A coating composition curable with a vapourized catalyst formed by mixing a poly-isocyanate cross linking agent with an acrylic polymer in a water free solvent, having a good evaporation rate in an acrylic urethane polymer system, said acrylic polymer having a molecular weight below 20,000, preferably less than 10,000 and a content of 15 to 50% by weight of an hydroxy unsaturated monomer and the remaining monomers being selected to provide the final polymer with a glass transition temperature in the range of -40°C to 55°C.
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Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

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ACYCLIC CROSSLINKED POLYMERS

This invention relates to surface coatings particularly to urethane crosslinked acrylic coatings.

Australian Patent 476,431 discloses the vapour catalysed curing process which enables a coating of an acrylic polymer - isocyanate mix to be cured at room temperature by the use of a vapourized catalyst.

U.K. Patent 2093049 provides a number of resin/isocyanate mixtures for use in the vapour catalysed curing process. These compositions provide conventional coating formulations particularly suited for vapour catalysis. Polyester, polyether and acrylic polyols are disclosed as being useful backbone polymers for use with the isocyanate. European Patent 0,029,598 discloses a coating composition having 50 to 95% of an acrylic polymer having a molecular weight from 500 to 10,000 and an hydroxyl content of at least 2% with 5 to 50% by weight of a polyisocyanate crosslinking agent.

It is an object of this invention to provide an improved composition for forming the cured acrylic-urethane coating so that the resulting coating exhibits improved toughness characteristics and has a quick drying time. Toughness is a combination of hardness and ductility or resilience which are desirable properties in coatings.

In particular it is an object of the invention to develop polymer formulations which exhibit the characteristic of early initial hardness so that the coatings are resistant to damage within half an hour of application.

To this end the present invention provides a coating composition curable with a vapourized catalyst and having high initial hardness characteristics formed by mixing a poly-isocyanate cross linking agent with an acrylic polymer in a water free solvent, having a good evaporation rate in an acrylic urethane polymer system, said acrylic polymer having a molecular weight below 20,000, preferably less than 10,000 and a content of 15 to
50% by weight of an hydroxy unsaturated monomer and the remaining monomers being selected to provide the final polymer with a glass transition temperature in the range of -40°C to 55°C, preferably -10°C to 30°C.

By maintaining a low molecular weight and having a relatively high number of hydroxyl groups the possibility exists for creating urethane crosslinks of length comparable to that of the acrylic backbone polymer. It is thought that it is this structure that results in a tougher coating film. Further, the predominance of these urethane linkages means that the crosslinked polymer is less soluble in the carrier solvent after curing and it is thought that this results in liberation of the solvent from the film which aids drying of the coating.

The hydroxyl containing monomer which is required to be present in the acrylic polymer comprises 15 to 50% by weight of total monomers and preferably comprises 25% to 35% by weight of total monomers. Preferably the hydroxyl containing monomer is an acrylic monomer and the most preferred monomers of this class are hydroxy ethyl acrylate (HEA), and hydroxy ethyl methacrylate (HEMA). With hydroxy ethyl acrylate the optimum initial hardness characteristics are obtained with polymers-in which HEA content is within the range of 25 to 35% moles on total moles of monomer and preferably about 30 mole %. The pot life optimum of at least 12 hours can be achieved within the range of 15 to 45% HEA content. It has been found that surprisingly HEA tends to provide better initial hardness and also equal to better final hardness than HEMA when used as the principal hydroxy monomer. Hydroxypropyl acrylate (HPA) and hydroxy propyl methacrylate (HPMA) may also be used, but as they contain a high proportion of secondary alcohols, they cure more slowly. They may be used in conjunction with HEA and HEMA to extend the pot-life.

As well as the acrylic and methacrylic hydroxy monomers other hydroxy monomers may be used, preferably in
admixture with acrylic or methacrylic hydroxy monomers. By using monomers which provide a longer hydroxyl terminated side chain preferably greater than 2 carbon atoms in length, the final cured urethane crosslinked polymer is thought to exhibit better flexibility characteristics in conjunction with hardness and is therefore less brittle. Suitably these other hydroxy monomers may be used up to 10% of the final polymer.

