The present invention relates to a triaza containing a triaza...
CONVENTION APPLICATION FOR A PATENT

APPLICATION ACCREDITED AND AMENDED

ALLOWED

8-2-25

We hereby apply for the grant of a Patent for an invention entitled: (1)

WOOD PRESERVATIVES

which is described in the accompanying complete specification. This application is a

Convention application and is based on the application numbered (2)

P30 40 499.0

for a patent or similar protection made in (4) Federal Republic of Germany

on 28th October 1980.

Our address for service is Messrs. Edwd. Yaters & Sons, Patent Attorneys,

50 Queen Street, Melbourne, Victoria, Australia.

DATED this 26th day of October 1981.

BASF AKTIEGESELLSCHAFT

Louis C. Gebhardt
Reg'd. Patent Attorney

To:

THE COMMISSIONER OF PATENTS.
DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

In support of the Convention Application made by BASF Aktiengesellschaft, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, (hereinafter referred to as the applicant) for a Patent for an invention entitled,

WOOD PRESERVATIVES

We, Friedrich Raemisch and Peter Barz, citizens of the Federal Republic of Germany, residing at 26 Burgermeister-Hörlicher-Strasse, 6700 Ludwigshafen, and 20 Hochfeldstrasse, 6700 Ludwigshafen, Federal Republic of Germany,
do solemnly and sincerely declare, as follows:

1. that we are authorized by the applicant for the patent to make this declaration on its behalf.

2. the basic application as defined by Section 141 of the Act was made in the Federal Republic of Germany under No. 30 40 499.0 on the 25th day of October 1980, by BASF Aktiengesellschaft.

3. ERNST-HEINRICH POMER, a citizen of the Federal Republic of Germany, residing at 4 Berliner Platz, 6703 Limburgerhof, Federal Republic of Germany, is/are the actual inventor of the invention and the facts upon which the applicant is entitled to make the application are as follows:
The applicant is the assignee of ERNST-HEINRICH POMER.

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at 6700 Ludwigshafen, Federal Republic of Germany this 7th day of October 1981.

BASF Aktiengesellschaft

To: THE COMMISSIONER OF PATENTS

Applicant DE-OS 2,201,063) and bis-phenyl-(3-trifluoromethyl-
Claim

1. A wood preservative comprising a solid or liquid carrier and a triazolyl methyl ketal of the formula

\[
\text{Cl} \quad \text{Cl}\quad \text{O} \\
\text{H}_2\text{O} - \text{A} \\
\text{N} \quad \text{N}
\]

where R is alkyl of 2 to 3 carbon atoms.
The following statement is a full description of this invention, including the best method of performing it known to: U.S.
WOOD PRESERVATIVES

The present invention relates to a wood preservative containing a triazolyl methyl ketal as active ingredient.

German Laid-Open Application DE-OS 2,551,560 discloses the use of 1-(beta-aryl)-alkyl-1H-1,2,4-triazole ketals as fungicides in agriculture for combating phytopathogenic fungi. The compounds may also be employed on animals and human beings suffering from diseases caused by pathogenic microorganisms.

We have now surprisingly found that triazolyl methyl ketals of the formula

\[
\text{C}_1\text{CH}_2\text{N} - \text{CH}_4
\]

where \( R \) is alkyl of 2 to 3 carbon atoms, have a very good action on wood-discoloring fungi, wood-rot fungi and wood-destroying fungi. The compounds 1-[2-(2,4-dichlorophenyl)-4-ethyl-1,3-dioxolan-2-yl-methyl]-1H-1,2,4-triazole (compound A) and 1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl-methyl]-1H-1,2,4-triazole (compound B) are particularly effective. The broad spectrum of action of the active ingredients in wood preservation could not have been foreseen, because other, prior art, triazole derivatives employed in agriculture, such as 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butane (compound 1) (German Laid-Open
Application DE-OS 2,201,063) and bis-phenyl-(3-trifluoromethyl-phenyl)-1-(1,2,4-triazolyl)-methane (compound 2), are virtually ineffective on wood-discoloring and wood-rot fungi, in spite of the fact that they have an excellent fungicidal action on phytopathogenic fungi.

For instance the following wood- and paint-discoloring fungi, wood-rot fungi and wood-destroying fungi may be combated with the wood preservatives according to the invention: Pullularia (Aureobasidium pullulans), Sclerophoma pityophila, Ceratocystis spec., Paecilomyces variotii, Hormiscium spec., Stemphylium spec., Phoma violacea, Cladosporium herbarum, Trichoderma viride, Chaetomium globosum, Hemicola grisea, Merulius lacrimans, Coniophora puteana, Lentinus lepideus, Lenzites trabea, Trametes versicolor, Stereum hirsutum, and Pomes annosus.

