**Title:** LOW TEMPERATURE-FLEXIBLE RADIATION-CURABLE UNSATURATED POLYSILOXANE COATINGS FOR FIBER OPTIC APPLICATION

**Abstract**

Optical fibers are coated with a radiation-curable liquid, polyethyleneically unsaturated coating composition consisting essentially of an organic polysiloxane having from 2 to 6 reactive side chains each of which carry a functional group providing one reactive site which has been reacted to provide a single radiation-curable monoethyleneically unsaturated side chain. There are about one such side chain for every 500 to 5,000 units of molecular weight. This provides a prime coating which has a modulus of elasticity at room temperature and at -60°C. below 3000.
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.

<table>
<thead>
<tr>
<th>Code</th>
<th>Country</th>
<th>Code</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT</td>
<td>Austria</td>
<td>LI</td>
<td>Liechtenstein</td>
</tr>
<tr>
<td>AU</td>
<td>Australia</td>
<td>LK</td>
<td>Sri Lanka</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
<td>LU</td>
<td>Luxembourg</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
<td>MC</td>
<td>Monaco</td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
<td>MG</td>
<td>Madagascar</td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
<td>MR</td>
<td>Mauritania</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td>MW</td>
<td>Malawi</td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
<td>NL</td>
<td>Netherlands</td>
</tr>
<tr>
<td>DE</td>
<td>Germany, Federal Republic of</td>
<td>NO</td>
<td>Norway</td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
<td>RO</td>
<td>Romania</td>
</tr>
<tr>
<td>FI</td>
<td>Finland</td>
<td>SE</td>
<td>Sweden</td>
</tr>
<tr>
<td>FR</td>
<td>France</td>
<td>SN</td>
<td>Senegal</td>
</tr>
<tr>
<td>GA</td>
<td>Gabon</td>
<td>SU</td>
<td>Soviet Union</td>
</tr>
<tr>
<td>GB</td>
<td>United Kingdom</td>
<td>TD</td>
<td>Chad</td>
</tr>
<tr>
<td>HU</td>
<td>Hungary</td>
<td>TG</td>
<td>Togo</td>
</tr>
<tr>
<td>JP</td>
<td>Japan</td>
<td>US</td>
<td>United States of America</td>
</tr>
<tr>
<td>KP</td>
<td>Democratic People's Republic of Korea</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
LOW TEMPERATURE-FLEXIBLE RADIATION-CURABLE UNSATURATED POLYSILOXANE COATINGS FOR FIBER OPTIC APPLICATION.

DESCRIPTION

Technical Field

This invention relates to radiation-curable liquid coating compositions which cure to form coatings which maintain their flexibility at temperatures as low as about -40°C. to -60°C., and to optical glass fibers coated therewith.

Background Art

Radiation-curable liquid coating compositions are well known, and many of these involve diacrylate-terminated polyurethane oligomers. However, these known compositions may, under some conditions, be relatively hard when cured. In these cases, one can dilute the diacrylate-terminated polyurethane with a large proportion of radiation-curable monomer of low T_g (glass transition temperature) so that radiation exposure will cure the coating and produce a soft layer instead of a hard one. However, these soft layers have little strength and, hence, are not useful for coating optical fibers.

In recent years, glass fiber has become important for the transmission of beams of light used for communication. These must be coated to protect the fiber surface against abrasion. The coating must also be able to resist microbending when the coated fiber is cabled and also when the coated fiber is subjected to large changes in temperature. These complex characteristics demand an unusual coating, namely, one which is both soft and tough. Moreover, this toughness must be achieved without introducing stiffness which would cause microbending when the coating contracts at low temperature. One effort to provide radiation-curable coatings having these properties is the subject of prior application Serial No. 170,148, filed July 18, 1980, but there the properties begin to fall off when exceptionally low
temperatures are encountered. It is desired to extend the range of low temperature which can be sustained without encountering unacceptable stiffness.