For example, one such monomer is an adduct of HEA and caprolactone. This monomer when used as a co-hydroxy monomer was found to be suitable.

Monomers prepared from poly-ethylene glycol ethers or secondary alcohol ethers such as poly-propylene glycol ethers, which give an hydroxyl terminated polyether side chain in the final polymer are also suitable in conjunction with shorter chain hydroxy acrylic or methacrylic esters. Particularly suitable are glycerol mono acrylate or poly-ethylene glycol mono methacrylate. These two monomers improve solvent resistance, flexibility and coating flow.

Also suitable is poly-propylene glycol mono methacrylate, which has a long poly-propylene glycol chain.

In order to ensure that the backbone polymer exhibits the basic characteristics of acrylic polymers and thus provide the desired durability, the polymer preferably contains at least 50% by weight, preferably 80% by weight, of acrylic monomers based on total monomers which will include the hydroxyl containing molecule when it is an hydroxy acrylic monomer. More preferably the acrylic content is about 80% of total monomer weight.

The selection of diluent monomers to be used in conjunction with the hydroxy containing monomer is primarily dependent on the effect of the monomers in maintaining the final polymers glass transition temperature (Tg) fall within the broad range of -40 to 55°C. The preferred Tg range for the acrylic polymers is -10°C to +30°C. Polymers with Tg values outside of this preferred
range exhibit either poor solvent resistance or poor initial hardness characteristics. For polymers in which HEA or HEMA are the principal hydroxy monomers a preferred Tg range is 0°C to 20°C.

As examples of suitable diluent monomers are:

1) Ethyl hexyl acrylate (EHA) and butyl acrylate are suitable for low Tg polymers;

2) Isobutyl methacrylate (IBMA) - provides good initial and final hardness values over the whole Tg range with solvent resistance improving at higher contents.

3) Lauryl methacrylate (LMA) is suitable in low quantities;

4) Ethyl acrylate (EA) is acceptable across the whole Tg range, and at levels 20% mole and greater, on total monomers, the solvent resistance improves at the expense of pot life.

5) Ethyl methacrylate (EMA) provides good initial cure rates but shorter pot life although solvent resistance is generally improved.

6) Acrylamide is acceptable in low concentrations however it will reduce the pot life.

7) Styrene provides optimum initial hardness values combined with cure rate and solvent resistance at Tg values of -10°C to 15°C with concentrations of 10 to 25%.

8) Methyl Methacrylate and Butyl acrylate are the preferred diluent monomers and have a preferred Tg range of 10°C to 20°C.

The acrylic backbone polymer may be formed by feeding the monomers to the refluxing solvent over a long period of time and using an excess of initiator to keep the molecular weight low. It is preferred that the average molecular weight of the acrylic backbone polymer be above 1000 and preferably below 10,000. In terms of viscosity it is preferred that the acrylic backbone polymer have a viscosity measured at 25°C and 65% non volatiles, within
the range 500 cP. to 5,000 cP.

Another means of reducing the chain length of the acrylic polymer is to use the addition of a chain transfer agent. By using an agent with a functional group active in crosslinking it is possible to obtain a crosslinked polymer of improved properties. Thus, a chain transfer agent with a hydroxyl functional group is preferred. However, a carboxylic functional group may also be used, but it will reduce the pot-life.

The initiator which is used in one embodiment is present in excess and may also contain a functional group, such as hydroxyl. Carboxylic functional groups may be used but they will reduce the pot-life. This means that there can be two sources of terminal functional groups for use in crosslinking, from the initiator or the chain transfer agent.

Peroxyde initiators have been proposed for acrylic polymers in U.S. Patent No. 4,075,242 (Rhum). However, the method of forming acrylic polymers as disclosed in that patent relied on the essential use of high boiling point alcohols as solvent. Such solvents are not suitable in the present invention because residual solvent will react with the isocyanate crosslinking reactants.