The novel active ingredients may be used in formulations, such as solutions, emulsions, pastes and oil dispersions. The formulations generally contain from 0.1 to 90, and preferably from 0.25 to 50, wt% of active ingredient. The application rates depend on the effect desired, and range from 0.5 to 8 g of active ingredient per m² of wood surface to be preserved, or 50 to 4,000 g of active ingredient per m³ of wood. Paints contain for example 0.5 to 2 wt% of active ingredient. To protect wood-base materials, the active ingredients may be added as an emulsion or simply mixed with the adhesive, for instance in amounts of from 2 to 6 wt%.

The active ingredients are applied by brushing, spraying, atomizing, dipping, or by pressure impregnation or diffusion methods.
To increase the spectrum of action, or to achieve special effects, the novel active ingredients may also be combined with other active ingredients. Mixtures with the following compounds are particularly favorable:

Organotin compounds, such as tributyltin oxide and tributyltin benzoate.

Methylene bis-thiocyanate.

Alkyl-dimethyl-benzylammonium chloride.

Cetylpyridinium chloride.

Chlorinated phenols, such as tetra- and pentachlorophenol.

tetrachloroisophthalic acid dinitrile.

2-halobenzoic acid anilide.

N-cyclohexyl-N-methoxy-2,5-dimethylfuran-3-carboxamide.

N,N-dimethyl-N'-phenyl-(N-fluoromethylthio)-sulfamide.

N-phenyl-N,N'-dimethyl-N'-fluorodichloromethylthiosulfonyl-diamide.

Methyl benzimidazole-2-carbamate.

2-thiocyanomethyl-thiobenzothiazole.

copper naphthenate.

copper-8-oxyquinoline.

Alkali metal and metal salts of N'-hydroxy-N-cyclohexyldiazenium oxide.

Mercaptobenzothiazole.

N,N-dimethyl-N'-(dichlorofluoromethylthio)-sulfamide.

p-chlorophenyl-3-propargyl-formal.

3-iodo-2-propynyl-butyl-carbamate.
EXAMPLE 1

To prepare an oily wood preservative containing 2% of active ingredient, 1 part (by weight) of compound A is first dissolved, with slight heating, in 55 parts of a gasoline fraction rich in aromatics. Subsequently, 10 parts of an alkyd resin is added, and the mixture is made up, at room temperature, to 100 parts with white spirit.

Oily wood preservatives containing 0.25 to 5 wt% of active ingredients A and B are prepared analogously.

To obtain water-resistant impregnation finishes, water repellents may be added to the oily wood preservatives. Examples of suitable substances are zinc stearate, aluminum stearate, and waxes. Color effects may also be obtained by incorporating inorganic or organic pigments or oil-soluble dyes into the formulations.

To protect wood against fungus attack, usually from 50 to 200 ml of the oily wood preservatives given in Example 1 is applied per m² of wood surface, by brushing, spraying or dipping.

EXAMPLE 2

Disc-shaped filter papers having a diameter of 13 mm and a thickness of 1 mm are impregnated with 0.2 ml solutions in acetone containing 200, 100, 50, 25 and 12.5 parts of active ingredient per million parts of solution (ppm). The discs are then placed on a 2% malt extract agar in Petri dishes which have been inoculated with spores of the wood-discoloring fungi Pullularia pullulans and Trichoderma viride (green wood mold). The dishes are then incubated for 3 days at from 22°C to 24°C. After this period, the fungi...
in the control dishes are well developed; the fungicidal action of the active ingredients is assessed from the fungus-free zones (halos) which have formed round the papers discs, as follows:

- no halo = no fungicidal action
+ small halo < 2 mm = slight fungicidal action
++ average halo 2-6 mm = good fungicidal action
+++ large halo > 5 mm = excellent fungicidal action.

a) *Pullularia pullulans*

<table>
<thead>
<tr>
<th>Active ingredient</th>
<th>ppm of active ingredient in solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td>A</td>
<td>+++</td>
</tr>
<tr>
<td>B</td>
<td>+++</td>
</tr>
<tr>
<td>1</td>
<td>+</td>
</tr>
<tr>
<td>2</td>
<td>+</td>
</tr>
</tbody>
</table>

Control (no active ingredient)

b) *Trichoderma viride*

<table>
<thead>
<tr>
<th>Active ingredient</th>
<th>ppm of active ingredient in solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td>A</td>
<td>+++</td>
</tr>
<tr>
<td>B</td>
<td>+++</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
</tr>
</tbody>
</table>

Control (no active ingredient)
EXAMPLE 3

Active ingredients A and B and comparative agents 1 and 2 are dissolved in acetone and added, in amounts of 0.4, 1.9 and 9.9 ppm, to a liquid, 5% malt extract agar. The agar is poured into Petri dishes, and, after it has solidified, the nutrient agar (containing the fungicides) is centrally inoculated with the mold and sap-stain fungus Chaetomium globosum. After the dishes have been incubated for 5 days at 25°C, the spread of the fungus colonies on the nutrient medium is assessed against the control (no active ingredient added):

