International Application Published Under the Patent Cooperation Treaty (PCT)

Applicant: GELORME, Joseph; Portsmouth, NE [US]; GELORME, Jeffrey, Donald [US/US]; IBM Corporation, MD 5E3, 3605 Highway 52 N, Rochester, Minnesota 55901-1407 (US).

Inventors: GELORME, Joseph; GELORME, Jeffrey, Donald

Abstract: The present invention is directed to silane coupling agents for printed circuit boards, such as high-temperature printed circuit boards (PCBs), a process for synthesizing the silane coupling agent, and (PCBs) with such coupling agents. The silane coupling agent is defined by the following formula: Formula (1) wherein at least one \( R' \) is an allyl and the other one is hydrogen, an alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl; and \( R^1 \) is an alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl.
SILANE COUPLING AGENTS FOR PRINTED CIRCUIT BOARDS

Field of the Invention

The present invention is directed to silane coupling agents, and more particularly, to silane coupling agents for printed circuit boards, such as high-temperature printed circuit boards.

Background of the Invention

The basic concept behind a coupling agent is to join two disparate surfaces. In the case of printed circuit boards (PCBs), a silane coupling agent is often used to join a coating, e.g., a varnish such as an epoxy-based resin, to a substrate, e.g. glass cloth, to define a laminate, or laminated structure. The silane coupling agent typically consists of an organofunctional group to bind to the coating and a hydrolyzable group that binds to the surface of the substrate. In particular, the alkoxy groups on silicon hydrolyze to silanols, either through the addition of water or from residual water on the inorganic surface. Subsequently, the silanols react with hydroxyl groups on the inorganic surface to form an oxane bond (Si-O-Si) and eliminate water.

One problem experienced with PCBs is conductive anodic filament (CAF), which is a copper corrosion byproduct that emanates from the anode of a circuit and "grows" subsurface toward the cathode, frequently along separated fiber-epoxy interfaces. With PCBs, anode/cathode pairs are typically plated through holes. CAF can result in catastrophic failure of PCBs, which in some instances can cause fires. The bond between the varnish and substrate is understood to be an important factor in CAF. Thus, the silane coupling agent is an important consideration in the laminate.

For the specific case of epoxy-based laminates, the organofunctional group that has been found to exhibit desirable performance based on numerous criteria is vinylbenzylaminoethylaminopropyl and also benzylaminoethylaminopropyl. Silane coupling agents, which include this organofunctional group, are thought to covalently bond to the epoxide functional groups of the traditional epoxy-based resin, such as the well known FR4 epoxy resins, through the secondary nitrogens of the amino groups. While a plethora of silane coupling agents exist, the industry workhorse for coupling epoxy-based resins has
been vinylbenzylaminoethylaminopropyl-trimethoxysilane (commercially available as Dow Corning Z-6032).

As the PCB industry has migrated away from traditional FR4 epoxy resins (due to lead-free requirements and the higher soldering temperatures associated with tin-silver-copper alloys), silane coupling agents originally developed for those epoxies have not kept pace. That is, vinylbenzylaminoethylaminopropyltrimethoxysilane is still the coupling agent utilized to couple, or bond, the glass cloth substrate to the laminate varnish. However, current varnishes are no longer comprised of FR4 epoxies, rather they are more likely to be bismaleimide triazine (BT) resins or polyphenylene oxide/trially-isocyanurate (PPO/TAIC) interpenetrating networks.

Consequently, a need exists in the industry for a silane coupling agent designed for current resin systems.

**Summary of the Invention**

In accordance with an embodiment of the present invention, a silane coupling agent for printed circuit boards is provided and defined by the following formula:

![Formula I](image)

**Formula I**

wherein at least one R’ is an allyl and the other is hydrogen, an alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl; and R₁ is an alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl. In one example, the silane coupling agent is:
In another embodiment, a process for synthesizing the silane coupling agent is provided.

The process includes, in the presence of heat and a catalyst, reacting $\text{HSi(OR}_1\text{)}_3$ and

wherein at least two $R$ groups are an allyl and the remaining $R$ group is hydrogen, an alkyl, a
cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl and $R^1$ is as
defined above so as to synthesize the silane coupling agent of Formula I. In one example,
the resulting silane coupling agent is diallylpropylisocyanurate-trimethoxysilane.