Most conventional initiators are suitable with tertiary butyl per-2-ethyl hexanoate (t-BPEH) being the most preferred. Other acceptable initiators are azo di-isobutyro nitrile (AIBN), benzoyl peroxide (BPO), tert-butyl per benzoate (t-BPB), di-t-butylperoxide and mixtures of these initiators.

One preferred method of this invention is to use an initiator containing an azo group and a chain transfer agent in combination to react the monomers slowly to form a low molecular weight polymer. In this method the reaction temperature is from 100 to 140°C and the azo initiator (preferably azo di-isobutyronitrile) is present in an amount of 3 to 4% by weight of the monomers.

An alternative method of this invention is to use
an initiator of the peroxide type (up to 8% by weight) with or without a chain transfer agent. These initiators are usually in the liquid form and are easier to dissolve in solvents or can be used without solvents. The temperatures required to activate these initiators are generally from 70°C to 140°C. In some cases higher boiling solvents may be required.

Preferred solvents are aromatic hydrocarbon solvents such as "PEGASOL" R100, ester solvents such as 'Cellosolve' acetate, hexyl acetate or butyl acetate and ketone solvents such as methylethyl ketone.

A particularly preferred solvent system utilizes an acetate either alone or in conjunction with a ketone solvent. This solvent system results in a faster cure rate because the solvent is more readily liberated from the polymer.

The ratio of initiator to chain transfer agent is preferably greater than 2.5 to 1. Generally, cure rate, hardness and pot life varies little with increasing initiator to chain transfer agent ratio's but solvent resistance does increase.

The preferred chain transfer agents are thiols such as
dodecylmercaptan (DDM), 3 mercapto-1,2 propanediol 2-mercaptopethanol, mercaptoacetic acid and isoocetyl-3-mercaptopropionate.

In selecting solvents for preparation of the acrylic polymers and also in selecting let down solvents for the coating formulations it is important to select solvents having good evaporation rates in an acrylic urethane systems. Thus, apart from the need to have good evaporation rates the solvent needs to be immiscible with the crosslinked resin coatings so that it is forced out of the coating onto its surface to aid fast evaporation. However the evaporation rate of the solvent system should not be too fast, as there should be sufficient open time
for the catalyst to enter the film.

Preferred solvents are aromatic hydrocarbon
solvents such as "PEGASOL" R100, ester solvents such as
'Cellosolve' acetate, hexyl acetate or butyl acetate and
ketone solvents such as methylethyl ketone. Other solvents
are xylene, n-amyl acetate, propoxymethylacetate, methyl
isobutyl ketone and toluene.

It is to be noted that hydroxyl solvents are not
suitable.

As solvents for the coating formulations any of
the solvents preferred for forming the acrylic resin may be
used. The preferred solvents for the coating formulations
are methyl ethyl ketone (MEK) mixed with cellosolve acetate
(CA) and Butyl acetate (BA) in equal quantities or MEK, CA
and xylene in equal quantities.

Examples of the acrylic backbone polymer of this
invention are illustrated in the following examples.

The reference to solvent resistance is a measure
of the hardness and the degree of crosslinking after 24
hours, which can be achieved when using these acrylic
polymers for urethane crosslinked coatings with the aid of
a vapour catalyst. The solvents used for the tests are
xylene and methyl ethyl ketone.

Initial hardness is a measure of the hardness of
the coating measured after completion of the vapourized
catalyst curing step. Final hardness of the coatings of
this invention is determined at 24 hours.

To form a coating composition from any of the
exemplified acrylic polymers, they are reacted with a
suitable poly isocyanate. Xylylene di-isocyanate or the
saturated form of xylylene diisocyanate may be used as the
crosslinking agent. Preferably trimethylol propane adducts
of the xylylene di-isocyanates are used.

