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(54) Title: PROCESS FOR THE MODIFICATION OF LIGNOCELLULOSIC MATERIAL IN VAPOUR PHASE

(57) Abstract

Reaction of Lignocellulosic material with Acetic Anhydride vapour greatly improves dimensional stability and resistance to biological attack and is according to this, invention made in the absence of any co-solvent or added catalyst in a simple way, very speedily with optimization of raw material feed and without the need for distillation/rectification. Partially dried or dry Lignocellulosic material heated is treated with Acetic Anhydride vapour for very short period of time. The time being adapted to suit the material dimension. The material is reacted and dried with or without gas flow and the resultant material is then by sample volatile analysis given a yield factor to pre-determined weight gain. Acetic Acid is only removed and further treated by known Ketene for re-vaporization.

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PROCESS FOR THE MODIFICATION OF LIGNOCELLULOSIC MATERIAL IN VAPOUR PHASE.

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Acetylated wood has been found to possess a high degree of dimensional stability and good decay resistance. Previous attempts at commercial process have been found to be expensive to attract industry and the processes have been used with wood of lumber thickness liquid phase treatments have tendered to cause problems with the large excess after acetylation of the acetylating solution.

This process deals specifically with the Acetylation of Lignocellulosic materials in their vapour phase using Lignocellulosic fibre, chip, shred, and veneer material. The Lignocellulosic material can then be resinated and pressed or moulded or extracted into all manner of products in an acceptable industrial scale.

Our Research and Development has culminated in an acceptable practical process for Acetylating Lignocellulosic material in vapour phase, for the production of all manner of finished products on existing industrial finishing equipment, the whole process maintaining sustainable cost variances with other none acetylated material.

The process of Lignocellulosic material being modified by vapour phase with Acetic Anhydride, and its derivatives greatly improves the stability, its resistance to moisture and its resistance to biological attack whilst the products can be fire proofed and coloured and have the ability to be recycled.

OBJECT AND ADVANTAGES OF THIS INDUSTRIAL SCALE PROCESS.

Process.

The primary objective of this industrial process scale invention is to present a process for large scale industrial continuous production use for acetylating all types of Lignocellulosic materials by vapour phase in a cost effective manner. The process does not use complex mixtures, the equipment is simple and user friendly and the materials of construction are non exotic easily fabricated thus not having the disadvantages of the prior inventions.

The process will continuously improve the (Linear % Swell %) stability I.B.S., M.O.R., and M.O.E. of the finished product, along with biological resistance to all manner of Lignocellulosic materials, in fibre, chip, shred and veneer form.

The present invention is believed to have several advantages over prior inventions in modification of wood its derivative materials, or other Lignocellulosic materials.

1. Speed of modification over liquid phase.
2. Simple equipment in standard classification materials. None exotic
3. Minimum cost of equipment manufacture.
4. Eliminates need for an added catalyst.
5. Minimum chemical usage.
6. Co-solvents or diluents not required.
7. No need for high pressure during modification.
8. No requirement for manifold excess or Acetic Anhydride.
9. Can be used to modify partially dry or dry Lignocellulosic material.
10. Simple recovery of excess reagents and by products.
11. Can be "bolt on" facility and compliment existing manufacturing equipment.

This process does not use a co-solvent or added catalyst and its most simple and user friendly to operate. The Lignocellulosic material is dried to its mean average using centrifugal filtration techniques. Existing drying facilities when centrifugal techniques are not used. Plume elimination to atmosphere when centrifugal techniques are used. The material is treated counter current wise with precise amount of Acetic Anhydride vapour for a very short period of time. The time is adapted to suit the material and final specification required. Excess acetylation solution is removed and recovered. The continuous chamber then completes the reaction and dries the Lignocellulosic material. The specification of the final product is related to its weight gain for the specific use required.

The Industrial Scale Process for the modification of Lignocellulosic material relates to the chemical modification of Lignocellulosic materials by Acetic Anhydride in vapour phase. This process in an industrial scale relates to the modification of all Lignocellulosic materials to obtain a high degree of moisture resistance, stability and greater resistance to infestation. The Industrial Scale Process can also deal with other Lignocellulosic materials such as :-

1. Palm
2. Peat
3. Wood Fibre
4. Baggass
5. Straw

and in materials from fibre to wood shred.

DESCRIPTION OF PREVIOUS INVENTIONS.

There are desirable and undesirable properties within Lignocellulosic material. The undesirable properties have limited their use for many products. Physical and chemical properties of Lignocellulosic materials are the result of the structure of the cell wall components both individually and collectively.

A good example being, wood changes its dimension with a changing moisture content. This is due to the cell wall polymers containing Hydroxyl and other oxygen containing groups. These groups attract moisture through hydrogen bonding. This moisture take up, swells the cell wall and therefore the wood expands until the cell wall becomes saturated with water. Beyond the saturation point the water is free water in the structure and as such does not take part in further expansion. This process is somewhat reversible i.e. as moisture is lost, shrinkage will occur.

Furthermore Lignocellulosic materials are bio degradable, organisms do recognize the polysacharides in the cell wall and they have very specific enzyme systems which are capable of changing these polymers into digestible units.

The high molecule or weight cellulose is the primary element responsible for strength in wood. The strength is lost as this polymer undergoes biological degradation through oxidation hydrolysis and dehydration reactions.

It has been noted that dimensional instability and biological degradation can be said to be a chemical phenomena. It is therefore possible to improve both of these undesirable properties with Lignocellulosic material by changing the basic cell wall polymer chemistry.

Chemical modification causes the cellulose and Hemi Cellulose elements, thus stability and biological reactions cannot take place because the chemical and molecular configuration/conformation of the substrate has been altered. Thus the packing of the cell wall by reacting chemicals to the cell wall polymers reducers the Lignocellulosic tendency to swell with changes in moisture because the Lignocellulosic material is already partially swollen by the reaction.

