**Title:** TRIVINYL ETHERS OF POLYOLS

![Chemical Structures](image)

**Abstract**

What is provided herein are trivinyl ethers of polyols having formula (I), which is the trivinyl ether of 1,1,1-tris(hydroxymethyl) ethane; and polyols having formula (II), where \(1 + m + n = 1 \text{ to } 20\); and \(X\) and \(Y\) are independently \(H\) or \(CH_3\). In the preferred forms of formula (II), \(1 + m + n = 3\) to 10, corresponding to an ethoxylated or propoxylated glycerol, respectively.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AT</td>
<td>Austria</td>
<td>ES</td>
<td>Spain</td>
<td>MG</td>
<td>Madagascar</td>
</tr>
<tr>
<td>AU</td>
<td>Australia</td>
<td>FI</td>
<td>Finland</td>
<td>ML</td>
<td>Mali</td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
<td>FR</td>
<td>France</td>
<td>MR</td>
<td>Mauritania</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
<td>GA</td>
<td>Gabon</td>
<td>MW</td>
<td>Malawi</td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
<td>GB</td>
<td>United Kingdom</td>
<td>NL</td>
<td>Netherlands</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
<td>GR</td>
<td>Greece</td>
<td>NO</td>
<td>Norway</td>
</tr>
<tr>
<td>BJ</td>
<td>Benin</td>
<td>HU</td>
<td>Hungary</td>
<td>PL</td>
<td>Poland</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
<td>IT</td>
<td>Italy</td>
<td>RO</td>
<td>Romania</td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
<td>JP</td>
<td>Japan</td>
<td>SD</td>
<td>Sudan</td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
<td>KP</td>
<td>Democratic People's Republic of Korea</td>
<td>SE</td>
<td>Sweden</td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
<td></td>
<td></td>
<td>SN</td>
<td>Senegal</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td></td>
<td></td>
<td>SU</td>
<td>Soviet Union</td>
</tr>
<tr>
<td>CI</td>
<td>Côte d'Ivoire</td>
<td></td>
<td></td>
<td>TD</td>
<td>Chad</td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
<td></td>
<td></td>
<td>TG</td>
<td>Togo</td>
</tr>
<tr>
<td>DE</td>
<td>Germany</td>
<td></td>
<td></td>
<td>US</td>
<td>United States of America</td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.
TRIVINYLS OF POLYOLS

This invention relates to trivinyl ether monomers and resin formulations thereof useful in applications which require high speed cationic initiated radiation curing.

Radiation curable coatings and films such as those formed from an acrylate oligomer are in great demand because of their rapid curing properties. However, these compounds are normally highly viscous liquids or solids and thus are unsuitable as diluents for other polymeric components of a radiation curable formulation. Indeed, such compounds themselves require the incorporation of a diluent or solvent for uniform substrate coating, control of coating thickness and curing at low temperatures. Accordingly, low viscosity monofunctional diluents are usually included in their formulations. While these diluents are reactive, they materially reduce the cross-linked density of the finished product and consequently lower abrasion resistance and ability to withstand chemical attack.

Although solvents have been used to reduce viscosity, they are detrimental in radiation curing due to their volatility which presents problems for uniform composition control unless their evaporation prior to radiant exposure is effected. Obviously, such procedure extends processing time and may pose environmental drawbacks.

To some extent, the drawbacks of high viscosity monomers can be reduced by curing at elevated temperatures. However, this alternative significantly adds to the cost of the overall operation in the expenditure of energy, temperature control and loss of more volatile components in the composition or blistering of the coating resulting from entrained volatiles.
Since acrylates are not conducive to cationically induced radiation curing, they require more costly free radical systems which are oxygen inhibited unless effected in an inert atmosphere, generally under a blanket of nitrogen. Although formulation with a photoinitiator which undergoes bimolecular reaction with a hydrogen donor minimizes the inhibitory effect of air, this benefit is realized at the expense of a greatly reduced cure rate. Also, it is found that polymerization or curing in free radical systems ceases almost immediately upon removal from the source of radiation; thus, the cured product usually contains significant amounts of unpolymerized components. Accordingly, it is an aim of research to develop a monomer having the beneficial properties of acrylates but which is amenable to radiation curing at a rapid rate by cationically induced polymerization which is not oxygen inhibited and which permits continued polymerization after removal from the source of radiation exposure.