Early coatings for optical fibers included silicone oils, cellulosic lacquers, blocked urethanes, and RTV silicones. Most of these materials present problems in handling, stability, durability, or application speeds, factors that have been quite successfully corrected by the use of radiation-curable coatings, (preferably ultraviolet-curable coatings) such as those described in the said prior application. However, none of the earlier ultraviolet-cured coatings provided the level of low temperature (-40°C. to -60°C.) flexibility shown by the conventionally cured RTV silicones. This invention seeks to provide radiation-curable coatings (preferably ultraviolet-curable) having the desired low temperature flexibility performance, and which, at the same time, give an almost unlimited pot life at temperatures up to 80°C. RTV silicones have a short pot life at 80°C. so they are applied at lower temperature where the viscosity is higher and application more difficult. The RTV silicones do not cure with great rapidity, and this adversely limits the speed of production.

Description of Invention

In accordance with this invention, optical glass filament is prime coated with a liquid, polyethylenically unsaturated, radiation-curable resin constituted by an organic polysiloxane having from 2 to 6 reactive side chains each of which carry a functional group providing one reactive site which is preferably selected from the group consisting of hydroxyl, amine, mercaptan, carboxyl or glycidyl, and said functional group having been reacted to provide a single radiation-curable monothylenically unsaturated side chain which preferably contains an acrylic or methacrylic group. Most preferably, the polysiloxane derivative is a polyacrylate or
polymethacrylate, terms which are used here to identify a plurality of acrylic or methacrylic groups which are preferably present as ester groups.

The unique properties desired herein are obtained by having the described polysiloxane possess about one such monoethylenically unsaturated side chain for every 500 to 5,000 units of molecular weight.

The organic polysiloxanes used herein include known compounds which are available in commerce. The polysiloxane backbone is substituted with organic radicals, some of which are inert, and here methyl, phenyl, or a mixture thereof is preferred, and some of which are reactive, like hydroxy propyl or hydroxy polyoxypropyl, which illustrate the side chain providing the hydroxy functional group which is the preferred group providing a single reactive site in the previous description of the organic polysiloxane.

The reactive organic radical may be joined to the silicon atoms of the polysiloxane backbone through oxygen, but it is preferred to have it joined to the silicon atoms by a direct carbon to silicon bond. This is because the direct carbon to silicon bond is more resistant to hydrolysis. The prime coatings of this invention are soft and it is preferred to topcoat them. The topcoating supplies improved hydrolysis resistance as well as improved abrasion protection, so the use of a topcoat minimizes the significance of hydrolysis resistance just as it minimizes the importance of toughness in the prime coating. Nonetheless, when the prime coating is hydrolysis-resistant and when it possesses good toughness as well as having a low modulus of elasticity which is retained at low temperature, the best overall properties are obtained.

While the functional group providing the single reactive site can be supplied by any organic radical,
aliphatic radicals are preferred, especially those which are saturated and which contain, except for the reactive functional group, only carbon and hydrogen, or carbon, hydrogen and oxygen. Thus, the preferred reactive side chains are saturated aliphatic hydrocarbon groups containing from two to four carbon atoms, especially 2-hydroxy propyl, and polyoxyalkylene ethers in which the alkylene group contains from two to four carbon atoms, such as hydroxy polyoxypropyl. Polyesters and polyether polyesters may be used in place of the more preferred polyethers noted above. A suitable polyester would be the reaction product of two moles of ethylene glycol or propylene glycol, with one mole of adipic acid or phthalic acid. This reaction product provides a diol which can be joined to the polysiloxane by one of its two hydroxy groups, leaving the other hydroxy group available to react with a compound which brings in the single ethylenically unsaturated group.

While aliphatic groups are preferred, the reactive side chain can be provided by an aromatic group such as the hydroxyethyl phenyl group.

If one were to use an hydroxy carboxylic acid, such as gamma hydroxybutyric acid, this could be joined to the polysiloxane by its hydroxy group, and then a single carboxyl group would be available to react with a compound which brings in the single ethylenically unsaturated group.

By starting with a polysiloxane containing a terminal carbinol group, this can be reacted with glycine (a carboxy amine) to provide, by direct esterification, a side chain having a primary amine group. While secondary amines are preferred because only one reactive functional site is provided, primary amines are effectively monofunctional when reacted with isocyanates, so they can be used and reacted with a monoethylenically unsaturated
monoisocyanate, like the reaction product of 2-hydroxyethyl acrylate with 2,4-toluene disocyanate or isophorone disocyanate which contain one isocyanate group which is far more reactive than the other so that equi-

molar proportions of reactants will provide the desired monoisocyanate.

