(54) Title: MOISTURE CURING HOT MELT ADHESIVES

(57) Abstract

A composition which comprises at least one isocyanate terminated polyester obtainable by enzyme catalysed polyesterification of one or more monomers selected from dicarboxylic acids, diols or polyols and/or hydroxyacids in the presence or absence of an inert organic solvent and a diisocyanate.
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Moisture Curing Hot Melt Adhesives

The present invention relates to compositions suitable for use as moisture curing hot melt adhesives.

The technology of hot melt adhesives and moisture curing hot melt adhesives is well known. Conventional hot melt adhesives are thermoplastic materials. They are applied molten at high temperatures and the adhesion comes entirely from the cooling of the material back to the solid state. Hot melt adhesives set immediately upon cooling from the liquid to the solid state, but may develop improved properties over minutes or days with crystallization. The two main drawbacks of this type of adhesive are the very high application temperatures, limiting the type of substrate, and the poor heat resistance of the final adhesive bond as reheating will again soften the material.

Moisture curing polyurethane hot melt adhesives have been developed to improve performance in these areas. These materials are polyester based and have terminal isocyanate groups which, after application, utilize the moisture in the air to cure (set) to produce a more heat resistant bond.

The molecular weight, and hence viscosity, of the polyurethanes used in moisture curing hot melt adhesives is significantly lower than that of the conventional thermoplastics used in conventional hot melt adhesives. This allows application of moisture curing hot melt
adhesives at much lower temperatures, for example 120°C, compared to 160°C for conventional hot melt adhesives, which causes much less damage to substrates. However, the lower molecular weight of the polyurethanes used in the moisture curing hot melt adhesives gives rise to other problems. Prior to any moisture curing taking place, moisture curing polyurethanes form an initial bond much more slowly than conventional hot melt adhesives, therefore the "green strength" (bond strength immediately after application) is lower.

The present invention seeks to overcome the problems of traditional moisture curing hot melt adhesives. The inventors have developed moisture curing hot melt adhesives with more rapid solidification and therefore greater "green strength" than other moisture curing hot melt adhesives on the market.

The present invention provides a composition, suitable for use as a moisture curing hot melt adhesive. The compositions of the present invention comprise at least one isocyanate terminated polyester obtainable by enzyme catalysed polyesterification of one or more monomers selected from dicarboxylic acids, diols or polyols and/or hydroxyacids in the presence or absence of an inert organic solvent and reacting the product with a diisocyanate and optionally at least one conventionally produced isocyanate terminated polyester. Preferably the diisocyanate is MDI (4,4′-diphenylmethane diisocyanate).
It is possible for isocyanate terminated polyester(s) used in the composition of the invention to be 100% polyester(s) obtained by enzyme catalysed polyesterification. However, it has been found that when up to 60% by weight of the polyester(s) are conventional polyester(s) the performance and physical properties of the composition are improved. Preferably at least 40% by weight, more preferably at least 50% by weight, more preferably at least 60% by weight, even more preferably at least 70% by weight, still more preferably at least 80% by weight and most preferably at least 90% by weight of the polyester(s) used are produced by enzyme catalysed polyesterification.

The composition may also contain additives conventionally present in moisture curing hot melt adhesives, for example antioxidants, oxazolidine, crosslinking agents and catalysts, in an amount of up to 5 parts per hundred (pph) of the overall composition per additive component.

The polyesters used in the composition of the invention may be produced by processes, such as those described in GB-A-2272904 and PCT/GB93/02461, involving an enzymatic polyesterification, either in the presence or absence of an organic solvent, which affords polyesters having high weight average molecular weight and low dispersity whilst also being extremely pure in terms of freedom from unwanted by-products. Polyesters produced by
this process comprise as repeating units

(i) residues of at least one aliphatic
hydroxycarboxylic acid, or derivative thereof; or

(ii) residues of (a) at least one aliphatic
dicarboxylic acid or derivative thereof, (b) at least one
aliphatic diol or polyol, and optionally (c) at least one
aliphatic hydroxycarboxylic acid, or derivative thereof.