Finally, it is noted that the unsubstituted acrylates are sensitizers and skin irritants as well as being carcinogenic, so that specialized safety precautions must be taken to protect operators from exposure.

Certain epoxy compounds also have been used as coatings; however these monomers and their oligomers are not readily curable by radiation. Thermal curing is generally required to increase the rate of polymerization. While vinyl ethers such as those ethers the polyethylene glycols are curable by UV light, their resulting coatings lack toughness and substrate substantivity. Also these materials have low viscosity such that it is difficult to obtain film build-up prior to curing.
Vinyl ether compounds, and methods for effectively cationically polymerizing such compounds, have been described in the literature. See, for example, U.S. Patents 4,161,405; 4,518,788; 4,751,273; 4,775,732; and 4,749,807. However, the art is limited with respect to multifunctional vinyl ether monomers, and to formulations thereof, for forming protective coatings.

What is provided herein is a trifunctional vinyl ether monomer having the formula (I):

\[
\begin{align*}
&\text{CH}_2\text{OCH=CH}_2 \\
&\text{CH}_3\text{-C-CH}_2\text{-OCH=CH}_2 \\
&\text{CH}_2\text{-OCH=CH}_2
\end{align*}
\]

which is the trivinyl ether of 1,1,1-tris(hydroxymethyl) ethane; and

trivinyl ethers of alkoxylated glycerol having the formula (II):

\[
\begin{align*}
&\text{X} \quad \text{Y} \\
&\text{CH}_2\text{(OCH-CH)}_l\text{OCH=CH}_2 \\
&\text{X} \quad \text{Y} \\
&\text{CH(OCH-CH)}_m\text{OCH=CH}_2 \\
&\text{X} \quad \text{Y} \\
&\text{CH}_2\text{(OCH-CH)}_n\text{OCH=CH}_2
\end{align*}
\]

where \( l + m + n = 1 \) to 20; and

\( X \) and \( Y \) are independently \( \text{H} \) or \( \text{CH}_3 \).

In the preferred forms of formula (II), \( l + m + n = 3 \) to 10, corresponding to an ethoxylated or propoxylated glycerol, respectively.
The radiation curable compositions of formula (II) include:

(a) between about 1 and 99.9 wt. % of a trivinyl ether of alkoxylated glycerol;
(b) between about 0.1 and about 5 wt. % of a cationic photoinitiator; and
(c) between about 0 and 99 wt. % of a polymerizable vinyl ether, epoxide, or acrylate oligomer.

The preferred compositions of formula (II) are those having from about 45 to about 95 wt. % of component (a) wherein:

\[ l + m + n = 3 \text{ to } 10; \]

from about 0.5 to about 2 wt. % of component (b); and from about 0 to about 50 wt. % of component (c).

Preferred trivinyl ether compounds (a) of formula (II) include the trivinyl ether of an ethoxylated glycerol having the formula:

\[
\begin{array}{c}
\text{CH}_2(\text{OCH}_2\text{CH}_2)_{1\text{OCH}=\text{CH}_2} \\
\text{CH(OCH}_2\text{CH}_2)_{m\text{OCH}=\text{CH}_2} \\
\text{CH}_2(\text{OCH}_2\text{CH}_2)_{n\text{OCH}=\text{CH}_2}
\end{array}
\]

and the trivinyl ether of a propoxylated glycerol having the formula:

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_2(\text{OCH}_2\text{CH})_{1\text{OCH}=\text{CH}_2} \\
\text{CH}_3 \\
\text{CH(OCH}_2\text{CH}_2)_{m\text{OCH}=\text{CH}_2} \\
\text{CH}_3 \\
\text{CH}_2(\text{OCH}_2\text{CH})_{n\text{OCH}=\text{CH}_2}
\end{array}
\]
The monomer of formula (I) may be prepared by direct vinylation of 1,1,1-tris(hydroxymethyl) ethane with acetylene. In the batch form of the reaction, the mole ratio of polyol to acetylene can vary between about 1:3 and about 1:4.5. In the batch or continuous form of the process, the acetylene gas is bubbled through the polyol liquid itself, or a solution of the polyol in a suitable solvent, such as the dimethyl ether of tetraethylene glycol. Other methods of preparation also may be used for synthesis of the compound of the invention, such as catalytic transetherification of the polyol with a suitable vinyl ether having a boiling point higher than the monomer product.

