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PATENT SPECIFICATION

1,092,909

NO DRAWINGS.

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COMPLETE SPECIFICATION.

Production of Laminated Sheet Material.

We, THE BORDEN CHEMICAL COMPANY (UK) LIMITED, (formerly Leicester, Lovell & Co. Limited, a British Company, of North Baddesley, Southampton, Hampshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of laminated sheet material, particularly plywood, using thermosetting adhesives.

In the manufacture of plywood and like laminated structures by hot pressing, it is common practice to employ aqueous solutions of synthetic resin condensation products such as phenol/formaldehyde or urea/formaldehyde resins. Such products have a tendency to penetrate into and, in some cases through, the substrate, before or during the pressing cycle, and in consequence much of the adhesive is removed from the region between the surfaces to be bonded, giving rise to the effect known as a "starved joint". In an attempt to minimise penetration and to retain as much as possible of the adhesive at the bonding surface, it is common practice to add filling materials to such adhesives. Such additions, however, while having a favourable effect in minimising penetration, contribute little or nothing to the adhesive properties of the composition, frequently give rise to an undesirable abrasive action on cutting tools and have, in particular, the disadvantage that they increase the viscosity of the adhesive so that difficulties arise in applying an economically thin spread.

40 playing the resins at a higher concentration. Apart, however, from the fact that it does not lend itself to the attainment of low spreads, it is also a disadvantage of such compositions that, within the range of concentrations that are practicable, the decrease 45 in the amount of penetration is generally inadequate. It is, moreover, known that the storage life of potentially thermosetting condensation products such as the urea and phenolic resins, decreases markedly with increase in concentration. Difficulties are 50 therefore encountered in shipping and storing such resins in highly concentrated form. It has been proposed, for example, in German Patent No. 641,928, to employ 55 comminuted powder adhesives, the adhesive being applied to one of the surfaces to be bonded after, or concomitantly with, the application to the surface of a moistening agent, such as water. Such a procedure 60 has, however, a number of disadvantages. Thus, apart from the fact that a moistening agent of the type envisaged does not always act adequately as an anchoring agent for the powder component, the introduction of 65 a moistening agent such as water is undesirable, since it tends to increase penetration and contributes nothing to the bond. We have now found that these several 70 disadvantages may be overcome by employing as an adhesive in the manufacture of laminated sheet material such as plywood, a composition comprising a liquid thermosetting resinous component in conjunction 75 with a subsequently applied, comminuted solid fusible potentially thermosetting component, the two components being stored separately and combined only at the time

Penetration can also be reduced by em-
[Price 4s. 6d.]

of use. In this way the storage and spreading problems associated with the use of high solids content condensation products are avoided.

5 Accordingly, the present invention comprises a method for the production of laminated sheet material, which comprises applying separately and successively to one or both surfaces to be bonded first, a liquid
10 resinous component as hereinafter defined, and secondly a comminuted, fusible, solid resinous or potentially resinous component, as hereinafter defined, bringing the surfaces to be bonded together and curing the
15 resinous material of the combined coating under heat and pressure, both the liquid and solid components being potentially thermosetting, at least in the presence of one another.

20 The term "liquid, potentially thermosetting, resinous component" is used herein to mean a condensation product of an aldehyde with urea or thiourea, or with a phenol which is unsubstituted in those positions
25 on the ring which are reactive towards formaldehyde, examples of suitable phenols being phenol, meta-cresol, 3,5-xyleneol and resorcinol. The term "liquid" should be taken as referring only to the form in which
30 the condensation product is presented. Thus the expression is to be construed as including solutions of normally solid condensation products.

35 The term "fusible, solid resinous or potentially resinous component" is used herein to mean products which are of themselves resinous, or are capable of becoming resinous either when heated or upon reaction
40 with one or more of the ingredients of the liquid resinous component, and which are thermosetting either when heated alone or when heated in conjunction with the liquid resinous component. Thus suitable
45 materials include condensation products of an aldehyde with urea, melamine or thiourea, or with a phenol which is unsubstituted in those positions on the ring which are reactive towards formaldehyde, for example, phenol, meta-cresol, 3,5-xyleneol and
50 resorcinol, said condensation product being solid at normal room temperature. The preferred products are those produced by spray drying aqueous solutions of urea or phenolic resins, though other methods known in
55 the art for producing fusible solid, potentially thermosetting, condensation products of the type described may be employed. It is also preferred to select both the liquid and the solid components from condensation
60 products of phenol with formaldehyde. It is further preferred that the phenol resin employed should be of the resole type, that is to say, produced by reacting 1 mol equivalent of phenol with more than 1 mol
65 equivalent of an aldehyde under alkaline

conditions. Good results may, however, also be obtained with phenolic resins of the novolak type, that is to say, with resins produced by condensing a phenol with less than an equimolecular amount of aldehyde.