The process comprises reacting the components defined
in (i) or the components defined in (ii) in the presence or
absence of a solvent and in the presence of a lipase such
that the molar ratio of acid groups to hydroxyl groups in
the reactants is 1:1 to 1:1:1.

As used herein the term "polyester" is intended to
encompass materials obtainable by this process from any
suitable combination of the monomers defined herein.

Aliphatic hydroxycarboxylic acids suitable for use in
this process include those of formula:

\[ \text{HOCH}_2 \cdot \text{R}^1 \cdot \text{CO}_2\text{H} \]

wherein \( \text{R}^1 \) is a bond or a divalent radical of a substituted
or unsubstituted \( \text{C}_1 \) to \( \text{C}_{12} \) alkyl group optionally having
one or more carbon - carbon double bonds and optionally
having one or more carbon - carbon triple bonds.

Suitable aliphatic dicarboxylic acids include those of
formula:

\[ \text{HO}_2\text{C} \cdot \text{R}^2 \cdot \text{CO}_2\text{H} \]
wherein \( R^2 \) is a bond or a divalent radical defined as for \( R^1 \).

Suitable aliphatic diols include those of formula:

\[
\text{HOCH}_2 - R^3 - \text{CH}_2\text{OH}
\]

wherein \( R^3 \) may be a bond or a divalent radical defined as for \( R^1 \).

Suitable aliphatic polyols include those of formula:

\[
\text{HOCH}_2 - R^4 - \text{CH}_2\text{OH}
\]

wherein \( R^4 \) is a divalent radical defined as for \( R^1 \) and bearing at least one hydroxyl substituent.

Each of the \( C_1 \) to \( C_{12} \) alkyl groups mentioned above may be substituted or unsubstituted and may be cyclic, branched or straight chain, optionally having at least one carbon-carbon double bond, either in the cis- or trans-conformation and optionally having at least one carbon-carbon triple bond. When the \( C_1 \) to \( C_{12} \) alkyl group has more than one double or triple carbon-carbon bond, these bonds may be conjugated or non-conjugated. The \( C_1 \) to \( C_{12} \) alkyl group is optionally substituted with one or more substituents (which, when there are two or more substituents, may be the same or different) each selected from halogen atoms, for example, fluorine, chlorine or bromine, hydroxyl, \(-\text{OR}^5\) where \( R^5 \) is hydrogen or a \( C_1 \) to \( C_{12} \)
alkyl, carboxyl, and \(-\text{CO}_2\text{R}^6\) where \(\text{R}^6\) is hydrogen or a \(\text{C}_1\) to \(\text{C}_{12}\) alkyl.

Preferably the diol has from 2 to 14 carbon atoms and is an \(\alpha,\omega\)-diol, for example 1,4-butandiol, diethylene glycol, ethylene glycol, propylene glycol, pentanediol, hexane-1,6-diol or dodecan-1,12-diol, most preferably 1,4-butanediol.

Diethylene glycol has a lower activity than other suitable diols so that, when diethylene glycol is used as a monomer, it is necessary to carry out the reaction either at higher temperature, in which case the dispersity is relatively wide, or at low temperature for a long period.

Preferably the diacid has from 2 to 14 carbon atoms, for example, oxalic acid, succinic acid, fumaric acid, citric acid, malic acid, malonic acid, maleic acid or adipic acid. Most preferably the diacid is adipic acid.

The hydroxy acids must have a non-sterically hindered primary or secondary hydroxyl. Tertiary hydroxyl and sterically hindered primary and secondary hydroxyls are unlikely to react under the conditions of the enzyme catalysed process. Preferred hydroxy acids are hydroxy-straight chain aliphatic carboxylic acids.

At high dilution certain hydroxy carboxylic acids tend to form lactones and it is therefore preferred that, when such hydroxy acids are used in the enzyme catalysed process, they are used only in high concentration in order to avoid the unwanted lactonisation reaction.
Preferably the hydroxycarboxylic acid has from 2 to 14 carbon atoms, for example glycolic acid, lactic acid, 2-hydroxybutyric acid, 2-hydroxy isobutyric acid, 2-hydroxy caproic acid, 2-hydroxy isocaproic acid, citric acid or malic acid.