The acetylene can be introduced into the reaction zone without dilution if present at low pressures; however, at elevated pressures, it is recommended that an inert non-oxygen containing gaseous diluent, such as nitrogen, a C$_1$-C$_3$ alkane or helium be used to dilute the acetylene reactant. When a diluent is employed, an acetylene concentration as low as 10% can be used, although between about 40 and about 60 wt. % acetylene in a diluent is most preferred.

The reaction is carried out in an oxygen free atmosphere which is generally achieved by purging with nitrogen and in the presence of a basic catalyst, such as an alkali metal hydroxide, e.g. potassium hydroxide, sodium hydroxide, and sodium, potassium or lithium metal, or hydride thereof. The concentration of catalyst employed can range from about 0.01% to about 5% by weight.

The process is effected at a temperature of between about 120° and about 180°C., under from about 10 to about 200 psig. total pressure, in a period of from about 2 to about 100 hours reaction time. Preferred conditions include a temperature of between about 140° to about 170°C., under between about 50 and about 100 psig. acetylene pressure and a reaction period of from about 4 to 70 hours.
The trivinyl ether monomers of formula (II) may be prepared by direct vinylation of an ethoxylated or propoxylated glycerol with acetylene to provide monomers of the general formula above.

In either the batch or continuous process of the invention, the acetylene gas is bubbled through the alkoxylated glycerol liquid itself, or a solution of the alkoxylated glycerol in a suitable solvent, such as the dimethyl ether of tetraethylene glycol.

Examples of the cationic photoinitiator, component (b), include the triphenyl sulfonium salt of phosphorous hexafluoride, diphenyl iodide salt, tetrazolium chloride, a phenyl onium salt and an alkyl aryl onium salt. A preferred cationic photoinitiator is triphenyl sulfonium hexafluorophosphate.

Suitable examples of the oligomer component (c), include any of the mono- and di- vinyl ethers of di-, tri- or tetra- ethylene or propylene glycols; C₂ to C₂₀ alkylene divinyl ethers; benzene divinyl ether; and the corresponding thioethers and epoxides; and acrylates such as pentaerythritol triacrylate. Mixtures of such compounds also may be used. Preferred oligomers are bisphenol diepoxide; triethylene glycol divinyl ether; acrylated epoxides; vinyl ether functionalized oligomers; and hexanediol diacrylate or methacrylate, pentaerythritol triacrylate and trimethacrylate.

The above compositions are readily prepared by mixing the components in any order until a uniform mixture is obtained. The resulting composition which is a viscous liquid is easily applied to a substrate in a thickness of from about 0.1 to about 20 mils, preferably from about 0.5 to about 10 mils. Suitable substrates include glass, ceramic, metal, plastic, wood, masonry and fabrics.
Because of the improved liquid viscosity, it is possible to retain higher thicknesses of film build-up on the substrate surface. By regulating the amounts of component (a) with respect to component (c), the desired viscosity, e.g. between about 30 and about 1,000 cps, is achieved without the introduction of extraneous chemical solvents and the like. The presence of the multifunctional vinyl ethers also permits rapid radiation curing, for example within a period of less than one second exposure to between about 100 to about 800 millijoules/cm² of UV light; between about 0.5 and about 5 megarads dosage of radiation from an electron beam or equivalent dosage from laser emissions. It is to be understood that many other sources of radiation can be used to effect curing. The radiation curing process is carried out at about room temperature under ambient pressure in the absence of solvent normally required with highly viscous materials.