70 Particularly suitable for use as a component of the potentially resinous type are the natural tannin extracts, such as mimosa, quebracho and wattle bark powders.

75 Where phenolic novolak resins or tannins are employed as the powdered component, it is preferred that a suitable aldehyde donor, such as hexamine or paraformaldehyde, should also be incorporated. The formaldehyde donor may, however, be
80 omitted in cases where the liquid component, onto which the powder component is deposited, contains a sufficient excess of uncombined aldehyde to react with the powder component so as to cause the latter
85 to thermoset.

It is to be understood that the powder component may contain in addition to the resinous or potentially resinous component and the aldehyde donor, other ingredients
90 such as powder conditioners, waxes, fillers and the like.

In the preferred method of carrying this invention into effect, the sheet material for example, wood veneer, is conveyed first
95 to a station at which a film of the liquid resinous component is deposited, and immediately thereafter to a second station at which the comminuted solid resinous component is deposited. The invention is not
100 limited to the deposition of the components by any particular method. Thus the liquid resinous component may be applied by means of a roller or by brushing or spraying. However, in order to obtain an
105 economically thin and even coating, we have found it particularly advantageous to employ a curtain coater in which the liquid is fed through a slot of adjustable width and is deposited in the form of a thin continuous
110 film, on the moving sheet material.

The comminuted solid resin may likewise be deposited by any convenient process. Suitable processes include, brushing or spraying
115 and we have found it particularly convenient to distribute the powdered material through a second curtain coater to which a vibrator is attached. Where the powder is deposited by spraying, improved results
120 can be obtained by employing an electrostatic coating process in which the particles are charged on leaving the spray head while the opposite electric charge is applied to the article to be coated.

The following examples illustrate the manner in which the invention may be carried into effect.

EXAMPLE 1

A phenolic resole was prepared by react-

ing phenol with 44% formalin in the ratio of 1 mol of phenol to 1.75 mols of formaldehyde in the presence of caustic soda (0.5 mol per mol of phenol). Reaction was effected by refluxing the ingredients together until the viscosity measured by diluting 375 parts by volume of the resin so formed with 50 parts by volume of 32% w/w caustic soda solution, reached a value of 800 centipoises at 25°C. The reaction was then stopped by adding additional caustic soda solution to bring the total molecular ratio of caustic soda to phenol to 0.818:1, and to reduce the solids contents of the resin to 43–45%. The resultant resin had a viscosity of 3 poises at 21°C. This resin was then charged to a curtain coater, the outlet of which was adjusted so that a continuous film of the resin was deposited at the rate of 1.25 lbs per 100 sq. ft on to the surface of a wood veneer fed beneath it. The coated veneer, which had a moisture content of 5% before coating, was then immediately passed beneath a

second curtain coater fitted with a vibrator and charged with a powdered resin obtained by spray drying the phenolic resin prepared as above. In this case, the coater aperture was adjusted so as to deposit the powdered resin evenly on the previously coated surface of the veneer at a rate of 0.8 lbs. per 100 sq.ft. The coated veneer was then assembled with a second, similarly coated, veneer and with a third uncoated veneer in such a way that the grain direction in adjacent veneers was at right angles, and the assembly placed under light pressure for 30 minutes following which it was fed into a hot press operating at a temperature of 115°C and a pressure of 200 pounds per square inch. After 6 minutes the assembly was removed from the hot press, cooled and tested.

Using the test procedures laid down in British Standard Specification No. 1203, the following results, which are average of six test pieces in each case, were obtained:—

DRY	342 pounds	(Specification minimum 250 lb f)
INT	269	" (" " 250 ")
MR	249	" (" " 200 ")
BR	252	" (" " 100 ")
WBP	248	" (" " 200 ")

The abrasive action of the glue line was found to be less marked than that of a similar panel produced using the liquid resin prepared as above in conjunction with a conventional filler, comprising 60 parts of coconut shell flour, 20 parts of chalk and 20 parts of mimosa powder.