Mercaptan functionality is illustrated in the examples. It can also be provided by reacting a dithiol, like 1,6-hexane dithiol or an hydroxy thiol, such as 1-hydroxy, 6-thiol hexane with a silanol-terminated polysiloxane. Similarly, glycidyl functionality can be employed in the glycidoxy propyl group since glycidoxy propyl-functional polysiloxanes are available in commerce. These can be reacted with acrylic acid to form a single acrylate ester group, the hydroxy group generated by the reaction being nonreactive under the conditions which enable ester formation with the glycidyl group.

It will now be evident that by a functional group providing a single reactive site we mean that it is feasible to react one site and not any other potentially reactive site. Nonetheless, it is preferred to employ a functional group which carries a single reactive hydrogen atom, like hydroxyl, carboxyl, mercaptan and secondary amine. These are desirably reacted with an acrylate or methacrylate carrying a single isocyanate group.

What is surprising is that the radiation-cured coatings of this invention in which the number of reactive side chains, the requirement that these be effec-
tively monoreactive, and the spacing of the groups provided by the molecular weight per reactive group, are both soft and physically tough. These characteristics are not generally useful in coatings, but they provide useful prime coatings for the optical glass filament.

These prime coatings possess a low modulus of elasticity which stays low at low temperatures. A room temperature modulus of 300 psi is typical in the present invention.
At -60°C, the modulus in a typical example increases to only about 1000. This is a very small increase in modulus for such a large reduction in temperature. This invention contemplates cured coatings which have a modulus of elasticity at room temperature and at -60°C. which are below 3000, preferably below 2000. The preferred modulus at -60°C. is between 400 - 1500.

One would think that the high cross-link density provided by radiation cure would produce a relatively high modulus which would be inconsistent with the needs of coated optical glass filament. To discover that the opposite is the fact when the polyacrylate or polymethacrylate is selected in accordance with this invention is something that would not have been foreseen.

One purpose of coating optical glass filament is to protect the surface of the filament before it might be abraded, and it is therefore preferred to apply the coating to the glass filament as it is initially formed. This is itself conventional.

As a matter of interest, the optical glass has the form of a continuous filament, but it is commonly referred to as a fiber, so these words are used interchangeably herein.

It is also preferred to overcoat the prime-coated filament of this invention to provide additional abrasion and/or hydrolysis protection, but this is also conventional, and the overcoats which may be used form no part of this invention.

It is desired to point out that the radiation used to provide the cure may be of diverse type, such as beta rays, electron beam and actinic radiation, but ultraviolet light is preferred because it is very rapid and does not significantly damage the optical glass filament. When ultraviolet light is to be used, the initiators and/or photosensitizers normally used for this purpose
will be employed herein, such as about 3% by weight of
diethoxy acetophenone. Since ultraviolet light is pre-
ferred, acrylic unsaturation is best, but since the
radiation character can vary, so can the specific charac-
ter of the unsaturation. Other useful ethylenic unsatura-
tions are illustrated by itaconic, crotonic, allylic,
vinylic, etc. These are in addition to the methacralic
unsaturation, provided by reaction with methacrylic acid
or 2-hydroxyethyl methacrylate, which has been noted
previously. Itaconic or crotonic unsaturation may be
introduced by using the corresponding acids in place of
acrylic acid. Allylic unsaturation may be introduced
using allyl alcohol in place of 2-hydroxyethyl acrylate.
Vinylic unsaturation may be introduced using hydroxy
butyl vinyl ether in place of 2-hydroxyethyl acrylate.

While it is preferred that the coating composition
consist of the radiation-curable polysiloxane deriva-
tives described herein, small amounts, up to about 15% of
the total weight of the composition, but desirably no
more than about 5% of the composition, may be constituted
by other materials, such as dissolved resins, like
melamine-formaldehyde condensates or unsaturated poly-
esters made from ethylene glycol, adipic acid and crotonic
acid, radiation-curable monomers like 2-hydroxyethyl
acrylate, or solvents like acetone. Since ultraviolet
cure is preferred, liquid mono- or poly-acrylates may be
added to adjust viscosity or for ancillary purpose. These
are illustrated by phenoxy ethyl acrylate, 2-ethylhexyl
acrylate, butyl acrylate, dodecyl acrylate, and the like.