The present compositions also lend themselves to thermal curing procedures effected at a temperature between about 70°C. and about 150°C. for a period of from about 5 to about 25 minutes in the presence of conventional initiators. Because of their sensitivity to curing by exposure to a source of radiation, the present products are also useful as photoresists when coated on a photographic film.

The compositions of this invention, when cured, provide clear films or coatings of superior toughness, abrasion resistance, and resistance to chemical attack in acid or basic media.
EXAMPLE 1

Preparation of the Trivinyl Ether of
1,1,1-Tris(Hydroxymethyl) Ethane

Tris(hydroxymethyl) ethane (1201.5 g), tetraethylene glycol dimethyl ether (1000 g) and potassium hydroxide, 85% pellets (30 g) were charged into a one-gallon autoclave. The autoclave was purged three times with nitrogen, heated to 110°C. and held under vacuum at 20 mm Hg for 10 mins. Propane (100 psig.) was then added and the temperature was raised to 140°C. The propane pressure was readjusted to 100 psig. and acetylene (100 psig.) was introduced to start the vinylation. The reaction was complete in 62 hours. The autoclave was then cooled to room temperature, purged two times with nitrogen and discharged. 2797 g of crude product was obtained which contained 86.4% of the trivinyl ether of tris(hydroxymethyl) ethane, as determined by glc analysis.

The crude product (2788 g) was distilled with a 30 plates Oldershaw column at a reduced pressure of 7 mm Hg. A total of 646.9 g of the trivinyl ether of tris(hydroxymethyl) ethane with 99% purity was collected between 69° and 71°C. The structure of the trivinyl ether was identified by nmr analysis.

EXAMPLE 2

Preparation of Trivinyl Ether of
Ethoxylated Glycerol (where 1 + m + n = 5)

Glycerol (870 g., 9.4 moles) and sodium hydroxide (1.0 g.) were charged into a one-gallon autoclave. The mixture was purged three times with nitrogen, heated to 140°C. and subjected to a vacuum of 30 mm Hg for one-half hour. The temperature of the solution was then brought to
155°C. and ethylene oxide (2080 g., 47.3 moles) was added at 30 psig. After all the ethylene oxide was consumed, the autoclave was cooled to 30°C., purged two times with nitrogen and discharged.

2,171 g. (7 moles) of the crude ethoxylated glycerol and 15.6 g. (0.28 moles) of potassium hydroxide then were charged into the one-gallon autoclave. The autoclave was again purged three times with nitrogen and subjected to a vacuum of 20 mm Hg at 140°C. for one-half hour. Propane (100 psig.) and then acetylene (100 psig.) were added. The autoclave was heated at 140°C. for 48 hours and then at 150°C. for 24 hours to give the trivinyl ether of ethoxylated glycerol.

**EXAMPLE 3**

**Preparation of Trivinyl Ether of Propyoxylated Glycerol (l + m + n = 6)**

Glycerol (552 g., 6 moles) and sodium hydroxide (0.6 g.) were charged into a one-gallon stainless steel autoclave. The autoclave was purged three times with nitrogen, heated to 115°C. and subjected to a vacuum of 30 mm Hg for one-half hour. Propylene oxide (2088 g., 36 moles) was added at 30 psig. After all the propylene oxide was consumed, the autoclave was cooled to 30°C., purged two times with nitrogen and discharged.

1,502 g. (3.4 moles) of the crude propyoxylated glycerol and 18.75 g. (0.29 moles) of 85% potassium hydroxide pellets were charged into the one-gallon autoclave. The autoclave was again purged three times with nitrogen and subjected to a vacuum of 30 mm Hg for one-half hour at 140°C. Propane (100 psig.) and then acetylene (100 psig.) were added. The vinylation reaction was continued
for 6 hours at 140°C. and 20 hours at 160°C. to provide the crude trivinyl ether of the propoxylated glycerol. The crude trivinyl ether was distilled with a thin film evaporator to give pure trivinyl ether of propoxylated glycerol as a clear liquid. The structure of the trivinyl ether was confirmed by nmr analysis.