Therefore the Hydroxyl groups in the cell wall polymers being esterified with Acetic Anhydride vapour, both dimensional stability and resistance to biological attack can be achieved. Reference works are as follows:-

1. Fuchs (BER.61B : 9481 : 1928).
2. Horn (BER.61B : 2542 : 1928).
3. Suida and Titsch (BER. 62B : 1599 : 1928).
4. Friese (BER.63B : 1902).
5. Suida (AUSTRIA PATENT 122.499 : 1930)
6. Ridgway & Vallington (BRITISH PATENT 579.255 : 1946)
7. Stamm and Tarkow (US PATENT 2417.995 : 1947).
8. Goldsteam & Weaver (US PATENT 3094.431).
9. Kling and Tarkow (TAPPI VOL 49 NO. 1 1966).
10. In 1985 Rowell and Simonson, Euro Patent 0213 252, showed by their invention that it was possible to acelytate Lignocellulosic material in liquid phase without catalyst or co-solvent. Whilst this liquid phase is possible, the process for industry tends to be too long leading to high costs.

Several methods of acetylation designed for stabilising the dimensions of and biological resistance of Lignocellulosic material have been suggested. All have presented great problems in the field of large scale industrial chemical modification due to their commercial significance. The previous attempts suffer from one or more of the following disadvantages.

The process is too large to suit existing industrial restraints. Is too time consuming. The process is too complicated, is excessively expensive, special drying facilities required, or the process inputs undesirable properties to the product.

Continuous large scale industrial process cannot tolerate any of the above disadvantages. It is not surprising therefore that modification of Lignocellulosic materials by Acetylation has not been more frequently used. Such high cost with other disadvantages in the past, have been a hindrance to the commercial realization of the application. Such application being in construction materials MDF - Particle Board, "Mopping up oil" spillages - sports goods, windows, doors, door/window frames and very many more uses.

CONTINUOUS / BATCH INDUSTRIAL PROCESS - FROM SCHEMATIC OF THE PROCESS FIGURE 1.

In relation to the foregoing it has now been established that post dried or dry Lignocellulosic materials in fibre, chip, shred or veneer can be acetylated in a continuous or batch process in vapour phase, which eliminates a catalyst or organic co-solvent. The procedures do not require high pressure, with very short reaction time and in this way high levels of dimensional stability, biological resistance are greatly enhanced hydrophobic characteristics are realised.

Lignocellulosic fibres, chip, shred, of all types and sizes practically or totally dried by continuous filtration or otherwise to mean average moisture content and below, are transported at temperature into a modifier either in continuous configuration or batch (1), (2). Anhydride vapour enters the modifier (3) at the opposite end or other and by plug formation technique in counter current fashion or other the anhydride vapour passes over and through the material and after a very short time (minutes) sufficient impregnation has taken place. Acetic Acid in the form of vapour is removed to (5) for further vaporization (7), using known ketene route.

Time scale for penetration depends on material being a fibre, veneer, board, structural member, chip or shred, to the degree of modification required but in minutes as apposed to hours.

Continuously the various Lignocellulosic material is heated to between 100 and 170°C for both continuous and batch modes of production according to the real adaptation of the real industrial process. The final drying in one hour using vacuum or gas flow, removes remaining Acetic Acid. Vacuum or gas flow is applied progressively. Vacuum or gas flow is held until complete drying is achieved. Gas flow as Nitrogen loop. Analysis by low volatile sampling confirms achieved specification. Veneer is modified in a vapour chamber, continuous or batch (without agitation). Resination can be in chamber (4) or for batch in single modifier/dryer/resinator.

PROCESS DEVELOPMENT.

The process development attributed to this patent covers all Lignocellulosic materials, as listed here in fibre - chip, shred and veneer.

1. Wood Fibre
2. Oil Palm
3. Straw
4. Flax
5. Sisal
6. Peat
7. Hemp
8. Baggass
9. Paper
10. Waste Paper
11. Rubber Plant
12. Waste Material

The process can use waste materials in all of the (1) to (7) areas and take a waste material into an area of added value.

The main attributes to this process development is a greatly simplified Acetic Anhydride in vapour phase process for Lignocellulosic materials to give dimensional stability and biological resistance with speed of operation.

CHEMICAL MODIFICATION

OF

LIGNOCELLULOSIC MATERIALS

INTRODUCTION

Lignocellulosic are naturally occurring materials consisting mainly of cellulose, hemicellulose, and lignin. Wood is one of the most commonly used of the lignocellulosics, and has traditionally been used as timber for constructional purposes. However, in the preparation of the timber much waste was produced. A means of converting this waste to a useful product was found in the form of composites, such as particle board. There are various types of particle board ranging from water board, strand board and orientated strand board through chip board to fibre board. Nearly all of these boards are conventionally produced by the dry forming process, resinating the almost dry wood particles and pressing to give a sheet product. The product is mainly flat sheet but some moulded products are also manufactured. The alternative is to wet form the sheet, either flat or moulded followed by pressing. This alternative method is normally only applied to fibre board.

The products formed by these procedures are widely used for construction purposes plus a variety of other end uses. There is one major drawback to all of these products, which is their lack of water resistance. As a consequence very few are able to be used for external use. However, it is possible to improve the water resistance of these products by chemical modification of the Lignocellulosic substrate. The chemical modification can be either a pretreatment or post treatment, depending on the desired property enhancement required and the type of product.

A further consequence of improving the water resistance is found to be an improvement of the strength properties of the product which is maintained after being subjected to high moisture environments. This is even observed after submersion in water, to have no detrimental effect on water resistance or strength properties.