Other monoethylenic monomers, like vinyl pyrrolidone,
diacetone acrylamide, isobutoxymethyl acrylamide, acryla-
mide, acrylic acid and dimethylaminoethyl acrylate may
be used.
The invention will be illustrated by the following example of preferred operation in which all proportions are by weight unless otherwise noted.

Example 1

Into a reaction vessel fitted with a stirrer and gas inlet tube is placed one mole (222 gms) of isophorone diisocyanate. 0.2% by weight of dibutyl tin dilaurate and 0.05% by weight of phenothiazine, based on the total weight of reactants, are added to the reaction vessel. The mixture is then blanketed with dry nitrogen gas and one mole (116 gms) of hydroxy ethyl acrylate are added over a period of from 4 to 5 hours while maintaining the temperature in the range of 25°C. to 30°C., cooling being used when needed. The stated temperature is maintained for one hour after acrylate addition is complete.

An addition reaction takes place with one of the two isocyanate groups in the isophorone diisocyanate to produce a urethane monoisocyanate containing acrylate unsaturation.

Example 2

One mole of tri(2-hydroxy polyoxypropyl) polysiloxane of average molecular weight 6000 and equivalent weight 2000 and which is 80% methyl substituted and 20% polyoxypropyl substituted (see note 1) is placed in a reaction vessel and heated to 60°C. Three moles of the Example 1 adduct are then added slowly while maintaining the temperature at 60°C. The reaction is continued until there remains no evidence of free NCO groups by infrared analysis. The product has a viscosity in the range of 10,000 to 15,000 centipoise.

The product of Example 2 is converted into an ultraviolet curable composition by the addition of 3% by weight of the photoinitiator diethoxy acetonaphone (no photosensitizer is needed). The product is then filtered through a 1 micron filter to remove particles.
and is then stored, ready for use.

In use, the liquid coating composition is coated upon freshly formed glass filament of optical quality and the freshly coated filament is irradiated with ultraviolet light to cure the coating. This coating is normally overcoated, which forms no part of this invention. The prime coating, however, has a very low modulus of 300 psi and, at -60°C., the modulus only increased to 1100 psi.

Note 1 - The Dow Corning product 1248 may be used.

Example 3

Into a 1 liter round bottom glass flask fitted with stirrer, reflux condenser, Dean Stark water removal trap and a gas inlet tube are placed 500 grams (0.083 15 mol) of the polysiloxane used in Example 2, 18.2 grams (0.253 mole) of acrylic acid, 0.82 gram of beta-nitrostyrene, 0.2 gram of phenothiazine, 175 grams of heptane and 7.22 gram of 40% sulfuric acid. The flask is heated with stirring to reflux and nitrogen gas is supplied to blanket the contents of the flask. Heating with stirring is continued for about 6 hours and 19 minutes to collect 9 ml. of water in the trap. Then 0.14 gram of p-methoxyphenol are added and a vacuum of about 29 inches of mercury is applied at 45°C.-55°C. for 50 minutes to remove the heptane. The nonvolatile content obtained is 93.5%, the acid value is 4.1, and the viscosity is 486 cps at 25°C. This product is made into an ultraviolet-curable coating composition by adding 3% by weight of the photoinitiator diethoxyacetophenone. The product is then filtered through a 1 micron filter to remove any particles which may be present.

Example 4

One mole (2400 grams) of tri(polyoxyethylene) polysiloxane having an equivalent weight of 800 (Dow Corning 193 fluid may be used) is placed into a reaction vessel. Three moles (1014 grams) of the isocyanate
-10-
adduct of Example 1 are added slowly while bringing the
temperature to about 60°C. Heating or cooling are
employed as necessary to maintain this temperature. The
reaction is continued until there remains no free
isocyanate groups by infrared analysis. 3% by weight of
diethoxyacetophenone are added and the product is filter-
ed to provide an ultraviolet curable coating for
optical fiber.
Example 5
10 Charge to a flask equipped with a stirrer, reflux
condenser and a dropping funnel 3 moles (666 grams) of
isophorone diisocyanate and 3 grams of dibutyl tin
dilaurate. With stirring add 2 moles (4800 grams)
of Dow Corning Q4-3667 (a polyoxyethylene terminated
dimethyl siloxane polymer) over a period of about 2
hours while maintaining the temperature at about 65°C.
After this addition is complete, maintain the tempera-
ture at about 65°C. for 1 hour. Then add 2 moles
(232 grams) of 2-hydroxyethyl acrylate and 1.7 grams of
phenothiazine and stir at 65°C. for one hour. The
resultant product may be used at this concentration or
it may be reduced with a liquid unsaturated diluent,
such as 2-hydroxyethyl acrylate, typically in an amount
of 5% by weight. For an ultraviolet curable coating
composition add between 1% and 10% of an appropriate
photoinitiator, like diethoxyacetophenone at 3% by
weight concentration.
Example 6
Charge to a suitably equipped reaction vessel
30 two moles of isophorone diisocyanate and 10 grams of
dibutyl tin dilaurate. Add to this mixture, slowly,
one mole of a carboxypropyldimethyl terminated poly-
dimethyl siloxane having a molecular weight of 5000
while maintaining the reaction temperature at about
35 60°C. The reaction is continued at about 60°C. until
the acid number is essentially zero. At this point, add 2 moles of 2-hydroxyethyl acrylate at such a rate that any exotherm does not bring the temperature above 65°C. Continue the reaction at 60°C - 65°C until no free NCO groups are evident using an IR spectroscopic analysis. The addition of 3% by weight of diethoxyacetophenone provides an ultraviolet curable coating composition.