0 = no fungus growth (fungus mycelium killed)
1 = slight fungus growth (up to one third of the surface of the agar covered)
3 = average fungus growth (up to two thirds of the surface of the agar covered)
5 = uncontrolled fungus growth (surface of agar completely covered)

<table>
<thead>
<tr>
<th>Active ingredient</th>
<th>ppm of active ingredient in nutrient agar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40</td>
</tr>
<tr>
<td>A</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Control (no active ingredient)</td>
<td></td>
</tr>
</tbody>
</table>
EXAMPLE 4

Active ingredients A and B and dissolved in acetone and added, in amounts of 80, 40, and 20 ppm, to a 5% malt extract agar as described in Example 3. The agar is poured into Petri dishes and, after it has solidified, the nutrient agar (containing the fungicides) is centrally inoculated with mycelium of the wood-destroying fungi Coniophora puteana and Trametes versicolor. After the dishes have been incubated for 5 days at 25°C, the spread of the fungus colonies on the nutrient medium is assessed against the control (no active ingredient added):

0 = no fungus growth (fungus mycelium killed)
1 = slight fungus growth (up to one third of the surface of the agar covered)
3 = average fungus growth (up to two thirds of the surface of the agar covered)
5 = uncontrolled fungus growth (surface of agar completely covered)

<table>
<thead>
<tr>
<th>Active ingredient</th>
<th>ppm of active ingredient in nutrient agar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coniophora puteana</td>
</tr>
<tr>
<td></td>
<td>80</td>
</tr>
<tr>
<td>A</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
</tr>
<tr>
<td>Control (no active ingredient)</td>
<td>5</td>
</tr>
</tbody>
</table>
The results of these experiments show that the prior art fungicidal triazole derivatives 1 and 2 have no, or only a very slight, action on fungi in wood, whereas the fungicidal triazole derivatives A and B surprisingly have a very good fungicidal action on fungi which attack wood.

EXAMPLE 5

10 parts by weight of compound B is dissolved in a mixture consisting of 90 parts by weight of xylene, 6 parts by weight of the adduct of 8 to 10 moles of ethylene oxide with 1 mole of oleic acid-N-monoethanolamide, 2 parts by weight of the calcium salt of dodecylbenzenesulfonic acid, and 2 parts by weight of the adduct of 40 moles of ethylene oxide with 1 mole of castor oil. By pouring the solution into water and uniformly distributing it therein, an aqueous dispersion of the active ingredient is obtained.

EXAMPLE 6

To determine the activity on the wood-destroying fungi Coniophora puteana and Trametes versicolor, pine sapwood blocks measuring 50x25x15 mm were coated at a rate of 100 g/m² of wood surface with oily wood preservative formulations containing 1 wt% of active ingredient B. After the treated blocks had been stored for 4 weeks, they were placed, together with untreated blocks, in glass dishes containing the fungi Coniophora puteana or Trametes versicolor in a nutrient agar. The dishes were then incubated in an atmospheric laboratory at 22°C and a relative humidity of 70%. After
3 months, the fungus mycelium attaching to the blocks was removed and the blocks were dried. The degree of wood destruction was then ascertained.

<table>
<thead>
<tr>
<th>Active ingredient</th>
<th>... % of active ingredient in the formulation</th>
<th>Degree of fungal attack after a test period of three months</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coniophora puteana</td>
<td>Trametes versicolor</td>
</tr>
<tr>
<td>Control (solvent only, without active ingredient)</td>
<td>3a/4b</td>
<td>4a</td>
</tr>
</tbody>
</table>

**Rating:**

1 undamaged
2a slight local attack
2b slight overall attack
3a severe local attack
3b severe overall attack
4a local complete destruction
4b overall complete destruction.

By attaching its blocks, in addition to the storage of wood blocks, it is stored in an atmosphere of 70% relative humidity. After
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A wood preservative comprising a solid or liquid carrier and a triazoly methyl ketal of the formula

\[
\begin{align*}
\text{Cl} & \quad \text{O} \quad \text{O} \\
\text{Cl} & \quad \text{O} \quad \text{O} \\
\text{H}_2\text{C-CH} & \quad \text{R} \\
\end{align*}
\]

where R is alkyl of 2 to 3 carbon atoms.

2. A process for protecting wood against discoloration and destruction by fungi, wherein the wood is treated with a triazolyl methyl ketal of the formula

\[
\begin{align*}
\text{Cl} & \quad \text{O} \quad \text{O} \\
\text{Cl} & \quad \text{O} \quad \text{O} \\
\text{H}_2\text{C-CH} & \quad \text{R} \\
\end{align*}
\]

where R is alkyl of 2 to 3 carbon atoms.

DATED this 26th day of October 1981.

BASF AKTIENGESELLSCHAFT

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