EXAMPLE 4

To a 4-ounce amber colored bottle is added 25 g. of trivinyl ether of ethoxylated glycerol prepared in Example 2 and 0.5 g. of triphenyl sulfonium hexafluorophosphate at a temperature of 60°C. with constant agitation. The formulation is coated onto a polyester plate by hand draw-down using a No. 3 Mayer bar to give a coating thickness of about 0.2 mil. The plate is subjected to a UV light exposure of 15 joules/cm² by passing it under two 200 watt/inch UV lamps at 700 feet/minute. This is followed by a thermal bake at 177°C. for 10 minutes. A protective chemical coating on the polyester is formed.

EXAMPLE 5

To a 4 ounce amber colored bottle is added 25 g. of bisphenol diepoxide having a molecular weight of 370-384 and 12.5 g. (0.062 moles) of triethylene glycol divinyl ether at a temperature of 45°C. with constant agitation. After a uniformly blended liquid mixture is obtained, 0.062 moles of trivinyl ether of propoxylated glycerol (Example 2) is added and agitation is continued for an additional 15 minutes at the blend temperature. After a uniform liquid mixture is obtained 0.25 g. of a fluorinated alkyl ester surfactant and 2 g. of triphenyl sulfonium hexafluorophosphate are added and mixed therein at about 45°C. This
formulation is coated on a aluminumn panel by hand
draw-down using a No. 3 Mayer bar to give a coating
thickness of 0.4 mil. The panel is subjected to a UV light
exposure of 15 joules/cm² by passing them under two 200
watt/inch UV lamps at 100 feet/minute. This was followed
by a thermal bake at 177°C. for 10 minutes. A highly
cross-linked protective polymer film is formed which is
chemical and abrasion resistant.

EXAMPLE 6

The formulation from Example 5 is repeated except
that an acrylated epoxy oligomer (Ebecryl 3700, Radcure
Specialties) is used in place of the bisphenol diepoxide.
Two grams of 1-hydroxycyclohexylphenyl ketone was also
added as a free radical photoinitiator. This formulation
is coated on an oak panel using a #24 Mayer bar to give a
coating thickness of 1.0 mil. The panel is subjected to UV
light exposure of 15 joules/cm² by passing them under two
200 watt/inch UV lamps at 100 feet/minute. A highly
cross-linked protective polymer film which is chemical and
abrasion resistant is formed.

EXAMPLE 7

The formulation from Example 5 is repeated except
that a vinyl ether functional urethane prepared from a
hydroxy vinyl ether and a toluene diisocyanate was used in
place of the bisphenol diepoxide.

This formulation is coated on a polyester film
using a #3 Mayer bar to give a coating thickness of 0.3
mil. The panel is exposed to UV light of 15 joules/cm²
by passing them under two 200 watt/inch UV lamps at 100
feet/minute. A fully cured protective coating is formed.
FIELDS OF USE

The compound of the invention exhibits a high speed cationic initiated radiation curing property, which enables its use in applications which require high speed curing, such as radiation curable coatings, photoresists in the electronic industry, and printing inks, which applications require ultraviolet or electronic beam activation.

It is to be understood that the above examples are provided to illustrate specific and preferred embodiments of the invention and that many modifications and alterations can be made in these examples without departing from the scope of the invention.
WHAT IS CLAIMED IS:

1. Trivinyl ether compounds having the formula (I):

\[
\begin{align*}
\text{CH}_2\text{OCH=CH}_2 \\
\text{CH}_3\text{-C-CH}_2\text{-OCH=CH}_2 \\
\text{CH}_2\text{-OCH=CH}_2
\end{align*}
\]

and formula (II):

\[
\begin{align*}
\text{X} \quad \text{Y} \\
\text{CH}_2\text{(OCH-CH)}_1\text{OCH=CH}_2 \\
\text{X} \quad \text{Y} \\
\text{CH(OCH-CH)}_m\text{OCH=CH}_2 \\
\text{X} \quad \text{Y} \\
\text{CH}_2\text{(OCH-CH)}_n\text{OCH=CH}_2
\end{align*}
\]

where \( 1 + m + n = 1 \) to 20; and

X and Y are independently H or CH\(_3\).