EXAMPLE 2

To further veneers coated by curtain coater with the liquid phenolic resin component as in Example 1 was applied, by means of a vibrating screen, an even layer of a powder composition comprising an intimate mixture of 100 parts by weight of mimosa powder and 20 parts by weight of paraformaldehyde, at the rate of 0.6 lbs per 100 sq. ft. After assembling and pressing as in Example 1, the resultant plywood panel was allowed to cool and was then tested in accordance with British Standard Specifications Nos. 1455 and 1203. Excellent results were obtained in the case of panels produced from veneers having an initial moisture content of 10%. Where the initial moisture content was only 5%, the resultant bonds were slightly inferior, but still complied with the specification requirements.

EXAMPLE 3

A phenolic novolac resin was prepared as follows: 1.432 lbs of 100% phenol, 850 lbs of 44% methanol-free formalin, 28 lbs of oxalic acid and 8 lbs of water were charged to a stainless steel kettle and heated to reflux temperature for 3 hours. The product was then dehydrated at atmospheric pressure until the residue reached a melting point of 53°C. It was then discharged into trays, allowed to cool and ground to approximately 200 mesh. The resultant powder was intimately mixed with paraformaldehyde in the proportion of 20 parts by weight of paraformaldehyde to every 100 parts by weight of the novolac powder.

Wood veneer was then sprayed with a phenolic resin solution as used in Example 1 so as to provide a coating weight of approximately 2 lbs per 100 sq.ft. and was then passed, while the coating was still wet, beneath a vibrating sieve from which the novolac/paraformaldehyde mixture, as above, was deposited at the rate of about 0.6 lbs per 100 sq.ft. After assembly and pressing as in Example 1, the panels produced were tested in accordance with British Standard Specification No. 1203 and gave the following results:—

DRY	389 pounds	(Specification minimum 250 lb f)
INT	294	" (" " 250 ")
MR	296	" (" " 200 ")
BR	202	" (" " 100 ")
WBP	243	" (" " 200 ")

EXAMPLE 4

The procedure of Example 3 was repeated except that the paraformaldehyde was replaced by hexamine (hexamethylenetetramine) in the proportion of 15 parts for

every 100 parts by weight of the novolak resin. On testing in accordance with British Standard Specification No. 1203 (DRY and WBP only) the following results were obtained:

DRY	300	pounds	(Specification	minimum	250	lb	f)
WBP	233	"	(	"	200	"	)

EXAMPLE 5

15 A wood veneer sheet was coated by roller with a liquid composition comprising:

20	*Casco Resin 'U'	—	100	parts by wt.
	China Clay	—	65.5	" "
	Water	—	30	" "
	Rye Flour	—	2	" "
	Tricalcium			
	Phosphate	—	2	" "
	Urea	—	10	" "
	Ammonium			
	Sulphate	—	0.5	" "

25 ("Casco" is a Registered Trade Mark. Casco Resin 'U' is a conventional liquid, aqueous urea-formaldehyde condensation product, having a solids content of 67% and a viscosity of 50 poises at 21°C).

30 While the coating was still wet, the veneer was sprinkled at the rate of 1 lb per 100 sq.ft with a powder composition consisting of:

	Melamine	— 50 parts by wt.
35	*Cascamite 6D	— 50 " "

(* "Cascamite" is a Registered Trade Mark. Cascamite 6D is a spray dried urea-formaldehyde condensation product).

The coated veneer was then assembled with a second similarly coated veneer and an uncoated veneer to form a conventional 3-ply panel assembly and placed under a pressure of 200 pounds per square inch in a hot press operating at a temperature of 100°C for 6 minutes.

On testing the panel was found to comply adequately with the requirements of British Standard Specification No. 1203/BR.

WHAT WE CLAIM IS:—

50 1. A method for the production of laminated sheet material, which comprises applying separately and successively to one or both of the surfaces to be bonded first a liquid resinous component as hereinbefore
55 defined, and secondly a comminuted, fusible

solid resinous or potentially resinous component, as hereinbefore defined, bringing the surfaces to be bonded together, and curing the resinous material of the combined coating under heat and pressure, both the liquid and solid components being potentially thermosetting, at least in the presence of one another.