CHEMICAL MODIFICATION

Lignocellulosic materials are potentially very reactive due to the abundance of functional groups on the polymeric hydroxyl group. The presence and availability of the hydroxyl group gives Lignocellulosics material their strength and versatility, but is also the reason for the problems that arise with lignocellulosics. The hydroxyl groups are in such large numbers that hydrogen bonding within and between the polymeric species occurs throughout the material. It is hydrogen bonding which binds wood together and leads to its strength but it is hydrogen bonding which allows hydrophilic substances like water to enter the structure and interact with the polymers and alter the properties of the lignocellulosic material. This gives rise to other problems such as micro-biological decay. If the natural reactivity of Lignocellulosics can be utilized to enhance the properties the resultant material would be superior in terms of performance and versatility.

The term chemical modification could be applied to any process in which a Lignocellulosic material is treated with another substance. This would cover all types of interactions from simple association with hydrophobic reagents, e.g. waxes, and hydrophilic reagents, e.g. inorganic salts, glycols.

These interactions do not give rise to covalent bonding and operate generally by either hydrophobic association, columbic interaction, or hydrogen bonding.

For the purposes of this patent chemical modification is more properly referred to as association by interaction to give covalent bond formation. The most common type of covalent bond formation that is possible with Lignocellulosics is the interaction with the abundant hydroxyl groups. Hydroxyl groups are available on all the polymeric species that occur in Lignocellulosics, i.e. on the cellulose, hemicellulose, and lignin, plus also the extractives.

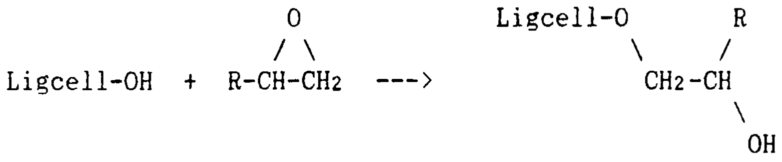
That are two basic types of chemical modification, one uses simple monofunctional modifying agents whilst the other uses difunctional, or even polyfunctional modifying agents. With the first type of process the Lignocellulosic substrate is modified then can be put through the conventional process to form the required product. In the second type of process the Lignocellulosic substrate is modified and pressed without addition of any further resin material, because the chemical modification also serves to bond the particles together during the pressing stage.

In the former process the Lignocellulosic is more activated and more compatible to the added matrix, i.e. the resin. whilst in the latter process the material is activated in such a way that no further additive is required to give a product comparable to but superior to conventional products. If an additional matrix is used with the latter process the product then becomes more comparable to glass reinforced plastic but with the possibility of being designed to be of superior performance and greater versatility.

Much work has been carried out on both types of procedures and the results obtained show that the products are of superior quality to the conventional products.

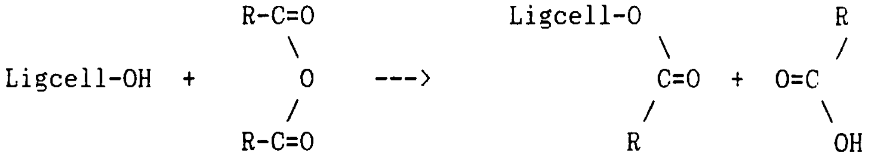
General types of modification

1. Reaction with Epoxides:



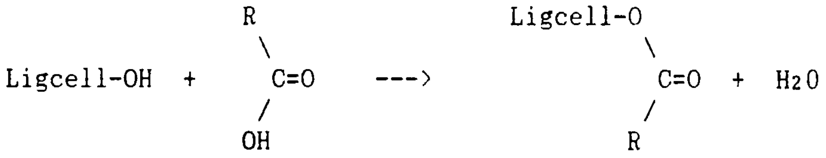
$$\text{Ligcell-OH} + \overset{\text{O}}{\text{R-CH-CH}_2} \longrightarrow \text{Ligcell-O-CH}_2\text{-CH(R)-OH}$$

2. Reaction with Anhydrides:



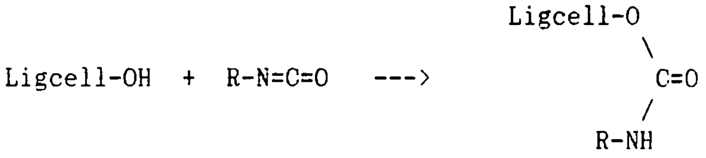
$$\text{Ligcell-OH} + (\text{R-C=O})_2\text{O} \longrightarrow \text{Ligcell-O-C(=O)-R} + \text{R-C(=O)-OH}$$

3. Reaction with Carboxylic acids:



$$\text{Ligcell-OH} + \text{R-C(=O)-OH} \longrightarrow \text{Ligcell-O-C(=O)-R} + H_2O$$

4. Reaction with Isocyanates:



$$\text{Ligcell-OH} + \text{R-N=C=O} \longrightarrow \text{Ligcell-O-C(=O)-NH-R}$$

LIGNOCELLULOSIC SUBSTRATES

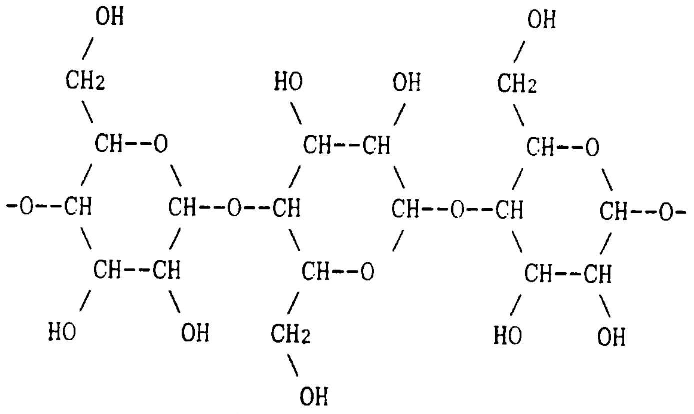
There is a whole range of Lignocellulosic substrates which are known to react with chemically modifying reagents to produce materials with enhanced properties.

