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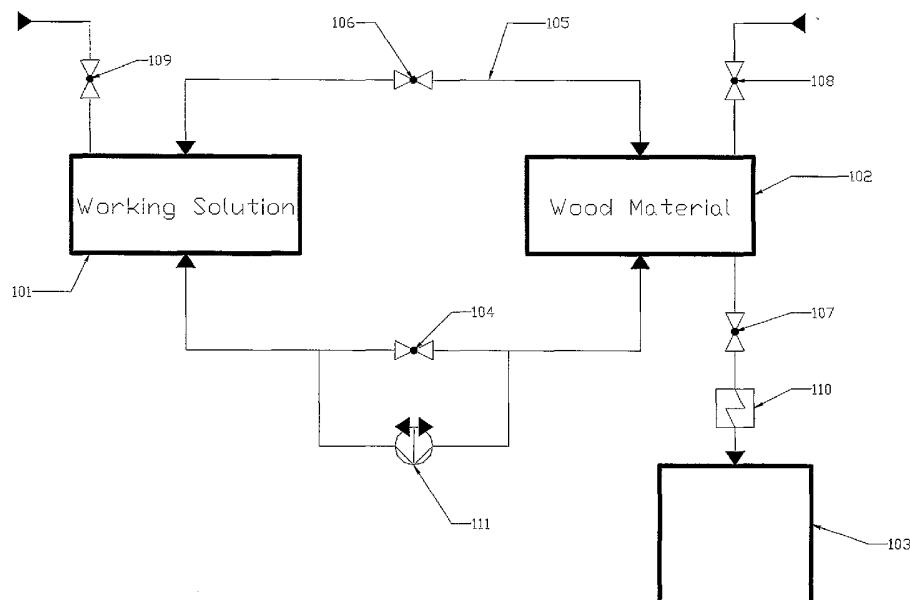
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(54) Title: IMPREGNATION PROCESS



(57) Abstract: The invention relates to a process for impregnating wood or wood based material. A working solution is preheated to a temperature above the atmospheric boiling point ("a super hot temperature") above the atmospheric boiling point ("a super hot temperature") of the working solution, at an elevated pressure sufficient to maintain the working solution in the liquid phase. The working solution is contacted with a wood or wood based material at a super hot temperature and an elevated pressure to cause impregnation of the solution into the wood or wood based material. The impregnated wood or wood based material and any remaining working solution, waste material and/or by-products are then separated.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

IMPREGNATION PROCESS

FIELD OF THE INVENTION

5 This invention relates generally to impregnation processes for impregnating wood or wood products to improve the decay resistance, dimensional stability and/or UV resistance of the wood and densify the wood and in particular but not exclusively to an acetylation impregnation process.

10 BACKGROUND

 Wood and wood based products have properties that may be improved to improve the performance characteristics of wood, and to extend their application to new fields, including, for example dimensional instability due to the hygroscopic nature of wood,
15 discoloration, biological degradation and degradation on exposure to UV light.

 Many of the conventional leading technologies for treating wood or wood based materials comprise impregnation with heavy metal preservatives. However, the utilization of heavy metals in preservatives for timber treatment is now not favoured due to toxicity
20 and environmental issues.

 Acetylation of solid wood has been extensively investigated in the past, but due to the lack of an appropriate processing system to impregnate, react and recover the by-product of impregnation in a time period to be feasible, its commercial application has
25 been limited. However acetylation is environmentally friendly and can improve all or some of the aforementioned shortcomings of wood

 Acetylation of the wood prevents water molecules from penetrating the cell wall by bulking the cell wall and substituting the hygroscopic hydroxyl groups of lignin and
30 hemicellulose with hydrophobic (less polar) acetyl groups. Acetylation treatment can improve dimensional stabilization and biological resistance, and may also improve resistance to weathering effects, discoloration, and UV degradation.

Acetylation of solid wood is traditionally practiced in several steps. Typically, impregnation is first performed in a pressure cylinder and the acetylation reaction is then performed in a separate dedicated plant to heat and reflux the acetic anhydride for a lengthy period until acetylation is complete. After treatment and heat reaction, the by-product, which is a mixture of unreacted acetic anhydride and acetic acid, is recovered.

European patent 0 213 252 discloses a process in which wood was "impregnated by acetic anhydride using a vacuum or vacuum pressure technique, the material was then drained of excess acetic anhydride and placed in a chamber heated to 120° C. The material was heated at this temperature for 2 to 8 hours".

European patent 0 680 810 A1 and B1 discloses a process in which wood was impregnated by acetic anhydride at a temperature in the range of 80 – 150°C preferably 90 – 130°C and then maintained at a temperature between 70-150°C for a period of time up to 24 hours (suitably about 3 hours) to cause the acetylation reaction within the wood.

The effect of different catalysts on the reaction rate has also been investigated, but heating to temperatures of up to 139°C, which is the boiling point of acetic anhydride, has proved to be the best option.

Gaseous acetylation of solid wood achieves insufficient loading or weight gain for improvement in stability and decay resistance. To achieve a 15% weight gain in acetylation theoretically 30% or more acetic anhydride is required. To impregnate gaseously this amount of acetic anhydride in solid wood requires an extremely long impregnation time. Gaseous acetylation of wood at high temperature has only been successful on very small wood particles such as fibers, flakes, chips or sawdust. United States patent 6,376,582 discloses use of vapour of the acetylating agent at a reaction temperature of around 140 to about 210°C at atmospheric pressure. Thus the gaseous acetylation of solid wood is restricted to very small wood dimensions as the rate of vapour-phase acetylation is determined by the rate of diffusion of vapours into wood and the acetylation time rapidly increases with the increase in the wood thickness. Application of gaseous acetylation has therefore remained restricted to thin veneers or solid wood only a

few inches long in the fiber direction, in relation to which acetylation can be achieved within a practical treating time.

Traditional acetylation processes that heat pre-impregnated, saturated wood to react
5 the acetic anhydride have poor heating efficiency due to the following problems:

- 1: The mass of acetic anhydride in the wood.
- 2: The poor heat conductivity of wood.
- 3: The fact that the wood heating is by conduction rather than convection.
- 4: Heat distribution is not uniform throughout the solid wood and thus
10 acetylation is uneven.
- 5: The total treatment, reaction and recovery period required is extremely long.

It is an object of the present invention to address at least some of these
aforementioned shortcomings or to provide the public with a useful choice.

15

SUMMARY OF THE INVENTION

In another aspect the invention provides a process for impregnating wood or wood
based material comprising the steps of:

- 20 a. preheating a working solution to a temperature above the atmospheric boiling point (“a super hot temperature”) of the working solution;
- b. contacting a wood or wood based material with the working solution at a said super hot temperature and at an elevated pressure such that the working solution is in the liquid phase, to cause impregnation of the liquid base
25 solution into the wood or wood based material; and
- c. separating the wood or wood based material and any remaining working solution, waste material and/or by-products.

Preferably the process includes the step of, after impregnation, recovering the by-
30 products by releasing the pressure to cause the by-products to boil off. Optionally a vacuum may be applied to improve the recovery of by-products.

Preferably pre-pressure is applied to the wood or wood based material prior to contact with the working solution at the super hot temperature to ensure the working solution remains in the liquid phase.

5 In another aspect the present invention provides a process wherein the solvent is selected from any one or more of water, isopropanol, methylene chloride, xylene, xylene mixed with paraffin wax, and acetic anhydride.

