a generalisation based upon experience in preparing a number of improved bonding agents according to this invention, the main features explained in Graph 2 being firstly that a very significant viscosity reduction results when the bark extract and preferred condensation product are combined, and that usually a very sharp viscosity reduction results from the combination of relatively small amounts of bark extract with the preferred condensation product. Accordingly the bark extract may be said to act as a viscosity reducing agent when present in minor amounts in the preferred condensation product, and conversely the preferred condensation product may be said to act as a viscosity reducing agent when present in minor amounts in the bark extract.

It will be seen from the foregoing that this invention provides a means of preparing useful improved bonding agents containing bark extract. That such bonding agents may be prepared at or near ambient temperatures without heated vessels or critical process control is of significant economic importance. Indeed, we have found that in most cases the adhesive mixing equipment normally found in a plywood mill or particle board mill can be used with little or no alteration thereto. If desired therefore the improved bonding agents of this invention may be prepared from the components as required, thereby eliminating problems of stability which have been often experienced in the prior art.

Alternatively the combination of bark extract and preferred condensation product may be supplied to the plywood mill or particle board mill in a dry powder form to be re-constituted by addition of water and/or other solvent as required. Surprisingly, although the improved bonding agents of this invention are of the heat curing type the combination of bark extract and preferred condensation product may be prepared and then

spray dried to facilitate storage and transportation. Accordingly, if desired, the preferred condensation product may be combined with aqueous bark extract in a bark extraction plant and then spray dried, to be supplied to users in dry powder form.

This invention is especially useful in enabling *Pinus radiata* bark extract, prepared from the predominant tree species grown in New Zealand to be used in bonding agents for the manufacture of various composite bonded materials such as particle board and plywood. Until the present time *Pinus radiata* bark extract has not been used commercially for bonding such materials on account of the many difficulties found and this invention goes a considerable way in overcoming the difficulties found.

The many examples shown herein being within the scope and spirit of this invention are not intended to be limiting but are provided by way of illustration only, and further examples will be apparent to those skilled in the art which we also deem to be included as being within the scope of the invention, as defined by the appended claims.

90 Claims

1. A bonding agent including bark extract (as defined herein) and at least one caustic free, phenol-aldehyde condensation product, which have been combined without the application of heat, said bonding agent having a pH of between 4 and 7.

2. A bonding agent as claimed in claim 1, wherein the phenol-aldehyde condensation product is or includes a preferred condensation product of group (a) as defined herein.

3. A bonding agent as claimed in claim 1 or claim 2, wherein the phenol-aldehyde condensation product is or includes a preferred condensation product of group (b) as defined herein.

4. A bonding agent as claimed in any one of the preceding claims wherein the phenol-aldehyde condensation product is or includes a preferred condensation product of group (c) as defined herein.

5. A bonding agent as claimed in any one of the preceding claims, wherein the phenol-aldehyde condensation product is or includes a preferred condensation product of group (d) as defined herein.

6. A bonding agent as claimed in any one of the preceding claims including at least one preferred condensation product selected from the groups (a), (b), (c) and (d), (as defined herein), treated with at least one compound capable of reaction with free formaldehyde.

7. A bonding agent as claimed in claim 6, wherein the compound is one or more of urea, thiourea and dicyanodiamide.

8. A bonding agent as claimed in claim 6 or claim 7, wherein at least one preferred condensation product selected from the groups (a), (b), (c) and (d), (as defined herein), is treated with at least one compound prior to the



an aqueous emulsion. For the purpose of constructing Graph 1 viscosities of various preferred condensation product and bark extract were determined at 20°C using a Brookfield RVF 100 instrument on the 50 revolutions per minute setting. Graph 1 shows the viscosity reduction effect resulting from various combinations of *Pinus radiata* bark extract in aqueous solution and preferred condensation product in aqueous emulsion. *Pinus radiata* bark extract in aqueous solution is prone to relatively high viscosities as explained hereinbefore and the viscosity reduction effect may be employed to enable bonding agents with a higher percent solids W/W to be prepared while still keeping viscosity reasonably low. The viscosity reduction effect is particularly useful when preparing improved bonding agents from *Pinus radiata* bark extract.

By way of further explanation and illustration the viscosity reducing effect which results when bark extract and preferred condensation product are combined, wherein the preferred condensation product is in the form of a solution not an emulsion, is shown in Graph 2. Graph 2 is also a generalisation based upon experience in preparing a number of improved bonding agents according to this invention, the main features explained in Graph 2 being firstly that a very significant viscosity reduction results when the bark extract and preferred condensation product are combined, and that usually a very sharp viscosity reduction results from the combination of relatively small amounts of bark extract with the preferred condensation product. Accordingly the bark extract may be said to act as a viscosity reducing agent when present in minor amounts in the preferred condensation product, and conversely the preferred condensation product may be said to act as a viscosity reducing agent when present in minor amounts in the bark extract.

It will be seen from the foregoing that this invention provides a means of preparing useful improved bonding agents containing bark extract. That such bonding agents may be prepared at or near ambient temperatures without heated vessels or critical process control is of significant economic importance. Indeed, we have found that in most cases the adhesive mixing equipment normally found in a plywood mill or particle board mill can be used with little or no alteration thereto. If desired therefore the improved bonding agents of this invention may be prepared from the components as required, thereby eliminating problems of stability which have been often experienced in the prior art.