As used herein the term "carboxylic acid derivative" refers to esters and acid anhydrides. An ester of a diacid may be a monoester or a diester, for example a mono or dialkyl ester. Preferably the alkyl groups are each of 1 to 4 carbon atoms, and more preferably the derivative is a methyl or ethyl ester or diester, most preferably methyl adipate or dimethyl adipate.

The polyols used herein have at least three hydroxyl groups of which at least two must be non-sterically hindered primary or secondary hydroxyl groups. Preferably the polyol has 3, 4 or 5 hydroxy groups. Tertiary hydroxyl and sterically hindered primary and secondary hydroxyls are unlikely to react under the conditions of the enzyme catalysed process but will nevertheless provide branch points when subsequently reacted with isocyanates. Suitable polyols include trimethylolpropane, pentaerythritol and triols, especially glycerol. Use of glycerol generally results in a linear polymer as the enzyme preferentially esterifies the primary hydroxyls, the secondary hydroxyl being sterically hindered, but branched products may be obtained using certain enzymes.

Owing to the low temperatures used in this
process compared with those of conventional chemically
catalysed polyesterifications, it is possible to use
diacids and hydroxyacids, such as oxalic acid, lactic acid
and glycolic acid, which decarboxylate at elevated
temperatures and it is thereby possible to produce
polyesters not generally accessible by other methods.

In one embodiment the polyesters produced by this
process may consist of repeating units of one or more
hydroxyacids.

In alternative embodiments the polyesters produced by
this process may comprise or consist of repeating units of
a diacid and a diol; a diacid and a polyol; a diacid, a
diol and a polyol; a diacid, a diol and a hydroxy acid; a
diacid, a polyol and a hydroxy acid; a diacid, a diol, a
polyol and a hydroxy acid, or any other suitable
combination of monomers, for example combinations in which
the diacid is replaced by its methyl ester or ethyl ester
derivative. Preferred combinations of monomers are
dimethyladipate/1,4-butanediol, adipic acid/glycerol,
adipic acid/1,4-butanediol, adipic acid/diethylene glycol,
adipic acid/diethylene glycol/glycerol, adipic
acid/diethylene glycol/trimethylolpropane, diethylene
glycol/adipic acid/dimethylolpropane, adipic acid/1,6-
hexanediol.

The reactive carboxylic acid groups and reactive
hydroxy groups of the reactants are generally present in
substantially equal numbers. The reaction may be carried
out with a stoichiometric imbalance, but this generally results in a product having a lower weight average molecular weight than if the reactants are used in equimolar amounts. However the proportions may be adjusted slightly such that a polyester having a predominance of terminal hydroxy units is obtained. In general the molar ratio of acid groups to hydroxyl groups should be from 1:1 to 1:1.1.

In the case where the resulting polymer is to have a predominance of terminal hydroxy groups the length of the polymer may be varied by varying the excess of hydroxyl present in the initial reaction mixture. For example, increasing the amount of hydroxyl groups relative to the number of acid groups in the reaction mixture will give rise to polymers of shorter chain length.

For further details of the enzymes and substrates which may be used see GB-A-2272904 and PCT/GB94/02461. When the polyesterification is carried out in the absence of a solvent the preferred enzyme is the lipase derived from *Candida antarctica*. When the polyesterification is carried out in a solvent the preferred enzyme is the lipase derived from *Mucor miehei*.

The activity of the enzyme may be affected by materials present in the reaction mixture, for example the lipase from *C.antarctica* is inhibited by glycerol. It is preferable not to include branched polyfunctional monomers, particularly secondary alcohols, in the initial reaction
mixture, but to delay their addition until after the
reaction is started to avoid reducing enzyme activity.
Preferably branched polyfunctional monomers are not added
to the reaction mixture until after the enzyme has been
removed, for example after completion of the initial
oligomerisation step. If a branched polyfunctional monomer
is added to the reaction mixture at least 12 hours, for
example at least 14 hours, 16 hours or 24 hours after the
start of the reaction, when the enzyme is still present in
the reaction mixture the enzyme activity will be reduced,
but not completely, and the reaction will continue at a
slower rate than if the branched polyfunctional monomer had
not been added.