10 In another aspect the present invention provides a process for impregnating wood or wood based material comprising the steps of:

- a. preheating a working solution to a temperature above the atmospheric boiling point ("a super hot temperature") of the working solution, at an elevated pressure sufficient to maintain the working solution in the liquid phase;
- 15 b. applying a pre-pressurise to a wood or wood based material prior to contact with the working solution at the super hot temperature, sufficient to maintain the working solution in the liquid phase;
- c. contacting a wood or wood based material with the working solution at a said super hot temperature and a said elevated pressure to cause impregnation of the solution into the wood or wood based material;
- 20 d. applying further pressure (the 'working pressure') to assist the impregnation of the working solution into the wood or wood based material; and
- e. separating the wood or wood based material and any remaining working solution, waste material and/or by-products.
- 25 f. reducing the pressure to remove any further working solution, waste material and/or by-products.

The term 'comprising' as used in this specification and claims means 'consisting at least in part of', that is to say when interrupting independent claims including that term, the features prefaced by that term in each claim will need to be present but other features can also be present.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is further described with reference to the accompanying figures in which:

- 5 **Figure 1** is a schematic illustration of a preferred impregnation process.
- Figure 2** is a chart of the boiling pressure at elevated temperature of water, acetic acid and acetic anhydride.
- Figure 3** shows the relationship between acetylation and volumetric Anti Shrink Efficiency (ASE).
- 10 **Figure 4** shows the relationship between acetylation and increase in oven dried volume.

DETAILED DESCRIPTION

15 In the process of the invention the solution is impregnated into the material in the liquid phase but at above the boiling point of the working solution, at a pressure which will maintain the working solution in the liquid phase. Typically the working solution will be preheated to a temperature above boiling point (“the super hot temperature”) under a pressure which ensures the working solution remains in the liquid phase. Alternatively the

20 working solution may be preheated to the super hot temperature at a pressure not sufficient to maintain the working solution in the liquid phase provided that pressure is subsequently applied so that when the working solution contacts the wood or wood based material it is in the liquid phase.

25 Also included within the scope of this invention is the preheating of the gaseous working solution which is subsequently condensed by the application of sufficient pressure so that the working solution is in the liquid phase when it contacts the wood or wood based material. Therefore the term working solution is to be interpreted to cover both gases and liquids.

30 The working solution is then released into a pressure impregnation vessel (which has been pre-pressured by a gas, for example nitrogen or air, to equal or above the pressure of the working solution) containing the wood or wood based material. The elevated

temperature will cause rapid reaction of the working solution in the wood while carrying out the impregnation in the liquid phase enables sufficient loading of acetic anhydride in the wood to be achieved to substantially enhance decay and insect resistance and dimensional stability of the wood, in a shorter processing time.

5

Any additional working solution and/or waste material is preferably subsequently separated from the wood or wood based material to protect the working solution from contamination by wood extractives and reaction by-product.

10 Wood or wood based materials which may be treated by the process of the invention include, but are not limited to solid wood, fiberboard, particle board, wood veneer, wood chips, OSB (oriented strand board), LVL (Laminated Veneer Lumber) and plywood.

15 Typically the process of the invention will be performed using two or more interconnected pressure vessels. Initially a first vessel contains the working solution and the wood is loaded into a second vessel. Optionally, a third vessel is connected to the second vessel to act as a reservoir for unreacted working solution and waste material.

20 Preferably the second vessel containing the wood or wood based material is evacuated and pressurized by a gas, such as air or nitrogen, prior to contact with the working solution. Suitable gases for applying pressure within the vessels include, but are not limited to, inert gases, for example nitrogen, argon and CO₂. The gas may also be a catalytic gas, for example acetic acid vapour at high temperature or acetic anhydride itself.

25 Desirably pressurized air is used. The main purpose of introduction of gas or vapours into this vessel is to eliminate boiling off of the super hot solution introduced and consequently stop the working solution cooling. It is believed that the high temperature and the oxidation free environment may induce some additional benefits on both stability and biodeterioration resistance of wood due to thermal treatment.

30

The composition of the working solution will depend upon the desired effect of the impregnation. Typically, the impregnation process will aim to improve dimensional instability caused by the hygroscopic nature of the wood, discoloration, biological

degradation and/or degradation by exposure to UV light. Examples of suitable working solutions include copper naphthenate in a solvent or solvents above their boiling point such as xylene, isopropanol and methylene chloride. Alternatively, xylene may be used as a heating medium by itself or in combination with paraffin wax. Since high temperature is involved in the process acetic anhydride may also be used to dissolve additional anhydrides, e.g. succinic anhydride. Preferably the working solution is acetic anhydride.

The working solution may be concentrated. Alternatively, the working solution may be diluted in an appropriate solvent, for example isopropyl alcohol (IPA), methylene chloride or water but is not limited thereto.

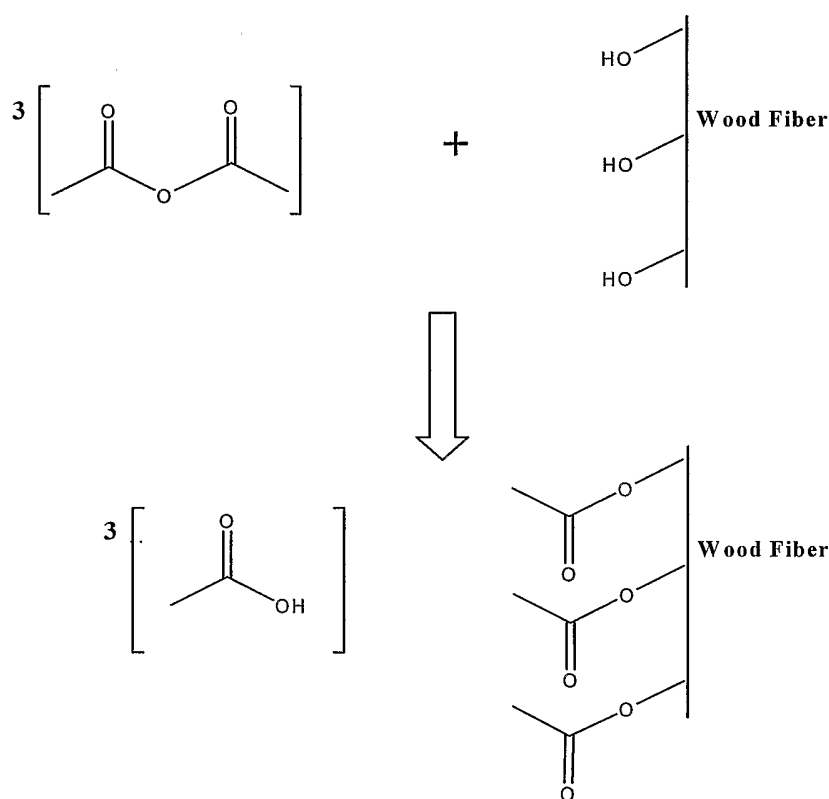
Desirably, the impregnation of the working solution within the wood or wood based material is assisted by the application of further pressure. The extra pressure can be either hydraulically or pneumatically applied.

Suitable pressure ranges for the pre-pressure stage are pressures sufficient to stop the solution from boiling at the elevated temperature, which can be from about 10 to about 1000kPa and preferably about 20 to about 700 kPa. Pressure can be applied by the vapour of the solvent used formed from the heated solvent, for example xylene, acetic anhydride and/or acetic acid. Pre-pressure can be inert gas or air.