Example 7
Charge to a suitably equipped reaction vessel one mole of a glycidoxypropylidimethyl terminated polydimethyl siloxane having an average molecular weight of 5000, 5 grams benzyl dimethyl amine and 5 grams phenothiazine. Add to this mixture, while raising the temperature to 90°C - 100°C., 2 moles of acrylic acid over a period of about 2 hours. Continue the reaction at 90°C - 100°C. until the acid number has dropped to about 1. Then cool and discharge. The addition of 3% by weight of diethoxyacetophenone provides an ultraviolet curable coating composition.

Example 8
Two moles of toluene diisocyanate are placed into a suitable reaction vessel. To this is added 5.7 grams of dibutyltindilaurate. The mixture is heated to 90°C. while one mole of a mercaptopropylidimethyl terminated polydimethylsiloxane having an average molecular weight of 2500 is added slowly. The reaction is continued at about 90°C. until there is no evidence of free SH groups by infrared spectrophotographic analysis. The reaction mixture is then cooled to 60°C and two moles of hydroxyethyl acrylate and 3 grams of phenothiazine are added. The reaction is continued at 60°C - 65°C. until no free isocyanate groups remain as determined by infrared spectrophotographic analysis. This product is a radiation-curable coating composition and can be made sensitive to ultraviolet light by the addition of 3% by weight of diethoxyacetophenone.
Example 9

One mole of polydimethylsiloxane, amino propyl-dimethyl terminated, of 4000 molecular weight is placed into a reaction vessel. Two moles of the isocyanate adduct of Example 1 is added rapidly, cooling if necessary to keep the temperature below 65°C. The reaction is continued at 60°C - 65°C until there is no evidence of free NCO group as determined by infrared spectro-photographic analysis. The addition of 3% by weight of diethoxyacetophenone provides an ultraviolet curable coating composition.
WHAT IS CLAIMED IS:

1. An optical glass fiber prime coated with a radiation-cured coating composition, said coating composition being a liquid, polyethylenically unsaturated, radiation-curable coating composition consisting essentially of an organic polysiloxane having from 2 to 6 reactive side chains each of which carry a functional group providing one reactive site which has been reacted to provide a single radiation-curable, monoethylenically unsaturated side chain, there being about one such side chain for every 500 to 5,000 units of molecular weight.

2. A coated optical glass fiber as recited in claim 1 in which said organic polysiloxane is hydrocarbon substituted except for said functional groups.

3. A coated optical glass fiber as recited in claim 1 in which said monoethylenically unsaturated side chain provides acrylate or methacrylate functionality.

4. A coated optical glass fiber as recited in claim 1 in which said polysiloxane carries a reactive group selected from the group consisting of hydroxyl, amine, mercaptan, carboxyl and glycidyl functional groups.

5. A coated optical glass fiber as recited in claim 1 in which said reactive group is hydroxyl.

6. A coated optical glass fiber as recited in claim 5 in which said hydroxyl group is reacted with an acrylate or methacrylate carrying a single isocyanate group.