2. The compound of formula (I) of claim 1 which is the trivinyl ether of 1,1,1-tris(hydroxymethyl) ethane.

3. The compound of formula (I) of claim 1 which is made by direct vinylation of 1,1,1-tris(hydroxymethyl) ethane.
4. The compound of formula (I) of claim 3 made by direct vinylation at about 120° to 175°C., in the presence of 0.5 to 2% KOH as catalyst, at about 50 to 100 psi. acetylene pressure, in an inert gas at about the same pressure as the acetylene, at a mole ratio of polyol to acetylene of about 1:3 to 1:4.5.

5. A compound of formula (II) of claim 1 wherein \( l + m + n \) is 3 to 10.

6. A compound of formula (II) according to claim 1 wherein both \( X \) and \( Y \) are \( H \).

7. A compound of formula (II) according to claim 1 wherein \( X \) is \( H \) and \( Y \) is \( CH_3 \).

8. A compound of formula (II) according to claim 1 wherein \( X \) is \( CH_3 \) and \( Y \) is \( H \).

9. A radiation curable composition comprising:

   (a) between about 1 and 99.9 wt. % of the trivinyl ether compound of formulas (I) or (II) of claim 1;

   (b) between about 0.1 and about 5 wt. % of a cationic photoinitiator; and

   (c) between about 0 and 99 wt. % of a polymerizable vinyl ether, epoxide or acrylate oligomer.
### INTERNATIONAL SEARCH REPORT

**I. CLASSIFICATION OF SUBJECT MATTER**

According to International Patent Classification (IPC) or to both National Classification and IPC

**INT CLASS:** C07C 43/16  C08F 2/46, 116/12, 216/12  
**US CLASS:** 568/616, 673, 675 522/31, 170 526/333

### II. FIELDS SEARCHED

<table>
<thead>
<tr>
<th>Classification System</th>
<th>Classification Symbols</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>568/616, 673, 675</td>
</tr>
<tr>
<td></td>
<td>522/31, 170</td>
</tr>
<tr>
<td></td>
<td>526/333</td>
</tr>
</tbody>
</table>

### III. 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>Y</td>
<td>US, A, 4,161,405 (CRIVELLO) Published 17 July 1979 Column 4, lines 55-56, Example 7</td>
<td>1-4</td>
</tr>
<tr>
<td>Y</td>
<td>US, A, 4,751,273 (LAPIN et al.) Published 14 June 1988 Column 3, lines 20-65; Column 4, lines 1-5</td>
<td>1-4</td>
</tr>
<tr>
<td>X</td>
<td>US, A, 4,766,252 (VARA et al.) Published 23 August 1988 Example 3</td>
<td>1, 5-8, 9</td>
</tr>
<tr>
<td>X</td>
<td>US, A, 4,828,873 (VARA et al.) Published 9 May 1989 Example 3, Column 5, line 44</td>
<td>1, 5-8, 9</td>
</tr>
<tr>
<td>A</td>
<td>US, A, 1,959,927 (REPP) Published 22 May 1934</td>
<td>1, 5-8</td>
</tr>
<tr>
<td>Y</td>
<td>US, A, 4,026,705 (CRIVELLO) Published 31 May 1977 Column 5, lines 55-68</td>
<td>9</td>
</tr>
<tr>
<td>Y</td>
<td>US, A, 4,885,319 (DOUGHERTY et al.) Published 05 December 1989</td>
<td>9</td>
</tr>
<tr>
<td>Y</td>
<td>US, A, 4,142,042 (GOBLE) Published 27 February 1979 Claim 10</td>
<td>1, 5-8</td>
</tr>
</tbody>
</table>

* 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
  - "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.
  - "Z" document member of the same patent family

### IV. CERTIFICATION

**Date of the Actual Completion of the International Search:** 19 November 1990

**Date of Mailing of this International Search Report:** 04 Feb 1991

ISA/US

Signature of Authorized Officer: [Signature]

Howard T. Mars

Form PCT/ISA/210 (second sheet) (May 1986)