Suitable pressure ranges for the working pressure, i.e. the extra pressure after flooding, are about 20 to about 4000kPa above the initial pre-pressure, but preferably about 20 to about 2000kPa. The working pressure will be partly determined by the permeability of the wood material being impregnated. Denser or refractory woods are less permeable and require higher pressures to achieve satisfactory impregnation of the working solution.

Suitable temperature ranges are about 10°C above the atmospheric pressure boiling point of the working solution and as high as recovery of excess solution warrants. In the case of acetic anhydride the temperature range is from about 150 to about 250°C, preferably from about 160 to about 220°C. The most preferred temperature is about 170 to about 200°C.

Preferably, once a desired pressure for maintaining the super hot working solution in a liquid phase has been attained, the pressure and/or temperature are held for a time sufficient to ensure reaction of the working solution within the wood or wood based product. The longer pressure is maintained, the greater the uptake of the working solution by the wood or wood based product. The term 'reaction' refers to any process which locks the working solution or part thereof within the wood or wood based product and may occur by biological, chemical or physical mechanisms. For example, when a working solution of acetic anhydride enters wood, it undergoes the substitution reaction below:



10

The acetyl group of acetic anhydride replaces the hydroxyl group of wood fibers with the formation of acetic acid by-product. The larger size of the acetyl group, compared to the hydroxyl group it replaces, causes a swelling of the wood which improves the properties of the wood, for example by reducing the moisture uptake of the wood.

15

Desirably any by-products formed by the reaction will have a boiling point lower than that of the working solution. Figure 2 shows that acetic acid (the by-product of the acetylation fixation reaction) has a boiling point lower than that of acetic anhydride. Therefore the pressure of acetic acid will be higher than that of acetic anhydride at any

time during holding at high temperature. This facilitates the preferential extraction of by-product from the reaction vessel. It is also believed that the removal of reaction by-product may further encourage the fixation reaction.

5 Typical waste materials, in addition to reaction by-products, may include naturally occurring wood sugars, hemicelluloses, saccharides and extractives, for example resin and fatty acids.

10 Desirably the pressure is maintained in the second vessel during the separation and drainage of the working solution and wood materials to prevent kickback from the wood affecting the working solution (the kickback is generally weaker and/or the ingredients are no longer in balance and it may also contain naturally occurring sugars and other molecules present in the wood which are carried back out of the wood). Kickback may occur during the release of pressure (“pressure kickback”) or during the application of a
15 vacuum (“vacuum kickback”).

 By draining the working solution after contact with the wood while maintaining a working pressure the extractives and by-product (for example acetic acid) contamination are reduced. Once the working solution has been drained from the second vessel, a vacuum
20 may be drawn through a condenser in a second vessel to facilitate the removal of further unreacted working solution from within the wood or wood based product together with any reaction by-products formed. Where the working solution comprises acetic anhydride, pressure kickback contains a mixture of acetic anhydride acetic acid and wood extractives and is coloured, typically red or brown, and vacuum kickback is colourless due to
25 vaporisation condensation of acetic acid rather than liquid flow. This is mainly due to the initial high temperature of the working solution which facilitates the removals of corrosive unwanted acetic acid.

 Extracted reaction by-products may optionally be separated, purified and recycled
30 by methods known in the art. For example, where acetic anhydride is the working solution acetic acid is the by-product. The acetic acid is extracted as a gas and may be collected by condensation. By dehydrating the acetic acid, acetic anhydride is formed suitable for reuse in the impregnation process. By separating only vacuum kickback some contamination of

the working solution by pressure kickback occurs which can be tolerated by adding more acetic anhydride to the working solution.

One embodiment of the impregnation process of the invention is shown in Figure 1. Vessel 101 containing working solution (in this example acetic anhydride) is preheated up to about 220°C at a vapour pressure of at least 600 kPa. Vessel 102 containing wood or wood-based material is evacuated and pre-pressurized using nitrogen through 108. Connecting lines 104 and 105 are opened allowing for the pressure between vessels 101 and 102 to equalize as the working solution enters vessel 102.

Once the pressure has equalised and flooding completed, valve 106 is closed and vessel 101 is placed under further pneumatic pressure through valve 109 which, via connecting line 104, in turn further pressurizes vessel 102. The final pressure shall be sufficient to ensure complete penetration of the product being impregnated. Alternatively a pressure pump (111) located in line 104 is used to pressurise cylinder 102. Pressure and temperature are held for a time to cause sufficient reaction of the working solution with the wood based material. Once the reaction is completed, excess working solution is drained from vessel 102 via connecting line 107 to vessel 103. Alternatively the solution can be returned to vessel 101, through line 104, by the pressure pump and/or pneumatic pressure.

Optionally, pneumatic pressure is applied to vessel 102 during draining of the working solution to avoid any kickback. This pressure can be vapour pressure of the super hot solution. Once the working solution has been drained, a vacuum is applied to vessel 102, through condenser 110, to remove any by-product liquid or gas (for example, where acetic anhydride is the working solution, the reaction by-product will be acetic acid. The acetic acid gas removed may be dehydrated to form acetic anhydride for reuse in the process).

In the process described above it is possible to effect treatment (impregnation), bulking (acetic anhydride reaction) and recovery all in one plant. This avoids the need to move the wood between a separate impregnation vessel and heat reaction plant, and also reduces the extra handling of corrosive chemicals.

It is believed that pre-impregnation of air or non-oxidative gas assists the deposition of chemicals where they are necessary (for example at “the cell wall”).

When compared to the existing prior art vapour phase acetylation processes, the
5 super hot temperature liquid phase acetylation process of the invention reduces the process
time that would otherwise be required at the temperature used to achieve reaction in a
single stage or vessel as in a vapour phase impregnation process, while achieving much
higher deposit of acetic anhydride in the wood, sufficient to significantly enhance wood
resistance to decay and insect attack and dimensional stability for example.

10

The process can also be used for other preservatives, solvents or combination of the
two. For example copper naphthenate can be dissolved in any solvent and pre-heated to
above the boiling point of solvent. After flooding and pressurizing using the super hot
solvent (above boiling point) the recovery of the solvent is greatly facilitated.

15

Heat curing at elevated temperature using different solvent or oil and recovery of
the solvent using the abovementioned process can bring dimensional stability, water
repellency and decay resistance to the wood.

20 The following description of experimental work further illustrates the invention:

Experiment 1: Acetylation

Radiata pine matched sapwood measuring 300x60x45 mm for ASE (Anti Shrink
25 Efficiency) and 300x20x20 mm for strength test was used in each run for the first nine
treatments referred to below. Radiata pine matched sapwood measuring 300x65x45 mm
for ASE and two 300x20x20 mm lengths for strength test was used for the treatments 10 to
20.

30 All wood samples were oven dried prior to treatments except treatments 6, 7 and
20.

Acetylation was conducted in three interconnected 2 litre stainless steel cylinders. Cylinders 1 and 2 had a heating jacket connected to PID controller to maintain temperature control. Pneumatic pressures were attained using compressed nitrogen gas.

- 5 The volumetric swelling coefficient was calculated according to the following formulae.

$$S = \frac{V_2 - V_1}{V_1} \times 100$$

where S = volumetric swelling coefficient

V₂ = wood volume at water saturation

V₁ = oven dried wood volume before saturation

10

Anti Shrink Efficiency was then calculated as follows:

$$ASE = \frac{S_c - S_M}{S_c} \times 100$$

where S_c is volumetric swelling coefficient of control and S_M is volumetric swelling coefficient of modified wood sample.