In yet another embodiment, a printed circuit board is provided which includes a substrate,
such as a glass cloth, and a varnish coating, such as a polyphenylene
oxide/triallylisocyanurate resin, on the substrate. The printed circuit board further includes a
silane coupling agent situated between the varnish coating and substrate so as to couple the
varnish coating to the substrate. The silane coupling agent is defined by the Formula I, as
discussed above.

In still another embodiment, a method of making a printed circuit board is provided which
includes applying a silane coupling agent to a substrate, such as a glass cloth. Next, a
varnish coating, such as a polyphenylene oxide/triallylisocyanurate resin, is applied on the
silane coupling agent so that the silane coupling agent is situated between the varnish
coating and substrate. Then, the substrate, coupling agent, and varnish coating are subjected to curing conditions, e.g., heat under vacuum, so as to define a printed circuit board. The silane coupling agent is defined by the Formula I, as discussed above.

**Detailed Description**

In accordance with an embodiment of the invention, there is provided a silane coupling agent for printed circuit boards (PCBs), such as high-temperature PCBs.

The silane coupling agent is defined by the following formula:

![Formula I](attachment:image)

**Formula I**

wherein at least one R' is an allyl and the other one is hydrogen, an alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl; and R^1 is an alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl.

In one example, each R' is an allyl. In another, example, R^1 is an alkyl group. In yet another example, each R is an allyl and R^1 represents an alkyl group having 1 to 18 carbon atoms. In another example, at least one R^1 group is a methyl group. In still another example, the silane coupling agent is:

![Diallylpropylisocyanuratetrimethoxysilane](attachment:image)
The silane coupling agent of Formula I incorporates an allylisocyanurate ligand as the organo functional group and is designed to interact with current resin systems, such as polyphenylene oxide (PPO)/triallylisocyanurate (TAIC) resins. In particular, the allyl group(s) of the silane coupling agent can co-react with the allyl group(s) of the TAIC as the varnish cures to form a crosslinked resin tightly bound to the glass fibers of the substrate.

Although the polyphenylene oxide (PPO)/triallylisocyanurate (TAIC) resins have been identified herein as suitable for coupling to glass fiber substrates via the silane coupling agent, it is contemplated that any ethylenic unsaturated monomer may be used as a varnish. To that end, in addition to TAIC (or its diallyl analog), vinyl- or methacryl-terminated PPO, any of the diallyl ethers of bisphenol (as described in U.S. Patent No. 4,774,282, the contents of which is expressly incorporated by reference herein in its entirety), or allyl-modified aryl cyanate esters (e.g., 1-allyl-2-cyanatobenzene), and the like, may be used.

And, while the silane coupling agent generally may be synthesized by methods known in the art, a schematic diagram outlining a proposed reaction mechanism for synthesizing the silane coupling agent of Formula I is shown below.

\[
\begin{align*}
\text{R} & \quad \text{N} & \quad \text{N} \\
\text{O} & \quad \text{C} & \quad \text{O} \\
\text{R} & \quad \text{N} & \quad \text{N} \\
\text{O} & \quad \text{C} & \quad \text{O} \\
\text{R} & \quad \text{N} & \quad \text{N} \\
\end{align*}
\]

\[+ \quad \text{HSi(OR')}_3\]

\[\Delta \quad \text{catalyst}\]

\[
\begin{align*}
\text{R}' & \quad \text{N} & \quad \text{N} \\
\text{O} & \quad \text{C} & \quad \text{O} \\
\text{R}' & \quad \text{N} & \quad \text{N} \\
\text{O} & \quad \text{C} & \quad \text{O} \\
\text{R}' & \quad \text{N} & \quad \text{N} \\
\end{align*}
\]

\[\text{Si(OR')}_3\]

Formula I
In the above schematic, concerning the allylisocyanurate ligand, at least two of the R groups are an allyl and the remaining R group is hydrogen, an alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl; and R\(^{1}\) is an alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl. In one example, the allylisocyanurate ligand is TAIC, i.e., each R group is an allyl, and the silicon hydride compound is trimethoxysilicon hydride, HSi(OCH\(_3\))\(_3\), i.e., R\(^{1}\) is a methyl, such that the resulting silane coupling agent is diallylpropylisocyanurate trimethoxysilane. In another example, each R is an allyl. In yet another example, R\(^{1}\) is an alkyl group. In still another example, each R is an allyl and R\(^{1}\) represents an alkyl group having 1 to 18 carbon atoms.