The trimethylol propane adducts of di-isocyanates
are preferred because they are less volatile than the di-
isocyanates. Also biuret compounds prepared from
di-isocyanates may be useful. Crosslinking agents, which are prepared from aromatic isocyanates will react faster than those prepared from aliphatic isocyanates however they are subject to greater yellowing.

Some examples of other isocyanates which may be useful, or which may be used to prepare useful polyisocyanates are:

Aliphatic and alicyclic di-isocyanates such as hexamethylene-1,6-di-isocyanate, 2,4- or 2,6-di-isocyanato-1-methylcyclohexane, tetramethylene-1,4-di-isocyanate, dicyclohexylmethane-4,4'-di-isocyanate, isophorone di-isocyanate, trimethylene-1,3-di-isocyanate, pentamethylene-1,5-di-isocyanate, dodecamethylene di-isocyanate, 1,2-di-isocyanato-cyclobutane, 2,2,4-trimethyl and 2,4,4-trimethyl-1,6-di-isocyanato hexane, dicyclohexyl-4,4'-di-isocyanate, dimer acid di-isocyanates, tetramethylxyylene di-isocyanate and alkyl esters of di-isocyanato-caproic acid containing an alkyl radical with one to eight carbon atoms.

Aromatic di-isocyanates such as toluene -2,4- and -2,6-di-isocyanate, diphenylmethane-4,4'-di-isocyanate, 3-methyl diphenylmethane-4,4'-di-isocyanate, m and p-phenylene di-isocyanates, naphthalene-1,5-di-isocyanate and chlorophenylene-2,4-di-isocyanate. The polyisocyanate is usually added in approximately a 1:1 stoichiometric ratio of isocyanate group to the hydroxy group in the acrylic polymers.

Using the vapour catalysed curing process the acrylic polymer isocyanate mix is sprayed or otherwise coated onto the surfaces and then the coated surfaces are placed in a curing chamber which contains vapourized amine catalyst which speeds up the reaction between the hydroxyl groups on the acrylic polymer and the isocyanate to form urethane crosslinkages.
Example 1

To the reactor was added

Butyl acetate : 10.79
Dodecyl mercaptan : .47

This mixture is heated to reflux at 120°C and subsequently over a six-hour period there is added:

Parts by Wt.

Styrene 9.37
Butyl acrylate 4.12
Methyl methacrylate 19.12
Hydroxy ethyl acrylate 12.38

Also, concurrently with the above addition but over an eight-hour period there is added:

Parts by Wt.

Butyl acetate 10
Methyl ethyl ketone 4.81
Genitron AZDN LMC (Azo di-iso butyronitrile) 1.25

heating is then continued for a further two hours.

The non volatile content of the resultant product is 65% w/w and its viscosity was 8500 cP at 20°C measured with a Brookfield LVF,S3 at 6 RPM.

The dodecyl mercaptan is used as a chain transfer agent.
(Calculated theoretical Tg is +42.0°C).

This polymer cured slowly and consequently did not have high initial hardness but did have good solvent resistance and hardness after 24 hours.
Example 2

This example demonstrates an alternative where an excess of peroxide initiator is used.

1. Heat to 150°C

5  Cellosolve Acetate
    (Ethylene glycol mono ethylether acetate)

2. Feed the following monomers over six hours

   Kg.
   Styrene 9.37
   Butylacrylate 4.12

10  Methyl methacrylate 19.12

Hydroxy ethyl acrylate 12.38

3. Feed simultaneously with 2. over six hours

   Kg.
   Pegasol R-100 22
   Di-tertiarybutyl peroxide 800 g.

15  Tertiarybutyl perbenzoate 2.1

Throughout the six hour feeding time the reaction mix is held at reflux temperature.

4. Then feed over one hour

   Kg.
   Pegasol R-100 900 g.

20  Tertiarybutyl perbenzoate 275 g.

and then hold at reflux temperature for a further two hours and subsequently allow to cool.

This polymer product exhibited good pot life and durability as a crosslinked film.