Details of all treatments are summarized in Table 1

Table 1: Treatment process, weight gain and ASE for experiment 1

Treatment	Solution Temperature Before (C°)	Extra Pressure kPa	Hydraulic Heating	Maximum Temp in Cylinder 2 (C°)	Hydraulic Time (minute)	Pneumatic Time (minute)	Bleeding Time (minute)	Vacuum Time (minute)	Including recovery of by-products	Weight Gain After Treatment (%)	Reacted Weight Gain 48 h oven (%)	Unreacted 48 Hour Oven (%)	Volumetric ASE (%)	Oven Dried Volume Increase (%)
Con														
2	155	200	Yes	162	30	30	40		100	24.6	19.4	5.1	73.5	7.4
3	175	200	Yes	180	30	30	40		100	28.3	22.4	5.9	87.5	7.6
4	180	200	Yes	175	15	25	30		70	25.4	23.2	2.2	87.4	9.6
5	200	200	Yes	159	20	20	15	25	80	32.1	20.6	11.6		
6*	170	200	Yes	158	10	20	20	35	85	20.9	7.6	13.4	72.1	
7*	200	200	Yes	183	15	25	10	16	66	11.4	2.9	8.5	50.6	
8	190	500	Yes	191	60	1	10	8	79	36.7	29.8	6.9	90.9	12.9
9	190	500	Yes	194	45	2	10	10	67	29.2	24.9	4.3	78.1	10.7
10	190	500	Yes	170	10	1	10	20	41	25.1	23.0	2.1	75.4	9.1
11	180	500	Yes	186	45	1	5	15	66	32.8	28.5	4.3	81.1	10.2
12	190	500	No	130	5	1	18	15	39	22.6	13.9	8.7	62.4	7.6
13	200	500	No	137	5	1	16	20	42	27.5	19.6	7.9	69.4	8.3
14	190	800	Yes	159	10	1	10	20	41	26.0	21.7	4.3	74.7	8.3
15	200	500	No	141	5	40	5	32	82	42.8	23.4	19.4	71.7	8.3
16	190	500	Yes	161	10	1	4	28	43	22.1	19.8	2.3	69.7	8.3
17	190	500	Yes	158	10	1	6	10	27	20.6	18.1	2.5	65.7	7.5
18	180	500	Yes	179	20	1	5.5	30	57	28.2	25.5	2.7	80.4	9.3
19*	180	500	Yes	178	20	1	7	30	58	10.4	6.6	3.7	64.3	

* Samples were not oven dried prior treatment

- 5 Net uptake, gross uptake, pressure and vacuum kickback of all treatments are summarized in Table 2.

Table 2: Net uptake, Gross uptake, Pressure and Vacuum kickback

Treatment	Net Uptake After Treatment (kg/m ³)	Pressure (kg/m ³)	Kickback	Vacuum (kg/m ³)	Kickback	Gross Uptake During Treatment (kg/m ³)
2	84.87	166.3		120.4		371.6
3	101.01	244.9		35.7		381.6
4	88.12	110.2		32.7		231.0
5	109.39	66.8		72.4		248.7
6		88.8		78.6		
7	44.31	57.1		85.7		187.2
8	128.99	150.0		140.8		419.8
9	155.38	176.6		125.7		457.7
10	129.51	217.9		54.7		402.1
11	163.78	170.8		103.6		438.3
12	119.27	241.8		84.5		445.6
13	140.89	195.8		91.2		427.8
14	132.38	305.2		118.0		555.6
15	210.58	77.7		99.8		388.1
16	113.40	206.3		92.1		411.9
17	108.94	172.7		77.7		359.4
18	137.61	205.4		102.7		445.7
19	68.46	185.2		91.2		344.9

Pressure kickback was a red brown colour due to extractives, but vacuum kickback was clear which indicates the vaporization of acetic acid from the wood due to its initial high temperature and its condensation rather than flowing out as liquid (note samples were not pre-extracted to remove extractives).

Figures 3 and 4 show the anti shrink efficiency (ASE) and oven dried volume increase of the wood samples. A limit of 28% weight gain is very close to the maximum theoretical reaction by acetylation. At higher temperatures adopted by this treatment process a weight loss due to solubilisation of wood extractives of up to 2% is probable, thus the actual weight gain due to acetylation is probably higher.

Figure 4 shows the close relation of bulking and ASE. Acetylation bulks the wood cell wall and thus the oven dried volume of wood increases. Figure 4 shows this effect,

which can be another way of measuring the extent of acetylation. In fact it is believed this volume increase is the main cause of ASE improvement.

Spectra of actual solutions were collected with horizontal ATR cell for treatment 5. Spectra showed that the solution before treatment was 100% acetic anhydride, after
5 treatment solutions showed that the majority of working solution was acetic anhydride, the majority of pressure kickback solution was acetic acid and the vacuum kickback solution was mostly acetic acid (by-product).

The results show that high acetylation of radiata pine sapwood can be achieved in a very short time.

10 **Experiment 2: Alternative Solvents with preservative agent**

Two solvents, Isopropyl alcohol and methylene chloride were tried with copper naphthenate as the preservative. One piece of radiata pine sapwood end-sealed 290x72x44mm was treated in each treatment.

A total of five treatments were conducted, three with Isopropyl alcohol and two
15 with Methylene Chloride. Treatment time for all treatments was 35 minutes. The plant described in experiment 1 was used and cylinder 102 was pre heated to 70°C for all treatments. Initial pneumatic pre-pressure for all treatments was adjusted to the boiling pressure of respective solvent at elevated temperature.

Table 3 shows the treatment process and solvent recovery for all treatments.

Table 3 Treatment Process, Net Uptake, Net Copper Naphthenate Uptake and Solvent remaining in the Wood

Treatment	Solvent Temperature (°C)/Pressure (kPa)	Hydraulic Pressure (kPa)	Net Uptake (Kg/m ³)	Net Copper Naphthenate Calculated (Kg/m ³)	Analytical Copper (% w/w) in Wood	Net Solvent Uptake Calculated (Kg/m ³)	Copper Penetration
Isopropyl 1	112/205	280	9.8	7	0.03	2.8	Complete
Isopropyl 2	112/190	290	18.4	13	0.08	5.4	Complete
Isopropyl 3	116/220	380	17.9	13	0.07	4.9	Complete
Methylene 1	88/300	440	16.6	12	0.08	4.6	Complete
Methylene 2	86/295	520	12.9	10	0.09	2.9	Complete

5 Experiment 3: Further Acetylation and Other Species

A further experiment was conducted on Sitka spruce, Scots pine and radiata pine as in Table 4.

- 10 Succinic anhydride also reacts to wood hydroxyl group in the same way as acetic anhydride, but creating no acidic by-product. In treatment 39, 10% succinic anhydride was dissolved in acetic anhydride working solution to observe the reduction of wood charring and effect on other wood properties.