Further concerning synthesis of the silane coupling agent, the allylisocyanurate ligand is reacted with the silicon hydride compound to reduce the alkene functionality of the allylisocyanurate ligand by adding across a double bond. This reaction takes place in the presence of heat (\(\Delta\)) and a catalyst, such as transition metal catalyst, e.g., chloroplatinic acid. Judicious selection of the reaction conditions and stoichiometry is thought to limit the reactivity to a single allyl group of TAIC. The catalyst can be used at the 3-20 weight percent range based on total weight of reactants. In another example, the weight percent range can be from 4-8 and, in another example, the weight percent can be 5. The reaction temperature can range from 55-120\(^{\circ}\)C. The completeness of the reaction can be determined by measuring the exotherm (via differential scanning calorimetry). Representative reaction times are in the 15-20 hr range. The reaction can be carried out in toluene or other suitable solvents. The reaction product can be isolated by stripping off the solvent via rotary evaporation or other suitable technique known to those skilled in the art. And, if necessary, fractional distillation can be used to separate the allylpropyl-isocyanurate derivatives.

Concerning the catalyst, transition metal catalysts, such as platinum catalysts, are suitable for use in the synthesis process. Examples of platinum catalysts include chloroplatinic acid as well as those disclosed in U.S. Patent No. 5,260,399, the contents of which is expressly incorporated by reference herein in its entirety. Also, Wilkinson’s catalyst, RhCl([C\(_5\)H\(_5\)])\(_2\)Pt, can be used. Ashby’s Catalyst (1.75 wt percent platinum in ethanol) can also be used for such hydrosilation reactions, as well as the Lamoreaux catalyst (3.5wt % platinum in octanol), and the Karstedt catalyst (Pt \(\left\{(CH=CHMe)Si\right\}\)\(_2\)O)\(_3\)). And, other representative examples include RhX(CO)(PR\(_3\))\(_2\); RhH(CO)([C\(_6\)H\(_5\)])\(_2\)P\(_3\); IrCl(CO)([C\(_6\)H\(_5\)])\(_2\)P\(_3\); M(CO)KC\(_6\)H\(_5\))\(_3\)P\(_2\); IrH(CO)([C\(_6\)H\(_5\)])\(_2\)P\(_3\); Pt([C\(_6\)H\(_5\)])\(_3\)P\(_4\); trans-Pt([C\(_6\)H\(_5\)])\(_3\)P\(_2\)Cl\(_2\);
CiS-Pt[(C₆Hs)₃P]₂C₁₂; Pt[(C₆Hs)₃P]₂(C₂H₄); Pt[(C₆Hs)₃P]₂O₂; trans-PtHCl[(C₆Hs)₃P]₂; cis-PtHCl[(C₆Hs)₃P]₂; Pt(PF₅)₄; Pd[(C₆Hs)₃P]₂C₁₂; Pd[(C₆Hs)₃P]₂Cl₂; Co[(C₆Hs)₃P]₂Cl₂; and Ru[(C₆Hs)₃P]₃Cl₂.

The resulting silane coupling agent of Formula I can couple, or bond, the varnish coating to the PCB substrate, e.g. glass cloth, to define a laminate, or laminated PCB. In particular, the resulting silane coupling agent can be applied to the substrate via known means, such as a dip coating process. Then, the treated substrate, e.g., glass substrate, is coated with a varnish, such as PPO/TAIC varnish, via means known in the art. After which, the laminate is subjected to curing conditions, e.g., heated under vacuum, as known in the art, which results in a crosslinked phase that is covalently bound to the glass fibers. And, as with the commercially available silanes, hydrolysis of the trialkoxy groups yields a silanol that reacts with hydroxyl groups on the glass surface to form Si-O-Si bonds upon loss of water.

Additionally, the propyl group to which the trialkoxysilane is attached is hydrophobic, further retarding ingress of water to the resin/glass interface and improving CAF resistance.

While the present invention has been illustrated by the description of one or more embodiments thereof, and while the embodiments have been described in considerable detail, they are not intended to restrict or in any way limit the scope of the appended claims to such detail. Additional advantages and modifications will readily appear to those skilled in the art. The invention in its broader aspects is therefore not limited to the specific details, representative product and/or method and examples shown and described. Accordingly, departures may be made from such details without departing from the scope of the general inventive concept.
CLAIMS

1. A silane coupling agent defined by the following formula:

\[
\begin{align*}
&\text{N} \quad \text{N} \\
&\text{O} \quad \text{O} \\
&\text{R'} \quad \text{R'} \\
&\text{Si(OR')}_3
\end{align*}
\]

wherein at least one R' is an allyl and the other is hydrogen, an alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl; and R\(^1\) is an alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl.