25  (Calculated theoretical Tg is + 42.0°C)

This polymer when cured did not have good initial hardness but exhibited excellent solvent resistance and hardness after 24 hours.
**Example 3**

To the reaction vessel was added:

- Methyl ethyl ketone 208.4
- Butyl acetate 683.5
- Dodecylmercaptan 19.8

Heat this mixture to 100°C and subsequently add dropwise, with stirring over 4 hours, a mixture of:

- Styrene 199.8
- n-Butyl methacrylate 199.8
- n-Butyl acrylate 992.0
- 2-Hydroxyethyl acrylate 528.0
- tert-Butyl per-2-ethylhexanoate (a 50% solution in aliphatics) 89.1

Then add dropwise over 2h a mixture of:

- Butyl acetate 159.9
- tert-Butyl per-2-ethylhexanoate (a 50% solution in aliphatics) 17.6

Hold the solution at 100°C for 1h and cool.

The non-volatile content is 63.3% to 65.3% (m/m)

20 (theoretical, 64.3%), and viscosity was 1200-1700 cP at 25°C measured with a Brookfield LVF, S3.

(Calculated theoretical Tg of Example 3 is -28°C.)

This polymer when cured-exhibited good initial hardness characteristics because of its fast curing rate but its solvent resistance was poor after 24 hours.
Example 4

1. To the reaction vessel was added:
   Methyl ethyl ketone 100.0
   Butyl acetate 34.0
   Dodecylmercaptan 3.7

2. Heat this mixture to 100°C and add dropwise with
   stirring, over 4 hours, a mixture of:
   Methyl methacrylate 87.1
   Butyl acrylate 71.8
   Styrene 54.4
   2-Hydroxyethyl acrylate 75.5
   Dodecylmercaptan 3.7

3. Feed simultaneously with 2., over four hours, eighty
   percent of a mixture of:
   Tert-butyl per-2-ethyl hexanoate
   (50% solution in aliphatics) 8.9
   Methyl ethyl ketone 26.0

4. Add the remaining twenty percent of mixture 3., over
   the next two hours, then hold at reflux temperature for a
   further hour and allow to cool.
   (Calculated theoretical Tg is +15°C).
   This polymer when cured exhibited a good cure rate and
   consequently also a good initial hardness and also had
   excellent solvent resistance after 24 hours.
EXAMPLE 5

To the reactor was added

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5 This mixture is heated to reflux at 120°C and subsequently over a six-hour period there is added:

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Also, concurrently with the above addition but over an eight-hour period there is added:

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<td>Methyl ethyl ketone</td>
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heating is then continued for a further two hours.

The non volatile content of the resultant product is 65.6% w/w and its viscosity was 6000 cp. at 25°C measured with a Brookfield-LVF, S3 at 6 RPM.

(Calculated theoretical Tg is +7.5°C)

This polymer when cured exhibits both good initial hardness and good solvent resistance after 24 hours.
Example 6

This example demonstrates an alternative where an excess of peroxide initiator is used.

1. Heat to 150°C Kg.
   Cellosolve Acetate 22
   (Ethylenglycolmonoethylether acetate)

2. Feed the following monomers over six hours Kg.
   Styrene 9.37
   Butyl acrylate 14.10
   Methyl methacrylate 11.31
   Hydroxy ethyl acrylate 12.38

3. Feed simultaneously with 2. over six hours Kg.
   Pegasol R-100 22
   Di-tertiarybutyl peroxide 800 g.
   Tertiarybutyl perbenzoate 2.1
   Throughout the six hour feeding time the reaction mix is held at reflux temperature.

4. Then feed over one hour
   Pegasol R-100 900 g.
   Tertiarybutyl perbenzoate 275 g.
   and then hold at reflux temperature for a further two hours and subsequently allow to cool.

   This polymer product exhibited good pot life and durability as a crosslinked film.
   (Calculated theoretical Tg is +7.5°C).