Table 4

	Treatment	Wood Moisture Content	Solution Temperature Before (C°)	Extra Pressure (kPa)	Maximum Temp (C°)	Hydraulic Time (minute)	Pneumatic Time (minute)	Bleeding Time (minute)	Vacuum Time (minute)	Total Time (minute) Including Recovery
	Radiata 37	OD	198	500	155	5	1.0	1.5	40	47.5
	Radiata 38	OD	190	500	167	15	1.0	2	40	58
10% SA*	Radiata 39	OD	191	500	169	16	1.0	2	38	57
Used AA**	Radiata 40	OD	193	500	168	15	1.0	2	38	56
Used AA	Radiata 41	9	190	500	168	16	1.0	2	40	59
	Radiata 48	OD	220	500	168	15	1.0	2	36	56
	Radiata 49	OD	220	500	150	5	1.0	2	50	59
	Scots 1	OD	190	800	162	10	1.0	5	33	49
	Spruce 1	OD	193	800	162	10	1.0	3	40	54
	Scots 2	OD	180	500	139	5	1.0	3	46	55
	Spruce 2	OD	182	500	143	5	1.0	3	44	53

* 10% succinic anhydride dissolved in acetic anhydride

** Acetic anhydride working solution was from previous treatments

The weight gain and ASE of third experiments are in Table 5 below.

5

Table 5

Treatment	Weight gain Aft Treatment (%)	Reacted Weight Aft Oven (%)	Un reacted (%)	Burning Inside 0 Min to 5 Max	ASE (%)
Scots Pine 1	29.10	23.18	5.92	2.00	82.10
Scots Pine 2	25.39	18.95	6.44	0.00	72.40
Spruce 1	26.33	16.21	10.11	2.00	70.80
Spruce 2	17.86	11.03	6.83	0.00	40.40
Radiata 37	19.11	17.01	2.10	0.50	63.56
Radiata 38	21.60	19.30	2.30	0.25	70.95
Radiata 39	25.10	22.80	2.30	0.00	70.10
Radiata 40	21.00	18.50	2.50	0.00	68.51
Radiata 41	5.50	8.10	5.40	0.25	39.34
Radiata 48	20.4	18.4	2.00	0.00	64.4
Radiata 49	16.95	15.58	1.37	0.00	39.5

Experiment 4: Further Heat Curing by Super Hot Solvent

Super heated xylene at 200°C was used as a medium for heat treatment. Two treatments were conducted, xylene and 5% paraffin wax dissolved in xylene. In both treatments radiata pine sapwood at 9% moisture content was used. Wood was light brown in colour after treatments and lost weight due to extractives dissolved in xylene. Treatment process is summarised in Table 6

Table 6

	Wood Moisture Content	Solution Temperature Before	Extra Pressure	Maximum Temp	Hydraulic Time	Pneumatic Time	Bleeding Time	Vacuum Time	Total Time
xylene	9	201	500	201	30	3.0	10	25	68
xylene+wax	9	202	500	210	30	3.0	8	30	71

10

ASE for xylene treated sample was 13.2% and for 5% wax dissolved in xylene was 7.8%.

Experiment 5 – Recycling acetic anhydride

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Further experiments were conducted in which the acetic anhydride used was a recycled solution from previous treatments and contained wood extractives and by-product acetic acid. A treatment schedule was followed and from treatment 71 onward working solution was not renewed but topped up by acetic anhydride. Thus in treatment 92 the working solution was used/topped up for 20 times. Xylene, a non-swelling solvent, was chosen to dilute this acetic anhydride working solution. Dilutions were performed on a weight/weight basis as shown in Table 7.

20

Table 7 : Dilution Summary

Treatment ID	Acetic anhydride (%)	Xylene (%)
92	100	0
93	80	20
95	60	40
96	40	60
97	20	80
94	0	100

Table 8 : Schedule Summary

Solution Temperature	°C	190
Initial Pressure*	kPa	300 – 400
Working Pressure	kPa	1100
Hydraulic Time	minutes	10
Hydraulic Temperature	°C	160
Pneumatic Time	minutes	1
Pressure Release	minutes	3
Vacuum Time	minutes	43

5

*Due to the solution being a mixture, the boiling point and subsequently pressure was different depending on the composition

Degree of Acetylation

The effect of percentage acetic anhydride on weight gain (degree of acetylation) is shown
10 in Table 9

Table 9 : Effect of Anhydride Concentration on Weight Gain

Acetic Anhydride %	Weight Gain After Treatment (%)	Un-recovered (%)	Actual Weight Gain (%)
100	28.4	3.7	23.7
80	25.2	3.3	21.2
60	20.8	2.6	17.8
40	17.7	3.3	13.9
20	12.2	3.8	8.1
0	1.2	0.7	0.5

These trials were conducted at a uniform total time of 60 minutes.

If time was not a limiting factor then an increased weight gain may have been achieved with the diluted working solutions.

Internal Burning

5

Impregnated 300mm long samples of wood were cut across their midpoint reveal their cross section. The exposed cross sections were sanded. Both the experiments using a 100% acetic anhydride working solution and experiments using a working solution diluted with xylene showed uniform colour and no sign of internal burning. This indicates that it is possible to avoid possible wood charring by dilution of the working solution with xylene and/or by process manipulation.

10

Experiment 6 - Acetylation treatments at 20 litre pilot plant

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In treatment 208 radiata pine heartwood and sapwood having different sizes were treated by pre-heating acetic anhydride to 173 °C and using the pressure of the gaseous acetic anhydride formed to pre-pressurise the acetic anhydride to 130 kPa thereby maintaining the liquid phase. The working pressure applied to the wood and acetic anhydride was 1000 kPa. The size and weight gains of the samples are illustrated in table

20

10.

Table 10

Treatment	Sample size			Weight	Un Reacted &
No. 208	Width	Thickness	Length	gain	By-product
Sample	(g)	(mm)	(mm)	%	%
A	90.07	45.75	645	27.55	3.08
B	90.05	45.14	645	27.28	2.73
C	89.76	45.16	645	26.55	3.48
D	89.62	45.19	645	31.65	6.16
D1	89.76	20.19	645	32.64	7.09
D2	90.04	19.71	645	31.14	5.24

In treatment 209 radiata pine heartwood and sapwood having two different thickness were treated by pre-heating acetic anhydride to 170°C and using the pressure of the gaseous acetic anhydride formed to pre-pressurise the acetic anhydride to 110 kPa thereby maintaining the liquid phase. The working pressure applied to the wood and acetic anhydride was 310 kPa. The size and weight gains of the samples are provided in table 11.

Table 11

Treatment	Sample size			Weight	Un Reacted &
No. 209	Width	Thickness	Length	gain	By-product
Sample	(g)	(mm)	(mm)	%	%
A	90.07	45.75	645	13.04	1.28
B	90.05	45.14	645	12.29	1.45
C	89.76	45.16	645	10.68	2.13
D	89.62	45.19	645	13.66	2.48
D1	89.76	20.19	645	18.61	0.87
D2	90.04	19.71	645	20.50	1.12

The foregoing describes the invention and a preferred form thereof. Alterations and modifications as will be obvious to those skilled in the art are intended to be incorporated within the scope hereof, as defined in the accompanying claims.

WHAT WE CLAIM IS:

1. A process for impregnating wood or wood based material comprising the steps of:
 - a. preheating a working solution to a temperature above the atmospheric boiling point (“a super hot temperature”) of the working solution;
 - 5 b. contacting a wood or wood based material with the working solution at a said super hot temperature and at an elevated pressure such that the working solution is in the liquid phase, to cause impregnation of the liquid base solution into the wood or wood based material; and
 - c. separating the wood or wood based material and any remaining
10 working solution, waste material and/or by-products.