The polyesters produced by this process generally have
a minimum weight average molecular weight of 200 Da,
preferably 600 Da, more preferably 1000 Da and most
preferably 4 kDa. The weight average molecular weight of
the polyester is measured using gel permeation
chromatography.

The polyesters produced by this process generally
comprise from 6 to 50 monomer units, preferably from 10 to
40 monomer units and most preferably from 30 to 40 monomer
units. Generally it has an acid number of from 0 to 50,
preferably from 0 to 25 and more preferably from 0.5 to 10.
Most preferably the polyester has an acid number of about
1.

The polyesters produced by this process generally have
a dispersity of 2 or less, preferably 1.5 or less, more preferably 1.3 or less. The dispersity is calculated as follows:

\[
\text{Disperisty, } d = \frac{\text{Weight Average Molecular Weight}}{\text{Number Average Molecular Weight}}
\]

and the number and weight average molecular weights may be obtained by conventional methods.

Whilst the enzymatic processes described above are preferred for production of the polyesters, any other process which produces polyesters having properties obtainable by the enzymatic process, may also be used.

The polyesters used in the present invention may be linear or branched. Branched polymers and linear polymers having pendant hydroxyl groups (which can act as branch points and lead to crosslinking on subsequent processing) are generally formed by introducing a small percentage of a branched polyfunctional monomer such as trimethylolpropane (TMP), dimethylol-propanoic acid (DMPA), pentaerythritol (PE) or glycerol. Incorporation of such monomers gives rise to both linear and branched polyesters.

For use in the present invention the polyesters, especially those having hydroxy terminal groups, are further reacted with at least one isocyanate to produce polyurethanes. Generally the enzyme is removed from the polyester before the reaction with isocyanate. This prevents the enzyme and its support from interfering with
the polyester/isocyanate reaction. Generally water 
produced during the polyesterification is removed before 
reaction with isocyanate.

Suitable isocyanates have the general formula:

\[ R' (NCO)_m \]

wherein \( R' \) is an \( m \) valent aliphatic, cycloaliphatic, 
heterocyclic or aromatic residue and \( m \) is 1 or 2. \( R' \) is 
preferably a divalent radical of formula:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{or} \\
\text{CH}_3 & \quad \text{or}
\end{align*}
\]

The isocyanate compound may be, for example, ethylene 
diisocyanate, propylene diisocyanate, tetramethylene 
diisocyanate, hexamethylene diisocyanate, decamethylene 
diisocyanate, dodecamethylene diisocyanate, 2,4,4-
trimethylhexamethylene-1,6-diisocyanate, phenylene 
diisocyanate, tolylene or naphthylene diisocyanate, 4,4'-
methylene-bis(phenylisocyanate), 4,4'-ethylene-bis(phenyl-
isocyanate), \( \omega,\omega' \)-diisocyanato-1,3-dimethylbenzene,
\( \omega,\omega' \)-diisocyanato-1,4-dimethylcyclohexane,
\( \omega,\omega' \)-diisocyanato-1,4-dimethylbenzene, \( \omega,\omega' \)-diisocyanato-
1,3-dimethylcyclohexane, 1-methyl-2,4-diisocyanato
cyclohexane, 4,4'-methylene-bis(cyclohexylisocyanate), 3-isocyanato-methyl-3,5,5-trimethylcyclohexyl isocyanate, dimer acid-diisocyanate, \( \omega,\omega' \)-diisocyanato-diethyl benzene, \( \omega,\omega' \)-diisocyanatodimethyl toluene, \( \omega,\omega' \)-diisocyanato-diethyl toluene, fumaric acid-bis (2-isocyanatoethyl) ester or 1,4-bis-(2-isocyanato-prop-2-yl) benzene, 1,3-bis-(2-isocyanatoprop-2-yl)benzene.