Alternatively the combination of bark extract and preferred condensation product may be supplied to the plywood mill or particle board mill in a dry powder form to be re-constituted by addition of water and/or other solvent as required. Surprisingly, although the improved bonding agents of this invention are of the heat curing type the combination of bark extract and preferred condensation product may be prepared and then

spray dried to facilitate storage and transportation. Accordingly, if desired, the preferred condensation product may be combined with aqueous bark extract in a bark extraction plant and then spray dried, to be supplied to users in dry powder form.

This invention is especially useful in enabling *Pinus radiata* bark extract, prepared from the predominant tree species grown in New Zealand to be used in bonding agents for the manufacture of various composite bonded materials such as particle board and plywood. Until the present time *Pinus radiata* bark extract has not been used commercially for bonding such materials on account of the many difficulties found and this invention goes a considerable way in overcoming the difficulties found.

The many examples shown herein being within the scope and spirit of this invention are not intended to be limiting but are provided by way of illustration only, and further examples will be apparent to those skilled in the art which we also deem to be included as being within the scope of the invention, as defined by the appended claims.

90 Claims

1. A bonding agent including bark extract (as defined herein) and at least one caustic free, phenol-aldehyde condensation product, which have been combined without the application of heat, said bonding agent having a pH of between 4 and 7.

2. A bonding agent as claimed in claim 1, wherein the phenol-aldehyde condensation product is or includes a preferred condensation product of group (a) as defined herein.

3. A bonding agent as claimed in claim 1 or claim 2, wherein the phenol-aldehyde condensation product is or includes a preferred condensation product of group (b) as defined herein.

4. A bonding agent as claimed in any one of the preceding claims wherein the phenol-aldehyde condensation product is or includes a preferred condensation product of group (c) as defined herein.

5. A bonding agent as claimed in any one of the preceding claims, wherein the phenol-aldehyde condensation product is or includes a preferred condensation product of group (d) as defined herein.

6. A bonding agent as claimed in any one of the preceding claims including at least one preferred condensation product selected from the groups (a), (b), (c) and (d), (as defined herein), treated with at least one compound capable of reaction with free formaldehyde.

7. A bonding agent as claimed in claim 6, wherein the compound is one or more of urea, thiourea and dicyanodiamide.

8. A bonding agent as claimed in claim 6 or claim 7, wherein at least one preferred condensation product selected from the groups (a), (b), (c) and (d), (as defined herein), is treated with at least one compound prior to the



condensation product being combined with bark extract.

9. A bonding agent as claimed in any one of the preceding claims, wherein the combination of
5 bark extract and phenol-aldehyde condensation product is treated with at least one acid or alkali.

10. An agent as claimed in claim 9, wherein the combination is treated with one or more of acetic or sulphuric acid or sodium hydroxide.
10 11. A bonding agent as claimed in any one of claims 1 to 9, wherein the combination is treated with one or more of benzene sulphonic acid, phosphoric acid and sulphuric acid.

12. A bonding agent as claimed in any one of the preceding claims, wherein at least one acid or alkali adjusts the pH range of the bonding agent to between pH4 and pH7.
15

13. A bonding agent as claimed in any one of the preceding claims, wherein the combination of bark extract and phenol-aldehyde condensation product, is spray dried.
20

14. A bonding agent as claimed in any one of the preceding claims, wherein an aldehydic or aldehyde donor material is included in the combination of bark extract and phenol-aldehyde condensation product.
25

15. A bonding agent as claimed in claim 14 including an aldehydic or aldehydic donor material in the form of para-formaldehyde.

- 30 16. A bonding agent as claimed in any one of the preceding claims including
1. Between 22% and 94% (solids by mass)

bark extract.

2. Up to 69% (solids by mass) condensation product (selected from (a), (b), (c), (d) as defined herein or a mixture thereof).
35

3. Up to 7% (solids by mass) compound capable of reacting with free formaldehyde.

4. Between 0.5% and 12% (solids by mass) aldehydic or aldehyde donor material.
40

17. A bonding agent as claimed in any one of the preceding claims 1 to 15 including:

1. 74% to 94% (solids by mass) bark extract.

2. Between 5% and 25% (solids by mass)
45

condensation product (selected from (a), (b), (c), (d) as defined herein, or a mixture thereof).

3. Between .1% and 2% (solids by mass) compound capable of reacting with free formaldehyde.

4. Between .5% and 10% (solids by mass) aldehydic or aldehyde donor material.
50

18. A bonding agent as claimed in any one of the preceding claims 1 to 15 including:

1. 86% (solids by mass) bark extract.

2. 8.7% (solids by mass) condensation product (selected from (a), (b), (c), (d) as defined herein, or a mixture thereof).
55

3. .3% (solids by mass) compound capable of reacting with free formaldehyde.

4. 5% (solids by mass) aldehydic or aldehyde donor material.
60

19. A bonding agent as claimed in claim 1, substantially as hereinbefore described.