Examples of the substrates used for this patent

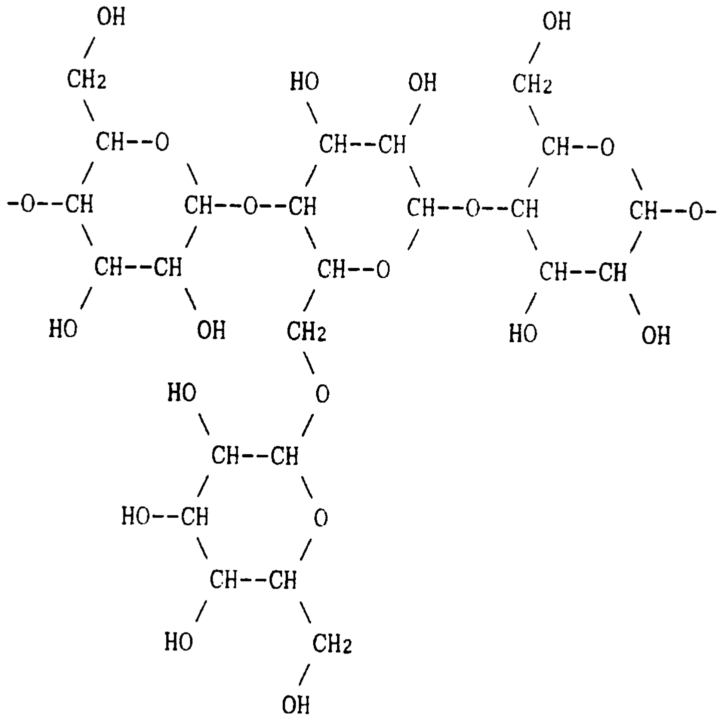
1. Wood Fibre
2. Oil Palm
3. Straw
4. Flax
5. Sisal
6. Peat
7. Hemp
8. Baggass
9. Paper
10. Waste paper
11. Rubber Plant
12. Waste Material

LIGNOCELLULOSIC POLYMERS

Cellulose:

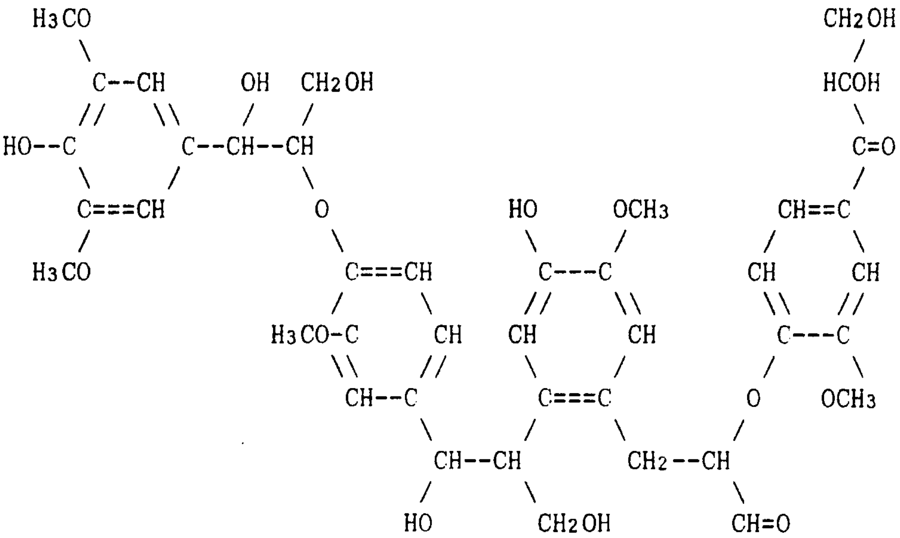


Hemicellulose:



LIGNOCELLULOSIC POLYMERS

Lignin:



POTENTIAL CHEMICAL MODIFYING AGENTS

As stated above simple modifying agents can be any material that will interact with the Lignocellulosic substrate. This would included any material that could form some weak interaction with any part of the Lignocellulosic. This type of modification can easily be reversed by simple solvent exposure, i.e. by leaching.

Examples:

waxes
resins
inorganic salts
metal salts of organic compounds
glycols - polyethylene glycol
alkanolamines

For chemical modification the interaction between the modifying agent and the Lignocellulosic is by way of covalent bond formation. Therefore, this type of interaction is permanent and cannot be extracted by exposure to solvent

Examples:

carboxylic acids - acetic acid
anhydrides - phthalic anhydride
epoxides - propyl epoxide
isocyanates - butyl isocyanate

These reagents can be either monofunctional or difunctional depending on the desired properties of the end product.

Examples:

allyl isocyanate
methylene diphenylisocyanate

The modifying reagents can be used with or without solvents and with or without catalysts.

Examples of solvents:

acetone
n-methyl pyrrolidinone

Examples of catalysts:

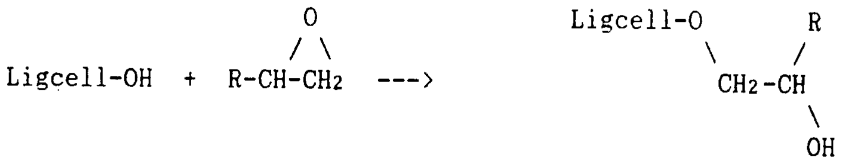
triethylamine
diazobicycl(2, 2, 2,)octane
n-methyl pyrrolidinone

THE TYPE OF MODIFYING REACTIONS

The modifying agents as outlined above are chosen because of the reactivity with the hydroxyl groups of the lignocellulosic material.