2. A process as claimed in claim 1 including applying sufficient pressure throughout the preheating step to ensure the working solution is maintained in the liquid phase.
15

3. A process as claimed in claim 1 or 2 including applying an initial pre-pressure to the wood or wood based material prior to contact with the working solution at the super hot temperature, sufficient to maintain the working solution in the liquid phase.
20

4. A process as claimed in claim 3 including applying the pre-pressure by a gas.

5. A process as claimed in claim 4 wherein the gas is selected from nitrogen, air, carbon dioxide, argon, acetic acid vapour or acetic anhydride vapour.
25

6. A process as claimed in any one of claims 3 to 5 including pre-pressurising the working solution to in the range of 10 to 1000 kPa.

7. A process as claimed in any one of claims 3 to 6 including pre-pressurising the
30 working solution to in the range of 20 to 700 kPa.

8. A process as claimed in any one of claims 1 to 7 including assisting the impregnation of the solution into the wood or wood based material by applying a further hydraulic or pneumatic pressure (the 'working pressure').
9. A process as claimed in claim 8 including applying the working pressure in the range of 20 to 4000 kPa above the initial pre-pressure.
10. A process as claimed in claims 8 or 9 including applying the working pressure in the range of 20 to 2000 kPa above the initial pre-pressure.
11. A process as claimed in any one of claims 8 to 10 including applying the working pressure for less than about 240 minutes.
12. A process as claimed in any one of claims 8 to 10 including applying the working pressure for less than 120 minutes.
13. A process as claimed in any one of claims 8 to 10 including applying the working pressure for between about 1 and about 60 minutes.
14. A process as claimed in any one of the preceding claims including subsequent to the impregnation, releasing pressure to separate any remaining working solution, waste material and by-products (the 'pressure kickback').
15. A process as claimed in claim 14 including subsequent to separating the wood or wood based material and any remaining working solution, waste material and/or by-products, releasing pressure to separate the pressure kickback.
16. A process as claimed in any one of the preceding claims including applying a vacuum to separate any remaining working solution, waste material and/or by-products (the 'vacuum kickback').
17. A process as claimed in claim 16 including recycling the pressure kickback, the vacuum kickback or both for reuse as the working solution.

18. A process as claimed in claim 17 including adding further of said working solution to the recycled working solution and reusing same.
19. A process as claimed in any one of the preceding claims wherein the boiling point of the reaction by-products is lower than the boiling point of the working solution.
- 5
20. A process as claimed in any one of the preceding claims wherein the wood or wood based material is selected from one or more of solid wood, fibreboard, particle board, wood veneer, wood chips, oriented strand board, laminated veneer board and plywood.
- 10
21. A process according to any one of the preceding claims including when carried out in a plant comprising:
- a. a first pressure vessel for initially containing and preheating the working solution; and
 - 15 b. a second pressure vessel for containing and contacting the wood or wood based material with the working solution.
22. A process as claimed in claim 21 wherein said plant also includes a third pressure vessel as a reservoir for unreacted working solution, waste material and/or by-products, said third pressure vessel communicating with said second pressure vessel.
- 20
23. A process as claimed in any one of the preceding claims including pre-heating the working solution to above about 10 °C above the atmospheric pressure boiling point of the working solution.
- 25
24. A process as claimed in claim 23 including pre-heating the working solution to in the range of 150 to 250 °C.
- 30
25. A process as claimed in claim 24 including pre-heating the working solution to in the range of 160 to 220 °C.

26. A process as claimed in claim 25 including pre-heating the working solution to in the range of 170 to 200 °C.
27. A process as claimed in any one of the preceding claims wherein the working solution is selected from any one or more of copper naphthenate, xylene, succinic acid and acetic anhydride.
28. A process as claimed in claim 27 wherein the working solution is acetic anhydride.
29. A process as claimed in any one of the preceding claims including combining the working solution with a solvent.
30. A process as claimed in claim 29 wherein the solvent is selected from any one or more of water, isopropanol, methylene chloride, xylene, xylene mixed with paraffin wax, and acetic anhydride.
31. A process for impregnating wood or wood based material comprising the steps of:
- a. preheating a working solution to a temperature above the atmospheric boiling point (“a super hot temperature”) of the working solution, at an elevated pressure sufficient to maintain the working solution in the liquid phase;
 - b. applying a pre-pressurise to a wood or wood based material prior to contact with the working solution at the super hot temperature, sufficient to maintain the working solution in the liquid phase;
 - c. contacting a wood or wood based material with the working solution at a said super hot temperature and a said elevated pressure to cause impregnation of the solution into the wood or wood based material;
 - d. applying further pressure (the ‘working pressure’) to assist the impregnation of the working solution into the wood or wood based material;
 - e. separating the wood or wood based material and any remaining working solution, waste material and/or by-products.

- f. reducing the pressure to remove any further working solution, waste material and/or by-products.
32. A process for impregnating wood or wood based material comprising the steps of:
- 5 a. preheating a working solution to a temperature above the atmospheric boiling point (“a super hot temperature”) of the working solution, at an elevated pressure sufficient to maintain the working solution in the liquid phase;
- 10 b. contacting a wood or wood based material with the working solution at a said super hot temperature and a said elevated pressure to cause impregnation of the solution into the wood or wood based material;
- c. separating the wood or wood based material and any remaining working solution, waste material and/or by-products; and
- 15 d. recycling any separated working solution, waste material and/or by-products as the working solution.
33. An impregnated wood or wood based material produced according to a process of any one of the preceding claims.