2. The silane coupling agent of claim 1 wherein each R' is an allyl.

3. The silane coupling agent of claim 1 wherein \(R^1\) is an alkyl group.

4. The silane coupling agent of claim 1 wherein each R is an allyl and \(R^1\) is an alkyl group having 1 to 18 carbon atoms.

5. A silane coupling agent of the following structure:

\[
\begin{align*}
&\text{N} \quad \text{N} \\
&\text{O} \quad \text{O} \\
&\text{Si(OCH}_3\text{)}_3 \\
&\text{Si(OR')}_3 \\
&\text{R'} \\
&\text{R'}
\end{align*}
\]

6. A printed circuit board comprising:
   a substrate;
   a varnish coating on the substrate; and
a silane coupling agent situated between the varnish coating and substrate so as to
couple the varnish coating to the substrate, the silane coupling agent defined by the
following formula:

\[
\begin{align*}
\text{R'} & \quad \text{Si(OR')}_3 \\
\text{R} & \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \\
& \quad \text{O} \quad \text{O} \\
\end{align*}
\]

wherein at least one R' is an allyl and the other one is hydrogen, an alkyl, a
cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl; and R is an
alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl.

7. The printed circuit board of claim 6 wherein each R' is an allyl.

8. The printed circuit board of claim 6 wherein R represents an alkyl group.

9. The printed circuit board of claim 6 wherein each R is an allyl and R represents an
alkyl group having 1 to 18 carbon atoms.

10. The printed circuit board of claim 6 wherein the silane coupling agent is

\[
\begin{align*}
\text{O} & \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \\
& \quad \text{O} \quad \text{O} \\
\text{Si(OCH}_3\text{)}_3 & \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \\
& \quad \text{O} \quad \text{O} \\
\end{align*}
\]

11. The printed circuit board of claim 6 wherein the substrate includes glass and the
varnish coating is a polyphenylene oxide/triallylisocyanurate resin.
12. A process for synthesizing a silane coupling agent comprising:
in the presence of heat and a catalyst, reacting

\[
\begin{array}{c}
\text{O} \\
N \\
\text{N} \\
\text{N} \\
\text{R} \\
\text{R} \\
\text{O} \\
\text{N} \\
\text{N} \\
\text{O} \\
\text{R} \\
\end{array}
\]

with HSi(OR\textsuperscript{1})\textsubscript{3}, wherein at least two R groups are an allyl and the remaining R group is hydrogen, an alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl; and R\textsuperscript{1} is an alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl, so as to synthesize a silane coupling agent defined by the following formula:

\[
\begin{array}{c}
\text{O} \\
N \\
\text{N} \\
\text{N} \\
\text{R} \\
\text{R'} \\
\text{O} \\
\text{N} \\
\text{N} \\
\text{O} \\
\text{R} \\
\text{Si(OR\textsuperscript{1})\textsubscript{3}} \\
\end{array}
\]

wherein at least one R is an allyl and the other one is hydrogen, an alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl; and R\textsuperscript{1} is the same as defined above.

13. The process of claim 12 wherein triallylisocyanurate is reacted with HSi(OCH\textsubscript{3})\textsubscript{3} to provide

\[
\begin{array}{c}
\text{O} \\
N \\
\text{N} \\
\text{N} \\
\text{R} \\
\text{R'} \\
\text{O} \\
\text{N} \\
\text{N} \\
\text{O} \\
\text{R} \\
\text{Si(OCH\textsubscript{3})\textsubscript{3}} \\
\end{array}
\]
14. The process of claim 12 wherein the heat is from about 55°C to about 120°C.

15. The process of claim 12 wherein the catalyst is a transition metal catalyst.

16. The process of claim 12 wherein each R is an allyl.

17. The process of claim 12 wherein R¹ is an alkyl group.

18. The process of claim 12 wherein each R is an allyl and R¹ represents an alkyl group having 1 to 18 carbon atoms.

19. A method of making a printed circuit board comprising:
   applying a silane coupling agent to a substrate, the silane coupling agent defined by the following formula:
   \[
   \text{wherein at least one } R' \text{ is an allyl and the other one is hydrogen, an alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl; and } R¹ \text{ is an alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl;}
   \]
   applying a varnish coating on the silane coupling agent wherein the silane coupling agent is situated between the varnish coating; and
   subjecting the substrate, silane coupling agent, and varnish coating to curing conditions so as to define a printed circuit board.