2. A method according to Claim 1 wherein the liquid resinous component is applied by means of a curtain coater.

3. A method according to either of Claims 1 or 2 wherein the solid resinous component is distributed by means of a vibrating sieve.

4. A method according to any of Claims 1 to 3 wherein the liquid resinous component is an aqueous solution of a phenol-formaldehyde resole.

5. A method according to any of Claims 1 to 4 wherein the solid component is a phenolic novolak resin.

6. A method according to any of Claims 1 to 5 wherein the solid component is prepared by spray drying an aqueous solution of a phenol-formaldehyde condensation product.

7. A method according to any of Claims 1 to 4 wherein the solid component is powdered mimosa extract.

8. A method according to either of Claims 5 or 7, wherein the solid component also includes an aldehyde donor.

9. A method according to Claim 8 wherein the aldehyde donor is paraformaldehyde.

10. A method according to any of the preceding Claims wherein the solid component also includes a filler.

11. A method for the production of laminated sheet material substantially as described in any of the Examples.

12. Laminated sheet material when prepared by the method claimed in any of the preceding Claims.

**STEVENS, LANGNER, PARRY
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EXAMPLE 4

The procedure of Example 3 was repeated except that the paraformaldehyde was replaced by hexamine (hexamethylene-tetramine) in the proportion of 15 parts for

every 100 parts by weight of the novolak resin. On testing in accordance with British Standard Specification No. 1203 (DRY and WBP only) the following results were obtained:

DRY	300 pounds	(Specification minimum 250 lb f)
WBP	233 "	(" " " 200 ")

EXAMPLE 5

A wood veneer sheet was coated by roller with a liquid composition comprising:

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Water	— 30	" "
Rye Flour	— 2	" "
Tricalcium Phosphate	— 2	" "
Urea	— 10	" "
Ammonium Sulphate	— 0.5	" "

(*Casco is a Registered Trade Mark. Casco Resin 'U' is a conventional liquid, aqueous urea-formaldehyde condensation product, having a solids content of 67% and a viscosity of 50 poises at 21°C).

While the coating was still wet, the veneer was sprinkled at the rate of 1 lb per 100 sq.ft with a powder composition consisting of:

Melamine	— 50	parts by wt.
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The coated veneer was then assembled with a second similarly coated veneer and an uncoated veneer to form a conventional 3-ply panel assembly and placed under a pressure of 200 pounds per square inch in a hot press operating at a temperature of 100°C for 6 minutes.

On testing the panel was found to comply adequately with the requirements of British Standard Specification No. 1203/BR.

WHAT WE CLAIM IS:—

1. A method for the production of laminated sheet material, which comprises applying separately and successively to one or both of the surfaces to be bonded first a liquid resinous component as hereinbefore defined, and secondly a comminuted, fusible

solid resinous or potentially resinous component, as hereinbefore defined, bringing the surfaces to be bonded together, and curing the resinous material of the combined coating under heat and pressure, both the liquid and solid components being potentially thermosetting, at least in the presence of one another.

2. A method according to Claim 1 wherein the liquid resinous component is applied by means of a curtain coater.

3. A method according to either of Claims 1 or 2 wherein the solid resinous component is distributed by means of a vibrating sieve.

4. A method according to any of Claims 1 to 3 wherein the liquid resinous component is an aqueous solution of a phenol-formaldehyde resole.

5. A method according to any of Claims 1 to 4 wherein the solid component is a phenolic novolak resin.

6. A method according to any of Claims 1 to 5 wherein the solid component is prepared by spray drying an aqueous solution of a phenol-formaldehyde condensation product.

7. A method according to any of Claims 1 to 4 wherein the solid component is powdered mimosa extract.

8. A method according to either of Claims 5 or 7, wherein the solid component also includes an aldehyde donor.

9. A method according to Claim 8 wherein the aldehyde donor is paraformaldehyde.

10. A method according to any of the preceding Claims wherein the solid component also includes a filler.

11. A method for the production of laminated sheet material substantially as described in any of the Examples.

12. Laminated sheet material when prepared by the method claimed in any of the preceding Claims.

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