The main type of reactions that occur are:

1. Reaction with Epoxides:

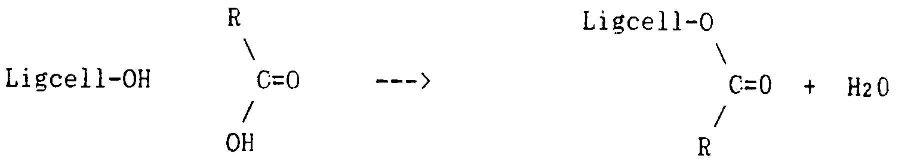


This gives an ether linkage to the substrate and simple epoxides can be employed:

2. Reaction with Anhydrides:

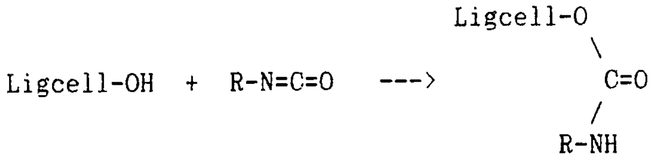
This gives an ester linkage to the substrate.

3. Reaction with Carboxylic acids:



As with the carboxylic acids these give an ester linkage.

4. Reaction with Isocyanates:



$$\text{Ligcell-OH} + \text{R-N=C=O} \longrightarrow \begin{array}{l}\text{Ligcell-O}\\ \qquad\quad \backslash\\ \qquad\qquad \text{C=O}\\ \qquad\quad /\\ \quad \text{R-NH}\end{array}$$

These modifying agents give a carbamate ester linkage to the substrate.

All the above reactions will proceed with or without catalyst, but the rate of reactions is obviously increased when a catalyst is present.

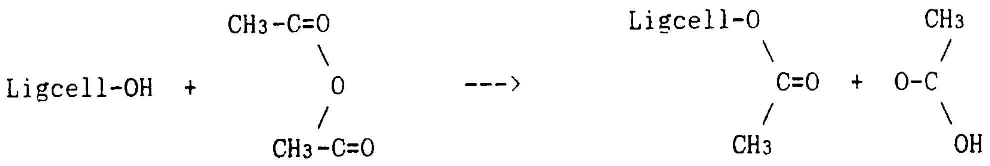
For some of the reactions it is better to use an additional solvent, whilst others give good results in the absence of an additional solvent.

When a solvent is required it is possible to choose one which will also catalyze the reaction.

The type of solvents tend to be commercial industrial solvents, typically paint solvents.

MODIFICATION USING ACETIC ANHYDRIDE VAPOUR

FOR THIS PARTICULAR PROCESS DEVELOPMENT AND PATENT THE TYPE OF MODIFICATION IS TO BE ACETYLATION USING ACETIC ANHYDRIDE VAPOUR.



$$\text{Ligcell-OH} + \begin{matrix} CH_3-C=O \\ \backslash \\ O \\ / \\ CH_3-C=O \end{matrix} \;\text{--->}\; \begin{matrix} \text{Ligcell-O} \\ \backslash \\ C=O \\ / \\ CH_3 \end{matrix} + \begin{matrix} CH_3 \\ / \\ O-C \\ \backslash \\ OH \end{matrix}$$

This gives an acetyl group linked to the substrate and a by-product of acetic acid.

The acetylated material will then be pressed into boards to give a superior medium density fibre board, or into mouldable products. By pressure moulding or extrusion techniques.

RESULTS TO DATE OF PILOT PLANT BOARD PREPARATION

PROPERTIES OF MODIFIED BOARDS IN COMPARISON TO CONTROL BOARDS

Static Bending

MOR

Modified	34.2 +/- 0.8 MPa	
Control	30.8 +/- 1.1 MPa	(density = 0.72)

MOE

Modified	2586 +/- 33 MPa	
Control	2932 +/- 92 MPa	(density = 0.72)

Work to failure

Modified	45.8 +/- 1.5 kPa	
Control	33.3 +/- 2.1 kPa	(density = 0.72)

PROPERTIES OF MODIFIED BOARDS

Internal Bond Strength

At 65%rh (density = 0.726)

	IBS MPa
Modified	0.94 +/- 0.03
Control	0.58 +/- 0.05

After conditioning to 93%rh

	IBS MPa (density = 0.725)	% of IBS at 65%rh (density = 0.726)
Modified	0.94 +/- 0.03	100
Control	0.33 +/- 0.01	57

After 1 hour 20°C water soak

	IBS MPa (density = 0.71)	% of IBS at 65%rh (density = 0.726)
Modified	0.91 +/- 0.04	97
Control	0.33 +/- 0.01	70

After 24 hours 95°C water soak

	IBS MPa (density = 0.74)	% of IBS at 65%rh (density = 0.726)
Modified	0.62 +/- 0.02	68
Control	0.035 +/- 0.001	7

Weight and density changes

Manufacture to 65%rh (density = 0.71)

	density increase %
Modified	2.79 +/- 0.08
Control	1.22 +/- 0.10

65%rh to 93%rh (density - 0.724)

	Weight increase %		volume increase %		density increase %	
	treated	residual	treated	residual	treated	residual
Modified	1.33 +/-0.09		0.08 +/-0.1		0.44 +/-0.04	
Control	5.26 +/-0.04		6.0 +/-0.4		-0.72 +/-0.36	

65% to 1 hour 20C water soak (density = 0.71)

	Weight increase %		volume increase %		density increase %	
	treated	residual	treated	residual	treated	residual
Modified	16.7 +/-0.3	0.01 +/-0.05	0.50 +/-0.02	0.02 +/-0.02	16.4 +/-2.1	-0.02 +/-0.06
Control	8.0 +/-1.0	1.10 +/-0.02	3.90 +/-0.3	3.40 +/-0.8	3.6 +/-1.3	-2.10 +/-0.5

65% to 24 hour 95°C water soak (density = 0.74)

	Weight increase %		volume increase %		density increase %	
	treated	residual	treated	residual	treated	residual
Modified	81.0 +/-0.3	0.10 +/-0.003	15.6 +/-1.1	10.8 +/-1.1	57 +/-1.0	-9.6 +/-0.9
Control	377 +/-16	-4.20 +/-0.3	247 +/-12	241 +/-13	38 +/-0.2	-72 +/-1.0

PROPERTIES OF MODIFIED BOARDS

Linear Expansion

65%rh to 93%rh (density = 0.724)

	expansion %	residual expansion %
Modified	0.078+/-0.005	
Control	0.163+/-0.008	

65% to 1 hour 20°C water soak (density = 0.71)

	expansion %	residual expansion %
Modified	0.060+/-0.03	0.06+/-0.01
Control	0.019+/-0.00	0.07+/-0.02

65%rh to 24 hour 95°C water soak (density = 0.74)

	expansion %	residual expansion %
Modified	0.06+/-0.03	-0.10+/-0.03
Control	0.78+/-0.1	0.72+/-0.05

PROPERTIES OF MODIFIED BOARDS

Thickness Swell

Manufacture to 65%rh (density = 0.71)

	Swell %
Modified	0.46+/-0.10
Control	2.27+/-0.14

65%rh to 93%rh (density = 0.724)

	Swell %	residual swell %
Modified	0.72+/-0.1	
Control	5.70+/-0.4	

65% to 1 hour 20°C water soak (density = 0.71)

	Swell %	residual swell %
Modified	0.37+/-0.02	-0.09+/-0.02
Control	3.90+/-0.3	3.20+/-0.8

65% to 24 hour 95°C water soak (density = 0.74)

	Swell %	residual swell %
Modified	15.3+/-3	11.0+/-1.1
Control	240+/-13	237+/-12

THE BENEFITS OF CHEMICAL MODIFICATION

Lignocellulosic materials are generally susceptible to degradation and water impregnation, which ultimately affect the performance.

Chemically modified Lignocellulosic material can be designed and engineered so that it is not susceptible to either of the above, i.e. degradation, or water impregnation, and included in the Industrial Process

The composite materials formed from a Lignocellulosic which has been chemically modified is superior to the unmodified composite in many respects. For chipboard the strength can be increased dramatically. The internal bond strength can be increased five fold, coupled with a doubling of the modulus of rupture. Similar results are obtainable with other composites such as medium density fibre board from this Process.

The resistance to swelling can be reduced to very low values, so that the material becomes compatible with metal veneers and other similar materials that are not affected by water from this process.

Chemical modification makes the material resistant to biological degradation, and resistance to ultra violet degradation can be engineered into the product, with this process.

Fire resistance is another quality that can be designed into the product when produced by chemical modification and is also non-leachable, unlike conventional processes from within this process.

The process is multipurpose for all Lignocellulosic materials as listed.

TYPICAL RESULTS.

% Linear Expansion

	N-UF	A-UF	N-MUF	A-MUF
Manufacture to 65%rh	0.5	0	0.25	0
65%rh to 93%rh	0.21	0.13	0.23	0.13
65%rh to 1 hour cold soak	0.03	0.06	0.06	0.03
65%rh to 2 hour boil	0.51	1.02	0.09	0.83

Thickness Swell %

	N-UF	A-UF	N-MUF	A-MUF
Manufacture to 65%	3.5	-0.2	3.0	-0.03
65% to 93%rh	7.3	1.5	8.2	1.3
65%rh to 1 hour cold soak	13.6	0.5	9.7	0.5
65%rh to 2 hour boil	238	274	121	111

Weight Gain %

	N-UF	A-UF	N-MUF	A-MUF
Manufacture to 65%rh	5.87	5.20	5.62	2.75
65%rh to 93%rh	4.88	2.40	5.02	2.19
65% to 1 hour cold soak	35	5.8	22	3.9
65% rh to 2 hour boil	414	464	229	212

IBS kPa

	N-UF	A-UF	N-MUF	A-MUF
65% rh	98+/-16	180+/-16	80+/-12	132+/-18
93% rh	91+/-20	202+/-16	68+/-10	162+/-29
1 hour cold soak	90+/-22	136+/-13	80+/-11	135+/-24

	N-UF	A-UF	N-MUF	A-MUF
MOR (MPa)	19+/-2	16+/-2	16+/-1	17+/-6
MOE (MPa)	1750+/-230	1860+/-180	1910+/-90	1790+/-140
IBS (kPa)	111+/-30	144+/-18	109+/-8	129+/-33

N = NON ACETYLATED

A = ACETYLATED

UF = UREA/FORMALDEHYDE

MUF = MELAMINE UF

TYPICAL RESULTS USING VAPOUR PROCESS DEVELOPMENT AVERAGED USING SUBSTRATES LISTED.

Linear Expansion

Manufacture to 65%rh

SAMPLE 1	0.2%
2	0.3%
3	0.2%
4	0.2%
5	0.08%
6	0.01%
7	0.09%
8	0.02%

65%rh to 93%rh

SAMPLE 1A	0.19%	0.20%
2A	0.23%	0.20%
3A	0.27%	0.26%
4A	0.20%	0.22%
5A	0.14%	0.17%
6A	0.14%	0.17%
7A	0.15%	0.13%
8A	0.13%	0.14%

Linear Expansion.