20. The method of claim 19 wherein each R' is an allyl.

21. The method of claim 19 wherein R¹ represents an alkyl group.
22. The method of claim 19 wherein each $R'$ is an allyl and $R^1$ represents an alkyl group having 1 to 18 carbon atoms.

23. The method of claim 19 wherein the silane coupling agent is

![Chemical Structure Image]

24. The method of claim 19 wherein the substrate includes glass and the varnish coating is a polyphenylene oxide/triallylisocyanurate resin.
1. A printed circuit board comprising:
   a substrate;
   a varnish coating on the substrate; and
   a silane coupling agent situated between the varnish coating and substrate so as to
couple the varnish coating to the substrate, the silane coupling agent defined by the
following formula:

   \[
   \text{Si}(OR')_2
   \]

   wherein at least one \( R' \) is an allyl and the other one is hydrogen, an alkyl, a
cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl; and \( R^1 \) is an
alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl.

2. The printed circuit board of claim 1 wherein each \( R \) is an allyl.

3. The printed circuit board of claim 1 wherein \( R^1 \) represents an alkyl group.

4. The printed circuit board of claim 1 wherein each \( R \) is an allyl and \( R^1 \) represents an
   alkyl group having 1 to 18 carbon atoms.

5. The printed circuit board of claim 1 wherein the silane coupling agent is
6. The printed circuit board of claim 1 wherein the substrate includes glass and the varnish coating is a polyphenylene oxide/triallylisocyanurate resin.

7. A method of making a printed circuit board comprising:
   applying a silane coupling agent to a substrate, the silane coupling agent defined by the following formula:
   \[
   \begin{align*}
   &\text{R'} \quad \text{N} \quad \text{N} \quad \text{R'} \\
   &\text{O} \quad \text{N} \quad \text{N} \quad \text{O} \\
   &\text{Si(OCH}_2)_3
   \end{align*}
   \]
   wherein at least one R' is an allyl and the other one is hydrogen, an alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl; and R$^1$ is an alkyl, a cycloalkyl, an aryl, a heteroaryl, a non-aromatic heterocyclic ring, or an allyl;
   applying a varnish coating on the silane coupling agent wherein the silane coupling agent is situated between the varnish coating; and
   subjecting the substrate, silane coupling agent, and varnish coating to curing conditions so as to define a printed circuit board.

8. The method of claim 7 wherein each R is an allyl.

9. The method of claim 7 wherein R$^1$ represents an alkyl group.
10. The method of claim 7 wherein each R' is an allyl and R^1 represents an alkyl group having 1 to 18 carbon atoms.

11. The method of claim 7 wherein the silane coupling agent is

![Chemical Structure](image)

12. The method of claim 7 wherein the substrate includes glass and the varnish coating is a polyphenylene oxide/triallylisocyanurate resin.
## A. CLASSIFICATION OF SUBJECT MATTER

INV. C07F7/18 C08J5/24

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)

C07F C08J

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)

EPO-Internal, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 3 517 001 A (BERGER ABE) 23 June 1970 (1970-06-23) examples 1-3</td>
<td>1-5, 12-18</td>
</tr>
</tbody>
</table>

## D

Further documents are listed in the continuation of Box C

See patent family annex

- **X** 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.
- **S** document member of the same patent family.

Date of the actual completion of the international search

24 March 2010

Date of mailing of the international search report

30/03/2010

Name and mailing address of the ISA/

European Patent Office, P B 5818 Patentlaan 2

NL- 2280 HV Rijswijk

Tel (+31-70) 340-2040,

Fax (+31-70) 340-3016

Autheorized officer

Rinkel, Bert

Form PCT/ISA/210 (second sheet) (April 2005)
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>GB 1202498 A</td>
<td>19-08-1970</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 3494951 A</td>
<td>10-02-1970</td>
</tr>
<tr>
<td>JP 2003138127</td>
<td>A</td>
<td>14-05-2003</td>
<td>NONE</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CN 1427039 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CN 1427034 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CN 1427053 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CN 1189843 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>DE 69614857 B1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>DE 69614857 T2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>WO 9701595 A1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TW 436496 B</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TW 482785 B</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TW 482786 B</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TW 482787 B</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TW 482788 B</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TW 482789 B</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>US 6696155 B1</td>
</tr>
</tbody>
</table>