It is essential that the polyesters used for the moisture curing hot melt adhesive compositions of the present invention have a hydroxyl value range of 5 to 110 mg. KOH/g, preferably 10 to 56 mg. KOH/g.

The polyurethanes used in the current invention generally have a NCO/OH ratio of 1.2 to 12, preferably 1.5 to 5.0.

The polyesters used in these polyurethanes have sharp melting points (unlike previously produced materials with wide dispersity) and impart to the polyurethanes excellent physical properties such as desirable combinations of hardness and flexural and tensile strength.

Compositions comprising one of the above polyurethanes have a viscosity of from 1 to 30, preferably 2 to 15, for instance 2 to 4 Pa.s at 120°C. Compositions with viscosities in this range, when used as moisture curing hot melt adhesive, have an application temperature of 80 to 200°C more preferably 100 to 150°C.

Polyesters produced by the enzyme technology of GB-A-2272904 and PCT/GB93/02461 exhibit a higher degree of
crystallinity than conventionally produced polyesters. A higher degree of crystallinity leads to a better green strength in the adhesive. The setting time for the compositions of this invention depend on the substrate and the ambient conditions.

The Examples below are included to illustrate the invention and is in no way intended to limit the scope of the invention.

Example 1 - Product A

Premelted pure 4,4’-diphenyl methane diisocyanate (100g) was quickly added to a premelted mixture of polyesters (conventional polyester: based on hexane adipate and having a hydroxyl value (OHv) of 28 (160g); enzymatic polyester: based on hexane adipate and having a hydroxyl value (OHv) of 17 (740g)) in a vessel equipped with nitrogen. The mixture was warmed to 75 – 80 °C and the reaction was carried out for approximately 2 hours until an isocyanate value of 2.0% was achieved.

The resulting product, product A, comprised:

- 4,4’-diphenyl methane diisocyanate 10 wt%;
- conventional polyester (based on hexane adipate having an OHv of 28) 16 wt%;
- enzymatic polyester (based on hexane adipate having an OHv of 17) 74 wt%.
Comparative Example 1 - Product B

Premelted pure 4,4′diphenyl methane diisocyanate (130g) was quickly added to the premelted polyester (conventional polyester: based on hexane adipate and having a hydroxyl value of 28 (870g)) in a vessel equipped with nitrogen. The mixture was warmed to 75 - 80 °C and the reaction was carried out for approximately 2 hours until an isocyanate value of 2.0% was reached.

The resulting product, product B, comprised:
- 4,4′-diphenyl methane diisocyanate 13 wt%;
- conventional polyester (based on hexane adipate and having an OHv of 28) 87 wt% .

The products of Example 1 and Comparative Example 1 were tested by conventional techniques, the results of which are set out below.

Shear Strength

The shear strength may be measured in accordance with British Standard BS 5350 Part C5 (1990)

Solidification Time

Samples of Product A and Product B were placed in an oven (at 100°C) until they were molten. Glass slides and a coating block were also warmed (to 100°C). Films (200μm) were then cast onto the warmed glass slides. The time for the sample to solidify was measured.
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<tr>
<td>Product B</td>
<td>conventional</td>
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<tr>
<td>Product A</td>
<td>blend of enzymatic and conventional</td>
<td>3 min 52 sec</td>
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**Crystallinity of Products**

The crystallinity of product A and product B was measured by Differential Scanning Calorimetry (DSC) and Wide Angle x-ray Diffraction (WAXD). The results of both these studies showed that product A has a higher degree of crystallinity that product B.

**Example 2 - Product C**

Pre melt and charge polyester (1144g enzymatic polyester having a hydroxyl value (OHv)=34.4 based on hexane adipate-AJH 1/151-0). Heat to 60-100°C and apply vacuum to reduce water content to <0.05% if necessary, then allow to cool to <40°C. Add premelted 4,4’ diphenyl methane diisocyanate (158 g) and warm to 75-80°C and hold for approximately 2 hours until an isocyanate value of 1.7% is reached.