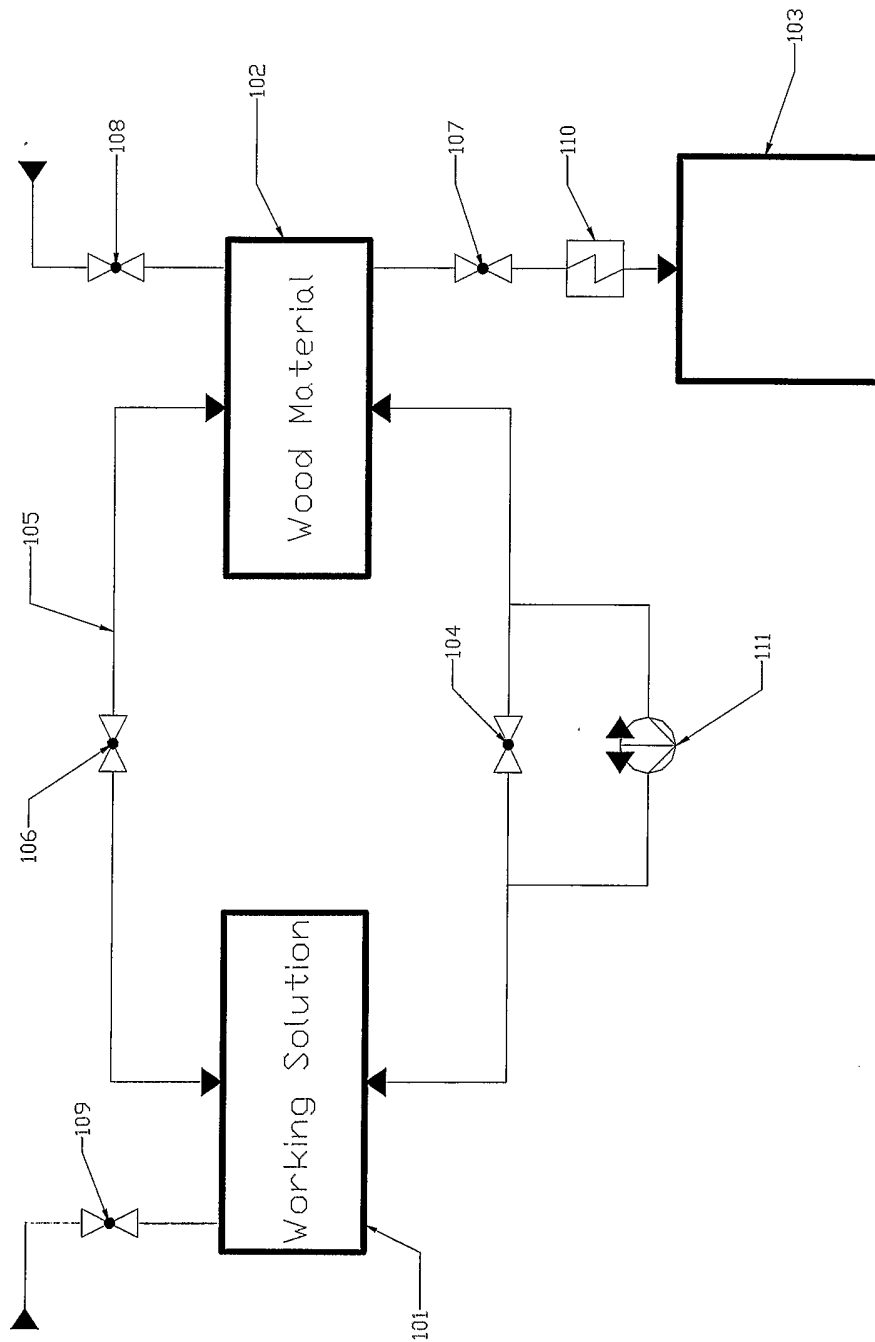


FIGURE 1

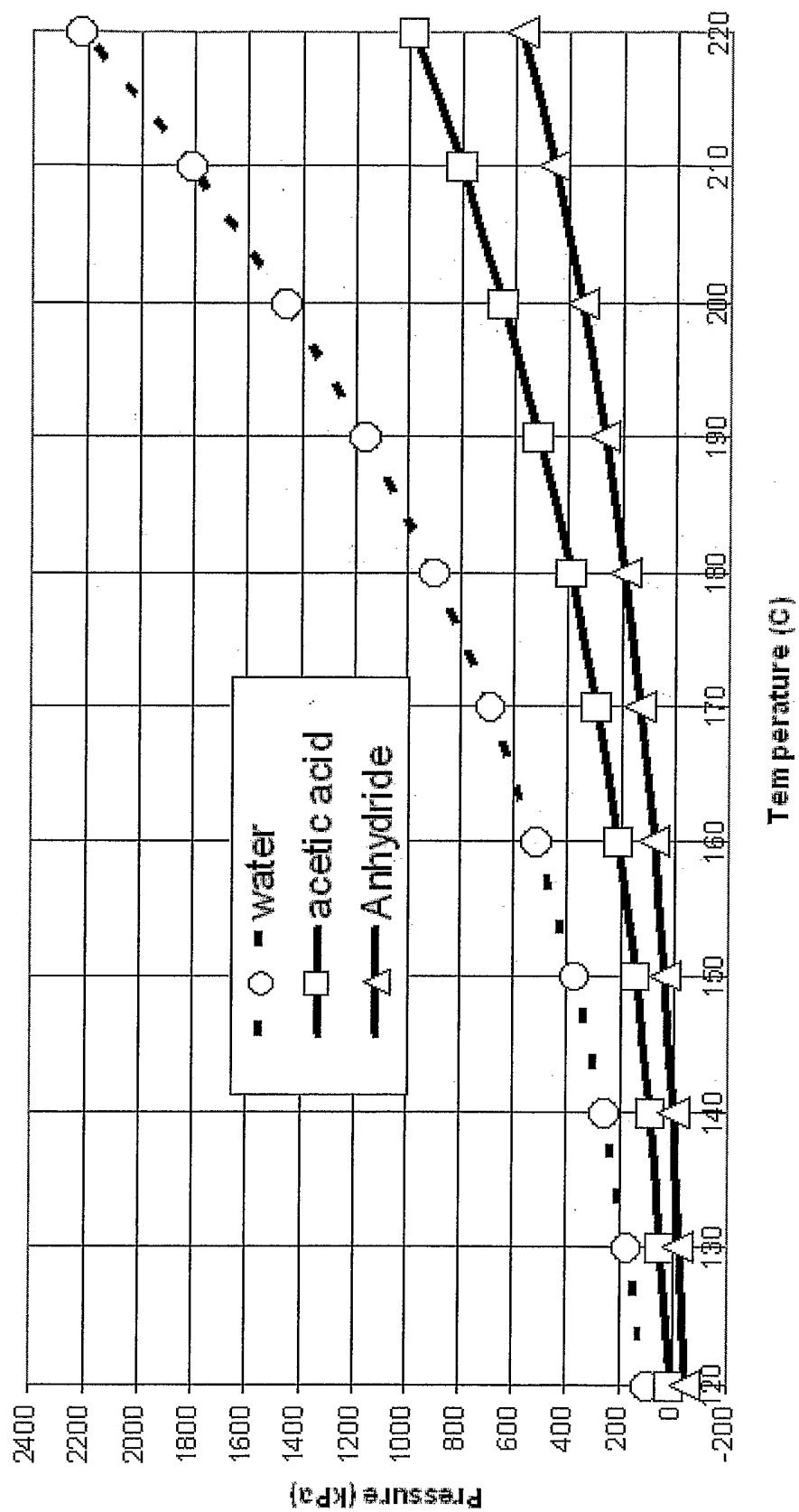


FIGURE 2

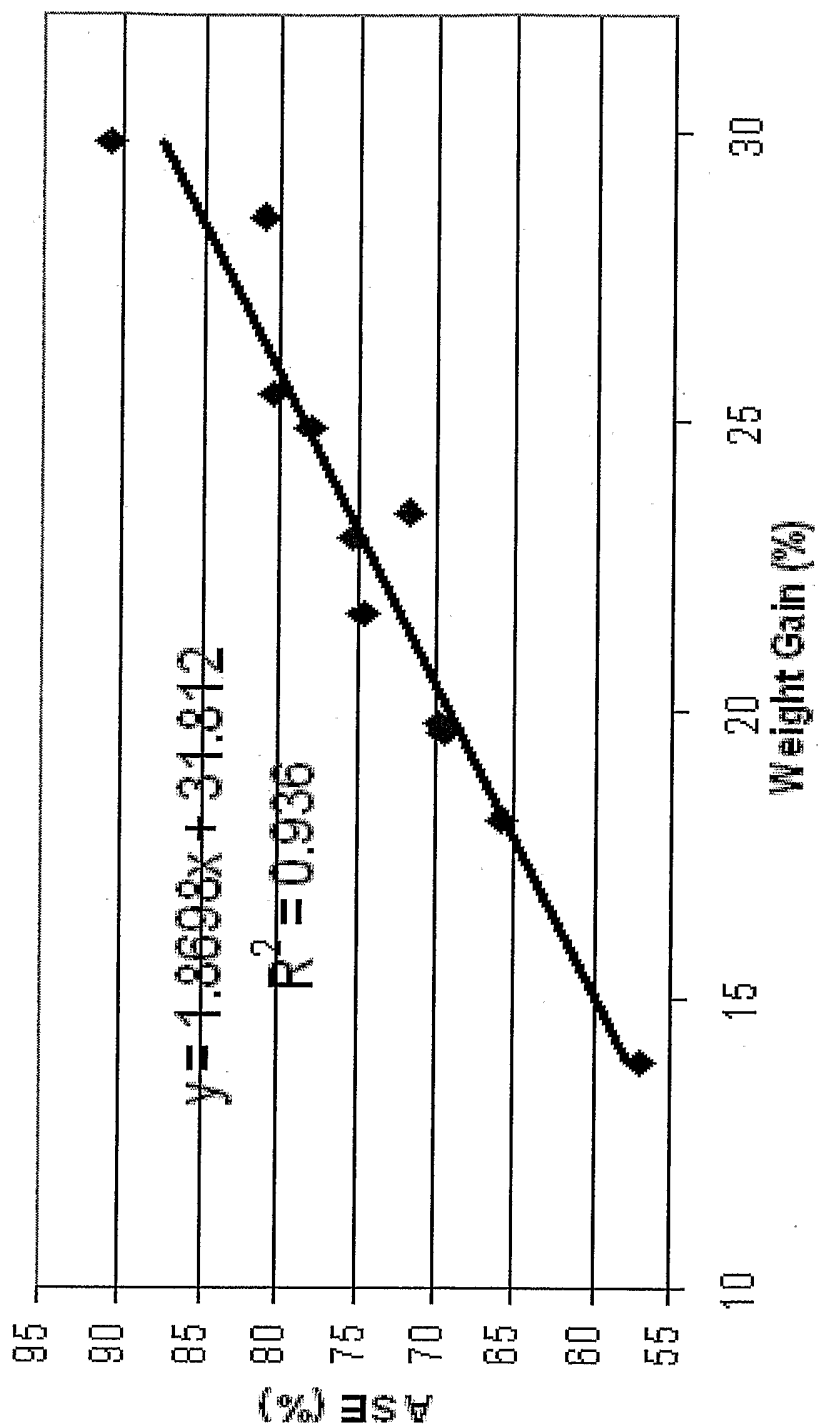


FIGURE 3

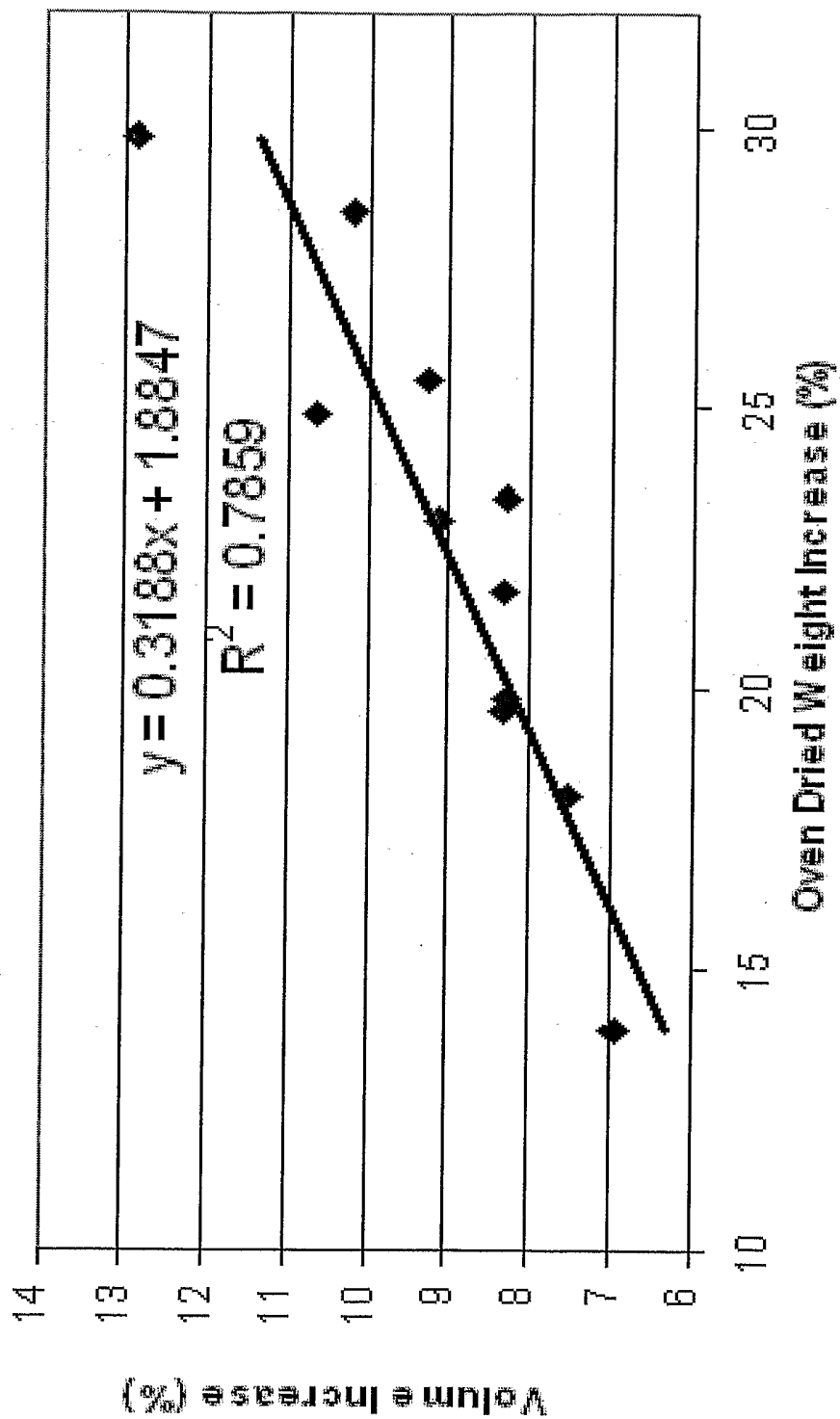


FIGURE 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ2005/000022

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl. ⁷ : B27K 3/08 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) B27K 3/08 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched NONE Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) B27K 3/08 and Keywords ((super(s)heat+) or boil+)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2001/024982 A (JARLASA FARGINDUSTRIER AB) 12 April 2001 Whole document	1-33
A	Derwent abstract accession No 2004-496208/47 Class P63 RU 2230658 C (KONTSEVOI S A) 20 June 2004 See abstract	1-33
A	EP 680810 A (STICHTING HOUT RESEARCH SHR) 8 November 1995 See abstract	1-33
<input type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family	
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 26 April 2005	Date of mailing of the international search report 28 APR 2005	
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustrialia.gov.au Facsimile No. (02) 6285 3929	Authorized officer GREGORY DIVEN Telephone No : (02) 6283 2992	

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NZ2005/000022

Information on patent family members

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
WO	2001/024982	AT	243096	AU	79766/00	CA	2386503
		CN	1377307	CZ	20021109	DE	60003460
		DK	1237687	EE	200200179	EP	1237687
		HU	0204152	JP	2003511258	NO	20021635
		NZ	518171	PL	354288	SE	9903622
		SK	4402002				
RU	2230658		NONE				
EP	680810	DE	69411887	DK	680810	ES	2122077

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX