

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

DECLARATION IN SUPPORT OF CONVENTION OR
NON-CONVENTION APPLICATION FOR A PATENT

Insert title of invention.

In support of the Application made for a patent for an invention
entitled: "PRESERVATIVE ELEMENTS CONTAINING ORGANIC BORON
COMPOUNDS AND THEIR USE"

Insert full name(s) and address(es)
of declarant(s) being the appli-
cant(s) or person(s) authorized to
sign on behalf of an applicant
company.

I Ian M. MacKinnon
We
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Cross out whichever of paragraphs
1(a) or 1(b) does not apply

1(a) relates to application made
by individual(s)

1(b) relates to application made
by company; insert name of
applicant company.

do solemnly and sincerely declare as follows:-

1. (a) ~~I am the applicant~~
or (b) I am authorized by

Manchem Limited

Cross out whichever of paragraphs
2(a) or 2(b) does not apply

2(a) relates to application made
by inventor(s)

2(b) relates to application made
by company(s) or person(s) who
are not inventor(s); insert full
name(s) and address(es) of inven-
tors.

the applicant..... for the patent to make this declaration on ~~their~~ ^{its} behalf.

2. (a) ~~I am the actual inventor~~

or (b) 1. Raymond Charles CASS
of 266 Malden Road, New Malden, Surrey KT3 6AR

AND 2. William Kenneth Houghton LAKIN
of 186 Withington Road, Manchester M16 8WA

Both of United Kingdom

~~is~~ the actual inventor(s)..... of the invention and the facts upon which the applicant.....
~~are~~ is
~~are~~ entitled to make the application are as follows:-

State manner in which applicant(s)
derive title from inventor(s)

By virtue of the employment of the inventors
by the applicant, the applicant would, if a
patent were granted upon an application made
by the aforesaid inventors, be entitled to
have the patent assigned to it.

Cross out paragraphs 3 and 4
for non-convention applications.
For convention applications,
insert basic country(s) followed
by date(s) and basic applicant(s).

3. The basic application..... as defined by Section 141 of the Act ^{was} ~~were~~ made
in Great Britain..... on the 13 October 1987
by Manchem Limited.....
in..... on the.....
by.....
in..... on the.....
by.....

Insert place and date of signature.

Declared at MANCHESTER this 20 day of JUNE 1989

Signature of declarant(s) (no
attestation required)

Ian M. MacKinnon

Note: Initial all alterations.

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(56) Prior Art Documents
AU 10598/88 B27K 3/39
GB 1560884
GB 2086726

(57) Claim

1. A method for preserving structural material from attack by fungus or insects said method comprising forming a cavity in the structural material, inserting therein a shaped preservative element containing a solid organic boron compound hydrolysable by water and then covering the element with a cap, plug or filler.

4. The method according to claim 2 wherein the boron ester is selected from mono (2-methyl-2, 4-pentanediol) - monoborate, triethanediol diborate, tri-(2,3-dimethyl-2,3-butanediol)diborate, tri-(2,5-dimethyl-2, 5-hexanediol)-diborate, tri-(2,6-dimethyl-4-heptanol) borate, triethanolamine borate, tri-isopropanolamine borate and tri-(2,2-dimethyl-1,3-propanediol) diborate.

12. The method according to any one of the preceding claims wherein the preservative element further contains at least one other water-soluble compound having fungicidal or insecticidal properties.

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(21) International Application Number: PCT/GB88/00845 (22) International Filing Date: 13 October 1988 (13.10.88) (31) Priority Application Number: 8724024 (32) Priority Date: 13 October 1987 (13.10.87) (33) Priority Country: GB (71) Applicant (for all designated States except US): MAN-CHEM LIMITED [GB/GB]; Borax House, Carlisle Place, London SW1P 1HT (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : CASS, Raymond, Charles [GB/GB]; 266 Malden Road, New Malden, Surrey KT3 6AR (GB). LAKIN, William, Kenneth, Houghton [GB/GB]; 186 Withington Road, Manchester M16 8WA (GB).	(74) Agents: MYERSCOUGH, Philip, Boyd et al.; J.A. Kemp & Co., 14 South Square, Gray's Inn, London WC1R 5EU (GB). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), DK, FI, FR (European patent), GB, GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), NO, SE (European patent), US. Published <i>With international search report.</i>	

(54) Title: PRESERVATIVE ELEMENTS CONTAINING ORGANIC BORON COMPOUNDS AND THEIR USE**(57) Abstract**

A preservative element, for timber or masonry, in the form of a shaped element containing an organic boron compound, especially a boro-organic ester. Preferably the element also contains inorganic boron salts or acids, and optionally also at least one other inorganic compound having fungicidal and/or insecticidal properties.

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PRESERVATIVE ELEMENTS CONTAINING ORGANICBORON COMPOUNDS AND THEIR USE

This invention relates to new preservative elements containing organic boron compounds and their use to protect structural materials, particularly timber and masonry susceptible to infestation by fungi or insects.

Inorganic boron compounds are well established as preservatives for timber and other materials against attack from fungi or insects. Recent developments have included the use of shaped rods, pellets or tablets of inorganic boron compounds for insertion into pre-formed cavities in timber. U.S. Patent 4,269,875 describes shaped timber preservative elements comprising fused monolithic bodies of wood preservative containing boron compounds, particularly boric oxide. These elements are most suitable in the treatment of timber such as new joinery, prior to fungal attack as a protective rather than remedial treatment, as they are only slowly soluble and have extensive lives in situ. A disadvantage of these elements is that they are



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expensive as they are difficult to manufacture except by casting.

U.K. Patent 2,114,003 proposes preservative tablets of inorganic boron compounds which are shaped by compression to fit in pre-formed cavities in timber or other materials. These tablets dissolve more rapidly than the fused products of U.S. Patent 4,269,875 in the moisture contained in the timber but suffer from the disadvantage of being mechanically weak except when prepared in the presence of a suitable adhesive binder such as starch.

Both the tablets and fused elements rely solely upon the moisture present in the location in which they are inserted within the timber to dissolve the preservative and transport it through the grain to the areas to be protected. Under some conditions this may lead to too little preservative being transported in time to prevent the onset of decay. This difficulty has been recognized and the use of highly concentrated solutions of inorganic borates and boric acid in glycols has been proposed to be used in conjunction with fused borate elements or borate tablets to overcome the problem. According to U.S. Patent 4,610,881, the glycol assists the borate in penetrating the outer parts of the wood more rapidly.

Other shaped bodies of inorganic borates capable of binding water by hydration, and their use as preservatives, are described in US Patent 4,661,157.

According to the present invention a shaped preservative element is provided containing solid organic boron compounds which are hydrolysed in the presence of moisture.

Accordingly, one aspect of the present invention provides a method for preserving structural material from attack by fungus or insects said method comprising forming a cavity in the structural material, inserting therein a shaped preservative element containing a solid organic boron compound hydrolysable by water and then covering the element with a cap, plug or filler.

The compounds have melting points preferably in the range of about 50°-200°C. These may be easily formed into shaped elements by fusion and casting or extrusion more easily and more economically than when the preservative element is composed of inorganic boron materials alone. This is particularly evident in the case of extrusion as they can be extruded at low temperatures by conventional means as used for example in the plastics industry.

Preferred organic boron compounds are boron esters having melting points in the desired range. Typical esters which may be used are mono (2-methyl-2,4-pentanediol)monoborate, triethanediol diborate, tri-(2,3-dimethyl-2,3-butanediol) diborate, tri-(2,5-dimethyl-2,5-hexanediol) diborate, tri-(2,6-dimethyl-4-heptanol)borate, triethanolamine borate and tri-iso-propanolamine borate. These materials are hydrolysed in



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the presence of the moisture typically found in timber and other structural materials to yield boric acid and the organic component which may be a diol, monohydric alcohol or an alkanol-amine. The organic component is miscible with water and penetrates the substrate and acts as a solvent for transporting the boric acid active ingredient and unhydrolysed organic boron compound through the substrate.

It is a particular feature of this invention that the presence of the free organic hydrolysis product facilitates the movement of the boric acid preservative through timber, particularly through the grain, in a manner similar to that described in U.S. Patent 4,610,881 for surface treatment and effectively brings boric acid into all areas susceptible to decay more rapidly than when using shaped products as described in earlier specifications. For example, on hydrolysis a free glycol and solution of boric acid enables diffusion to commence immediately, whereas with an element comprising solid inorganic materials the active ingredient has to dissolve in moisture present in the substrate before diffusion will occur.

Thus in the prior disclosures it is a comparatively slower process for the integrity of the shaped products to disappear. Fast availability of the preservatives is essential to reduce the risk of continued infestations by fungi or insects in remedial treatments and also for protective measures. This

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early penetration by preservative materials through substrates having moisture contents considered conventional for surface protected timber is valuable in case of early breakdown of surface coating.

In practice, the products of the invention are manufactured preferably in the shape of cylindrical rods or pellets. They are used by establishing a cavity by boring a hole to the desired depth in the substrate to be protected, inserting one or more rods or pellets, and sealing the hole with a cap, plug or conventional filler.

The products of the present invention can be used to advantage in both protective and remedial treatments. In the United Kingdom new joinery typically has an average moisture content of between 12% and 15%. This is maintained under normal circumstances in external conditions where the joinery is protected by an appropriate surface coating. When the joinery is inadequately maintained, the moisture content will rise to about 25-30% and it is only then that conditions are suitable for the germination of fungi such as those causing dry and wet rot which are responsible for most cases of decay.

Within a comparatively short time when brought into contact with the substrate, the products of this invention will commence to disintegrate, initially into a pasty mass which

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adheres to the walls surrounding the pre-formed cavity where diffusion occurs through the walls over their whole area into substrate. In time the pasty material diminishes as the boric acid and the organic material diffuses but it can easily be replenished by periodic inspection and insertion of new rods or pellets into the cavity. In practice in timber containing 12-15% moisture, disintegration of the compositions can occur in as little time as a few weeks.

In one aspect of the invention mixtures of organic boron compounds may be used to control the availability of boric acid from the shaped products. Ideally, the protection system should deliver initially a rapid high level amount of preservative to arrest the activity of decay organisms followed by a long term low level release of preservative to maintain protection. Thus a combination of organic boron compounds showing different rates of hydrolysis may be used to vary the rate of diffusion of boric acid through the substrate.

The organic boron compounds used according to this invention typically contain 2.5-7.5% boron which is all available as boric acid as the compounds are totally prone to hydrolysis.

In a second preferred aspect of this invention the available boron can be increased by dispersing water-soluble

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inorganic borates into the organic boron compounds during manufacture of the shaped elements.

The inorganic borates are preferably selected from alkali metal borates, such as sodium tetraborate or sodium octaborate tetrahydrate, boric acid and boric oxide. In particularly preferred compositions the dispersed inorganic boron compounds are mixtures of discrete particles which have different rates of dissolution in the moisture present in the substrates so as to provide elements giving protection over longer periods. Of these compounds, boric acid is most readily available while boric oxide, being glassy in nature is very slow to dissolve.

An example of a composition of a preferred element in parts by weight comprises:

mono hexylene glycol monoborate	20
boric acid	20
borax	30
boric oxide	30

The ratios between the borate components depends on the rate of dissolution required for a particular application. For example, in damp conditions leaching of water soluble preservatives is more rapid, thus more of a slow dissolving preservative such as boric oxide would be necessary to provide

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effective protection over long periods.

In general, a ratio of boric oxide to other borates and boric acid of between 10:1 and 1:10 is desirable.

However, this aspect of the invention is not limited to the use of inorganic boron compounds as other water-soluble compounds having fungicidal or insecticidal properties may also be dispersed within the organic boron compound matrix. Examples of suitable compounds are copper, arsenic and chromium salts and fluorides such as sodium fluoride.

It is evident that the more available preservative there is in the shaped elements, the greater the area radiating the element may be protected before decomposition is complete and the preservative leaches from the substrate. Advantageously, we have found that up to five parts by weight of particulate inorganic preservative to one part by weight of organic boron compound can be used without adversely affecting the structure or mechanical stability of the elements during their manufacture or use. Therefore, the organic boron compounds not only provide a more rapid access to boric preservative elements than possible heretofore with solid preservative elements, they are also very effective matrices for dispersing other preservatives to form elements by more economical processes.

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The invention will be further illustrated by reference to the following example:

Example I

Samples of tri-(2,2-dimethyl-1,3-propanediol)diborate and tri-(2,3-dimethyl-2,3-butanediol)diborate were melted and cast into cylindrical rods having a diameter of 13 mm.

Joinery quality pine pieces 450 mm long with dressed dimensions of 44 x 94 mm were prepared. At the mid-point of each piece a 13 mm hole was drilled through the 94 mm dimension to within 6 mm of the bottom surface. The rods were inserted into the holes with a sufficient upper gap for plugging to enable them to be periodically inspected. Comparative samples were prepared using commercially available rods comprising 67% sodium octaborate tetrahydrate preservative.

Replicate pieces were stacked in layers, with wooden stickers placed between each layer, in thermostatically controlled air circulation cabinets having relative humidities of 65% and 100% respectively. These gave average moisture contents in the timber pieces of approximately 12% and 24% for the duration of the tests.

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At monthly intervals over an exposure period of six months, the timber pieces were examined to establish the condition of the rods and diffusion distance of boron using the curcumin test. The results obtained are shown in the following Table 1.

TABLE 1

Sample	Time Mths	Diffusion distance mm		Condition of rod	
		65% RH	100% RH	65% RH	100% RH
Tri-(2,2-dimethyl-1,3-propanediol)diborate	1	25	50	disintegrated ^c	disintegrated
	3	75	75 ^a	small residue ^c	small residue
	5	75	75	small residue	small residue
	6	75	75	small residue	small residue
Tri-(2,3-dimethyl-2,3-butanediol)diborate	1	50	75	disintegrated	disintegrated
	3	50	75 ^a	small residue	small residue
	5	50	75	small residue	small residue
	6	75	75	small residue	small residue
Sodium octaborate tetrahydrate	6	- b	- b	largely unchanged	largely unchanged

a - Increase in lateral diffusion over cross-section

b - No indication at 25 mm

c - disintegrated - reduced volume with crumbly texture
small residue - largely dissipated, small quantity of residual material

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Example II

Samples of mono(2-methyl 2,4-pentanediol) mono-borate and tri-(2,3-dimethyl-2,3 butanediol)diborate were melted and cast into cylindrical rods having a diameter of 13 mm. Similar samples were prepared using these compounds, but with the incorporation of finely divided inorganic boron compounds as indicated in Table 2 prior to casting.

These samples were obtained by melting the organic boron compound and adding the inorganic boron compound to the melt. The pourable mix was then cast into rods as before.

Rods were inserted into pine pieces and placed in thermostatically controlled air circulation cabinets as described in Example I.

The rods were examined bimonthly over an exposure period of six months. The results obtained are shown in Table 2.

Table 2

Sample	Boron Content (wt.%)	Time (Months)	Diffusion Distance mm		Condition of Rod	
			65% RH	100% RH	65% RH	100% RH
Mono(2-methyl-2,4-pentanediol monoborate)	7.24	2	-	25	no visable change	some powdering
		4	25	50	powdering exterior	powdery exterior
		6	25	50	powdering exterior	powdery exterior
Mono(2-methyl-2,4-pentanediol monoborate) (1 part) and boric acid (2 parts)	14.00	2	-	25	some powdering	some powdering
		4	25	50	powdery exterior	powdery exterior
		6	25	50	powdery exterior	powdery exterior
tri-(2,3-dimethyl-2,3-butanediol) diborate	6.15	2	75	75	small residue	small residue
		4	100	100	small residue	small residue
		6	100	100	small residue	small residue
tri-(2,3-dimethyl-2,3-butanediol)diborate(2 parts) and boric oxide (3 parts)	21.10	2	-	25	some powdering	soft texture
		4	25	50	pasty exterior	pasty throughout
		6	25	50	pasty exterior	pasty throughout

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method for preserving structural material from attack by fungus or insects said method comprising forming a cavity in the structural material, inserting therein a shaped preservative element containing a solid organic boron compound hydrolysable by water and then covering the element with a cap, plug or filler.
2. The method according to claim 1 wherein the structural material is timber or masonry.
3. The method according to claim 1 or 2 wherein the organic boron compound is a boron ester having a melting point of 50° to 200°C.
4. The method according to claim 2 wherein the boron ester is selected from mono (2-methyl-2, 4-pentanediol) - monoborate, triethanediol diborate, tri-(2,3-dimethyl-2,3-butanediol)diborate, tri-(2,5-dimethyl-2, 5-hexanediol)-diborate, tri-(2,6-dimethyl-4-heptanol) borate, triethanolamine borate, tri-isopropanolamine borate and tri-(2,2-dimethyl-1,3-propanediol) diborate.
5. The method according to any one of the preceding claims wherein the preservative element is in the form of a rod or a pellet.
6. The method according to any one of the preceding claims wherein the preservative element contains two or more organic boron compounds having different rates of hydrolysis.
7. The method according to any one of the preceding claims wherein said organic boron compound contains between 2.5 and 7.5% boron by weight.



8. The method according to any one of the preceding claims wherein the element also contains a water-soluble inorganic boron compound.

9. The method according to claim 8 wherein the inorganic boron compound is one or more of alkali metal borates, boric oxide and boric acid.

10. The method according to claim 9 wherein the weight ratio of boric acid to other borates is between 1:10 and 10:1.

11. The method according to claim 9 which comprises 20 parts by weight mono hexylene glycol monoborate, 20 parts by weight boric acid, 30 parts by weight borax and 30 parts by weight boric oxide.

12. The method according to any one of the preceding claims wherein the preservative element further contains at least one other water-soluble compound having fungicidal or insecticidal properties.

13. The method according to claim 12 wherein said other water-soluble compound is selected from metal salts of copper, arsenic or chromium and inorganic fluorides.

14. A method for preserving structural material from attack by fungus or insects substantially as hereinbefore described with reference to the Examples.

DATED this 7th day of August, 1991
MANCHEM LIMITED
By Its Patent Attorneys
DAVIES & COLLISON



INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 88/00845

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC
IPC4: B 27 K 3/34, 3/52, 3/00, C 04 B 41/46, A 01 N 55/08, 59/14

II. FIELDS SEARCHED

Minimum Documentation Searched *

Classification System Classification Symbols

IPC4 B 27 K, A 01 N

Documentation Searched other than Minimum Documentation
to the extent that such Documents are included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages **	Relevant to Claim No. **
P,X	WO, A1, 88/04601 (LAPORTE INDUSTRIES LIMITED) 30 June 1988, see the whole document --	1-8,13
X	GB, A, 1560884 (BASF AKTIENGESELLSCHAFT) 13 February 1980, see page 2, line 7 - line 9; page 2, line 25 - line 34; page 2, line 100 - line 101; claims 1-4,16 --	1-3,5
Y	Derwent's abstract, No. 83 781 577/40, SU 979 109, publ. week 8340 (AS LATV ORG SYNTHESIS) --	1,7-9
Y	US, A, 4076871 (BUDDY M. SHORT ET AL) 28 February 1978, see column 1, line 40 - line 41; column 2, line 33 - line 46; column 3, line 2 - line 28 --	1-3,7,8

* Special categories of cited documents: **

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

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"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

"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 docu-
ments, such combination being obvious to a person skilled
in the art.

"A" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search
5th January 1989

Date of Mailing of this International Search Report

03 FEB 1989

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

M. VAN MOL

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	GB, A, 2086726 (BORAX HOLDINGS LIMITED) 19 May 1982, see page 1, line 39 - line 51; page 1, line 63 - line 67; page 1, line 82 - line 88; claims 1-12 --	1,4,7,8, 11-13
Y	US, A, 4269875 (CARL C. BECHGAARD ET AL) 26 May 1981, see abstract --	1,8,13
Y	EP, A1, 0184663 (BIO-KIL CHEMICALS LIMITED) 18 June 1986, see claims 1-10 --	1,8,13
Y	GB, A, 2114003 (BIO-KIL LABORATORIES) 17 August 1983, see page 1, line 109 - line 114; claims 1-12 -- -----	1,7,8,9, 13

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

PCT/GB 88/00845

SA

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 02/11/88
The European 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	Publication date	Patent family member(s)	Publication date
WO-A1- 88/04601	30/06/88	AU-D- 10598/88	15/07/88
GB-A- 1560884	13/02/80	NONE	
US-A- 4076871	28/02/78	NONE	
GB-A- 2086726	19/05/82	NONE	
US-A- 4269875	26/05/81	NONE	
EP-A1- 0184663	18/06/86	US-A- 4661157	28/04/87
GB-A- 2114003	17/08/83	NONE	