**Comparative Example 2 - Product D**

Pre melt and charge polyester (1317g conventional
polyester having a hydroxyl value (OHv) = 30.5 based on hexane adipate). Heat to 60-100°C and apply vacuum to reduce water content to <0.05% if necessary, then allow to cool to <40°C. Add premelted 4,4’ diphenyl methane diisocyanate (161g) and warm to 75-80°C and hold for approximately 2 hours until an isocyanate value of 1.7% is reached.

The products of Example 2 and Comparative Example 2 were tested by conventional techniques as described below.

**Material Characteristics**

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<td>13,700 cps</td>
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<td>%NCO</td>
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<tr>
<td>OH value of Polyester</td>
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<td>Reaction index</td>
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**Lap Shear Tests**

**5 Minute Test**

Samples were warmed to 125°C for 4 hours to ensure constant temperature throughout the sample. The coating bar was also warmed. The substrate was coated with sample to approx. 150μm (subject to expansion of the bar at
- 18 -
elevated temperature). The substrates were placed together immediately and a weight of 1kg was applied to the sample and left at room temperature for 4 minutes. A further minute was allowed for placing the sample in the tensometer jaws.

Substrate: Beech wood to BS5350 part C5
moisture content - 9.83% (spec - 12±2.5%)
Conditioned for 24 Hours at 50% relative humidity, 22±2°C.

Open time 2-3 seconds. Testing was carried out to BS5350 part C5 1990, results are given below quoted in Newtons.

In general the mode of failure in the 5 minute test was cohesive.

24 Hour Test
Lay up as above but samples were left for at least 24 hours in humidity cabinet 23±2°C 50% RH.

In general the mode of failure in the 24 hour test was cohesive with some of the higher shear strengths showing wood failure.
## Results

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1) A composition which comprises at least one isocyanate terminated polyester obtainable by enzyme catalysed polyesterification of one or more monomers selected from dicarboxylic acids, diols or polyols and/or hydroxyacids in the presence or absence of an inert organic solvent and a diisocyanate.

2) A composition according to claim 1 which comprises at least 40% by weight of at least one isocyanate terminated polyester obtainable by enzyme catalysed polyesterification.

3) A composition according to claim 1 or 2 which comprises at least 50% by weight of at least one isocyanate terminated polyester obtainable by enzyme catalysed polyesterification.

4) A composition according to any one of the preceding claims wherein the diisocyanate is 4,4′-diphenylmethane diisocyanate (MDI).

5) A composition according to any one of the preceding claims additionally comprising one or more of
   a) an antioxidant;
   b) oxazolidine;
   c) a crosslinking agent, and
   d) a catalyst

in an amount of up to 5 parts per hundred (pph) of the overall composition per additional component.
6) A composition according to any one of the preceding claims wherein the isocyanate terminated polyester is linear 1,6-hexane adipate.

7) A composition according to any one of the preceding claims wherein the polyester(s) have terminal isocyanate groups and a NCO/OH ratio of 1.2-12.

8) A composition according to any one of the preceding claims, wherein the viscosity of the composition is from 1 to 30 Pa.s at 120°C.

9) Use of a composition according to any one of the preceding claims as a moisture curing hot melt adhesive.

10) A process for the use of a composition according to any one of claims 1 to 7, as a hot melt adhesive, which comprises applying the composition at a temperature of from 80 to 200°C.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08G18/42

According to International Patent Classification (IPC) or to both national classification and IPC:

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbol(s))

IPC 6 C08G

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):

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C.
[X] Patent family members are listed in annex.

* Special categories of cited documents:

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'E' earlier document published on or after the international filing date

'I' document which may throw doubts on priority claim(s) or which it 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 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

25 July 1997

Date of mailing of the international search report

05.08.97

Name and mailing address of the ISA

European Patent Office, P.B. 3818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl
Fax (+ 31-70) 340-3016

Authorized officer

Neugebauer, U

Form PCT/ISA/210 (second sheet) (July 1992)

page 1 of 2
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