7. A coated optical glass fiber as recited in claim 6 in which said hydroxyl group is reacted with the reaction product of one mol of 2,4-toluene diisocyanate or isophorone diisocyanate with one mol of 2-hydroxy ethyl acrylate.
8. A coated optical glass fiber as recited in claim 1 in which said reactive group is selected to include a single reactive hydrogen atom.

9. A coated optical glass fiber as recited in claim 8 in which said reactive hydrogen atom is reacted with an acrylate or methacrylate carrying a single isocyanate group.

10. A coated optical glass fiber as recited in claim 4 in which said functional group carrying one reactive site is a saturated aliphatic radical containing, except for the reactive functional group, only carbon and hydrogen, or carbon, hydrogen and oxygen.

11. A coated optical glass fiber as recited in claim 2 in which the hydrocarbon substituent is selected from the group consisting of methyl, phenyl, and mixtures thereof.

12. A coated optical glass fiber as recited in claim 11 in which said functional group is connected to said polysiloxane by a carbon to silicon bond.

13. A coated optical glass fiber as recited in claim 1 in which said liquid coating composition contains initiators and/or photosensitizers rendering the composition curable by ultraviolet radiation, and the coating composition is cured with ultraviolet light.

14. A coated optical glass fiber as recited in claim 1 overcoated with a topcoat to protect the prime coat from abrasion and hydrolysis.

15. A method of producing an optical glass fiber prime coated with a coating having a modulus of elasticity at room temperature and at -60°C. below 3000 comprising, applying to the freshly formed glass filament the radiation-curable coating composition of claim 13 and exposing the coating to ultraviolet light to cure the same.
**INTERNATIONAL SEARCH REPORT**

**I. CLASSIFICATION OF SUBJECT MATTER**

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

<table>
<thead>
<tr>
<th>Class.</th>
<th>Classification System</th>
<th>Classification Symbols</th>
</tr>
</thead>
<tbody>
<tr>
<td>INT. CL.3</td>
<td>6028 5/14</td>
<td>C08F 2/50 C08F 30/08</td>
</tr>
<tr>
<td>U.S. CL.</td>
<td>204/159.13</td>
<td>526/279</td>
</tr>
</tbody>
</table>

**II. FIELDS SEARCHED**

Minimum Documentation Searched

<table>
<thead>
<tr>
<th>Classification System</th>
<th>Classification Symbols</th>
</tr>
</thead>
<tbody>
<tr>
<td>U.S.</td>
<td>204/159.13</td>
</tr>
</tbody>
</table>

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched

**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, 2,956,044, Published 11 October 1960 Merker</td>
<td>1-13</td>
</tr>
<tr>
<td>Y</td>
<td>US, A, 3,650,811, Published 21 March 1972 Nordstrom et al</td>
<td>1-13</td>
</tr>
<tr>
<td>Y</td>
<td>US, A, 4,201,808, Published 6 May 1980 Cully et al</td>
<td>1-13</td>
</tr>
<tr>
<td>Y</td>
<td>US, A, 4,290,869, Published 22 September 1981 Pigeon</td>
<td>1-13</td>
</tr>
<tr>
<td>Y</td>
<td>US, A, 4,293,678, Published 6 October 1981 Carter et al</td>
<td>1-13</td>
</tr>
<tr>
<td>Y</td>
<td>US, A, 4,348,454, Published 7 September 1982 Eckberg</td>
<td>1-13</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) and 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

• 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

• document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

• 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

**IV. CERTIFICATION**

Date of the Actual Completion of the International Search 14 September 1983

International Searching Authority ISA/US

Date of Mailing of this International Search Report 20 SEP 1983

Signature of Authorized Officer A. Koeckert

Form PCT/ISA/210 (second sheet) (October 1981)
FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y  US, A, 4,359,369, PUBLISHED 16 NOVEMBER 1982  1-13
   TAKAMIZAWA ET AL
P,Y  US, A, 4,367,918, PUBLISHED 11 JANUARY 1983  1-15
    PINNOW
    CARTER
Y  GB, A, 1,323,869, PUBLISHED 18 JULY 1973  1-13
Y  JP, B, 55-4770, PUBLISHED 31 JANUARY 1980  1-13

V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSearchABLE

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:
1. Claim numbers .......... because they relate to subject matter not required to be searched by this Authority, namely:

2. Claim numbers .......... because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this international application as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest
- The additional search fees were accompanied by applicant’s protest.
- No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (supplemental sheet (2)) (October 1981)