1 hour cold soak

SAMPLE 1B	.02%	0.11%
2B	.02%	0.04%
3B	0.1%	0.12%
4B	0.003%	0.04%
5B	0.003%	0.04%
6B	0.003%	0.04%
7B	0.06%	0.06%
8B	0.02%	0.01%

2 hour boil

SAMPLE 1C	0.3%	(-) 0.1%
2C	0.6%	0.4%
3C	0.03%	(-) 0.6%
4C	0.01%	(-) 0.4%
5C	0.7%	0.3%
6C	0.7%	0.3%
7C	0.7%	0.3%
8C	0.7%	0.3%

Thickness Swell

Manufacture to 65%rh

SAMPLE 1D	1.0%
2D	1.0%
3D	1.0%
4D	1.8%
5D	(-).1%
6D	(-).3%
7D	(-).1%
8D	(-).1%

65%rh to 93%rh

SAMPLE 1E	1.0%
2E	1.0%
3E	2.0%
4E	0.8%
5E	0.8%
6E	0.5%
7E	0.5%
8E	0.4%

Thickness Swell

1 hour cold soak

		After Re-conditioning
SAMPLE 1F	1%	1.2%
2F	1%	1.2%
3F	1%	1.2%
4F	0.5%	(-) 1.1%
5F	0.4%	(-) 0.2%
6F	0.1%	0.12%
7F	0.1%	0.12%
8F	0.1%	0.12%

2 Hour boil

		After Re-conditioning
SAMPLE 1G	5%	4%
2G	4%	4%
3G	4%	4.5%
4G	5%	5%
5G	5%	5%
6G	5%	4%
7G	5%	4%
8G	3%	4%

Internal Bond Strength (kPa)

65%rh

	Density KG/M^3	IBS KPa	Density KG/M^3	IBS KPa
SAMPLE 1H	653	550	740	630
2H	651	561	735	630
3H	617	525	730	620
4H	609	515	745	600
5H	650	550	750	630
6H	700	450	730	650
7H	712	445	735	650
8H	715	455	740	650

93%rh

SAMPLE 1J	700	580	690	620
2J	700	580	685	625
3J	715	530	685	625
4J	720	520	712	680
5J	750	530	710	675
6J	715	525	708	675
7J	730	560	700	675
8J	700	560	690	680

MEAN INTERNAL BOND STRENGTH AND SWELLING DATA

ORIGINAL BOILED RET - COLD SOAK

DEN	IBS	IBS	GAINED	WT
KG/M^3	KPa	KPa	% GAIN	%
790	650	580	98	50

2 HOUR BOIL RECONDITIONED

SWELL	WEIGHT	SWELL	WEIGHT	SWELL	SWELL %
%	GAIN %	% GAIN	%	%	%
0.8	98	20	- 0.0	7	0.02

CONCLUSION

Chemical modification of Lignocellulosic materials can be carried out to the level required to achieve the desired end product.

The end product can have the desired properties designed and engineered into it by a combination of modifications.

Chemical modification treats a Lignocellulosic as a mixture of polymeric materials which can be altered to suit the end purpose.

A chemically modified material can have reactivity towards specific agents designed into it.

In short chemical modification takes Lignocellulosic materials from being a low grade material into the area of high grade polymers.

DOCUMENTS CONSIDERED TO BE RELEVANT

- CHEMICAL ABSTRACTS, vol 98, no. 4, 13th June 1983, page 91, no. 200096w, Columbus, Ohio, US; & JP - A - 58 32 807 (DAIKEN KOGYO CO., LTD.) 25-02-1983

  * Abstract *

CHEMICAL ABSTRACTS, VOL. 81, NO. 8, 26th August 1974, Page 113, no. 39277t, Columbus, Ohio US; & SU - A-391 923 (INST. OF WOOD PULP CHMISTRY, ACADEMY OF SCIENCES, LATVIAN S.S.R., LATVIAN AGRICULTURAL ACADEMY) 27-07-1973

* Abstract *

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  * Abstract *

MODIFICATION OF LIGNOCELLULOSIC MATERIALS IN VAPOUR PHASE

ACETIC ANHYDRIDE AND ITS DERIVITIVES

1.	TRANSFER SYSTEM.
2.	STORAGE.
3.	JACKETED MODIFIER.
4.	JACKETED MODIFIER (WITH OR WITHOUT GAS FLOW).
5.	RECOVERY SYSTEM.
6.	COLLECTOR.
7.	ANHYDRIDE VAPORIZER SYSTEM.
8.	CONDENSOR.
9.	RECEIVER.
10.	VACUUM SET.
11.	RESINATOR.
12.	OUTPUT TO FURTHER BATCH / CONTINUOUS PROCESS.
13.	RESIN STORAGE.
14.	FLOW METER.
A.	MEDIUM PRESSURE HOT WATER IN.
A.	MEDIUM PRESSURE HOT WATER OUT.
B.	MEDIUM PRESSURE HOT WATER IN.
B.	MEDIUM PRESSURE HOT WATER OUT.

NITROGEN LOOP OPTION

C.	HEAT EXCHANGE UNIT.
D.	TRANSFER SYSTEM.
E.	RECEIVER TANK (PART ACID).
F.	CONDENSOR.

CLAIMS

1. A process for the acetylation of Lignocellulosic materials, directly for improving dimensional stability and biological resistance all in vapour phase - with or without gas flow, using acetic anhydride.

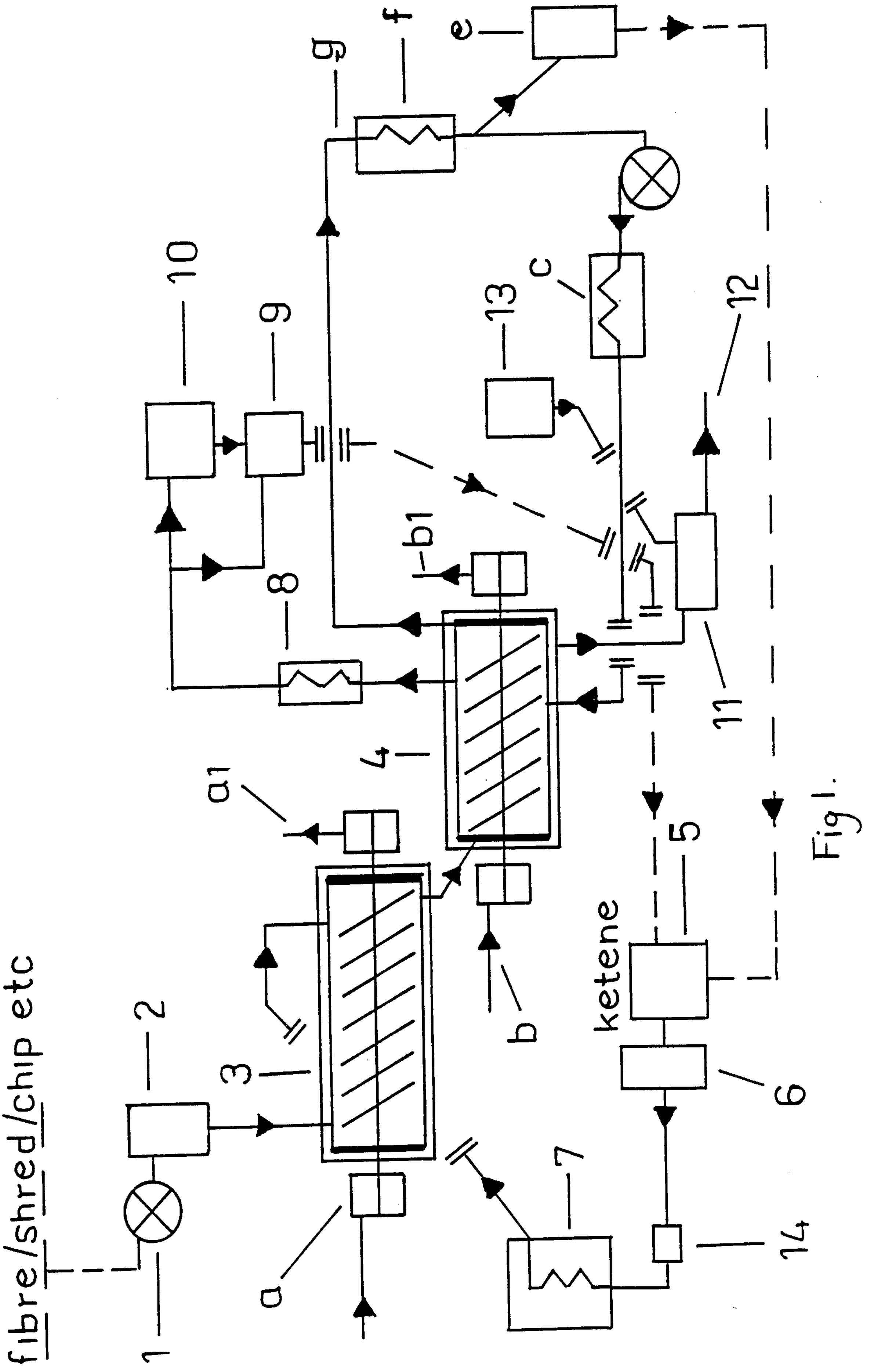
2. Reduction of reaction time (minutes) as opposed to hours, as characterised in claim one.

3. Optimization for the exact need for raw material, which was impossible previously in a liquid phase, as characterised in claims one and two.

4. No extra requirement for recovery as distillation/rectification, as characterised in one, two, three.

5. Material can be reacted and dried in gas flow, as characterised in one.

6. The process can be achieved using a single for batch or double for continuous modifier, with or without agitation, as characterised in claim one.


fibre/shred/chip etc
1
2
3
a
a1
4
b
b1
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14
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Fig 1.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 93/01576

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08H5/04 D21C1/04

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)
IPC 5 D21C C08H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE PAPERCHEM THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY, ATLANTA, GA, US AN 53-00384 FAHMY, Y. A. ET AL 'Acetylation in Particle Board Making' see abstract & EGYPTIAN J. CHEM. 20, NO. 4: 397-403 (1977). [ENGL.;ARABIC SUM.] --- -/--	1-6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"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)

"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

"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

"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

"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.

"&" document member of the same patent family

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Date of the actual completion of the international search 4 November 1993	Date of mailing of the international search report 25. 11. 93
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Authorized officer SONGY, O

Inte nal Application No
PCT/GB 93/01576

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE PAPERCHEM THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY, ATLANTA, GA, US AN 49-02000 KORCHEMKIN, F. I. ET AL 'METHOD OF EXTENSIVE ACETYLATION OF BOARD' see abstract & SB. TR. TSENTR. NAUCH.-ISSLED. INST. BUMAGI NO. 10: 130-134 (1975). (RUSS.) ---	1-6
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X	DATABASE WPI Section Ch, Week 7534, Derwent Publications Ltd., London, GB; Class A11, AN 75-56732W & SU,A,451 707 (CELLULOSE PAPER IND RES) 12 March 1975 see abstract ---	1-6
X	DATABASE WPI Section Ch, Week 8603, Derwent Publications Ltd., London, GB; Class A82, AN 86-018161 & JP,A,60 242 003 (DAIKEN KOGYO KK) 2 December 1985 see abstract ---	1-6
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int onal Application No

PCT/GB 93/01576

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		AU-A- 6097986	05-03-87
		CA-A- 1284563	04-06-91
		FI-A- 8603443	01-03-87
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		US-A- 4804384	14-02-89