   This polymer when cured has a good initial hardness and solvent resistance after 24 hours.
Example 7

1. To the reaction vessel was added:
   
   Methyl ethyl ketone 36.0
   Butyl acetate 100.0
   Dodecylmercaptan 6.8

2. Heat this mixture to 100°C and subsequently add dropwise, with stirring over 4 hours, a mixture of:
   
   Styrene 55.2
   Methyl methacrylate 80.9
   n-Butyl acrylate 81.8
   2-Hydroxyethyl acrylate 94.3
   tert-Butyl per 2-ethylhexanoate (a 50% solution in aliphatics) 13.7

Then add dropwise over 2h a mixture of:

   Butyl acetate 44.0
   tert-Butyl per-2-ethylhexanoate (a 50% solution in aliphatics) 3.4

Hold the solution at 100°C for 1h and cool.

The non-volatile content is 62.5% to 64.5% (m/m)

20 (theoretical, 63.5%), and viscosity was 10,000 to 14,000 cP

at 25°C measured with a Brookfield LVF, S3.

(Calculated Theoretical Tg is +10°C).

This polymer when cured has good initial hardness characteristic and also exhibits good solvent resistance

and hardness after 24 hours.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A coating composition curable with a vapourised catalyst and having high initial hardness characteristics formed by mixing a poly-isocyanate crosslinking agent with an acrylic polymer in a water free solvent having a good evaporation rate in an acrylic urethane polymer system, said acrylic polymer having a molecular weight below 20,000, and a content of 15 to 50% by weight of an hydroxy unsaturated monomer and the remaining monomers being selected to provide the final polymer with a glass transition temperature in the range of \(-40^\circ\text{C}\) to \(+55^\circ\text{C}\).

2. A coating composition as claimed in claim 1 wherein the hydroxy monomer is an hydroxy acrylic or methacrylic monomer.

3. A coating composition as claimed in claim 2 wherein the hydroxy acrylic or methacrylic monomer is present in an amount of 25 to 35% by weight.

4. A coating composition as claimed in claim 3 wherein the hydroxy monomer is selected from hydroxy ethyl acrylate or hydroxy ethyl methacrylate.

5. A coating composition as claimed in claim 1 wherein a proportion of the hydroxy monomers provide a final polymer having pendant hydroxy terminated chains greater than 2 carbon atoms in length.

6. A coating composition as claimed in claim 4 wherein the remaining monomers are selected to give a polymer with a glass transition temperature in the range of 0 to \(20^\circ\text{C}\).

7. A composition as claimed in claim 1 wherein the acrylic polymer is formed in a solvent having a good evaporation rate in an acrylic urethane polymer system in
the presence of a chain transfer agent and a free radical initiator the ratio of initiator to chain transfer agent being at least 2.5 to 1.

8. A composition as claimed in claim 1 wherein the solvent used is an acetate or a ketone.

9. A composition as claimed in claim 1 wherein the isocyanate crosslinking agent is selected from aliphatic or alicyclic di-isocyanates, aromatic di-isocyanates or trimethylol propane adducts of di-isocyanates.
### INTERNATIONAL SEARCH REPORT

**Classification of Subject Matter**

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

- **Int. Cl.** C08G 18/62, C09D 3/72

**Fields Searched**

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**Minimum Documentation Searched**

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

**AU:** IPC as above; Australian Classification 094.79, 094.80

### DOCUMENTS CONSIDERED TO BE RELEVANT

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**Continued**

**Certification**

**Date of the Actual Completion of the International Search**

6 April 1986 (06.04.86)

**Date of Mailing of the International Search Report**

15 May 1986 (15.05.86)

**International Searching Authority**

Australian Patent Office

**Authorized Officer**

D. J. Shepherd

Form PCT/ISA/210 (second sheet) (January 1990)
FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y, P
US, A, 4517222 (BLEGEN) 14 May 1985 (14.05.85) (1-9)
See example 3

Y
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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:

3. □ Claim numbers ......... because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

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/218 (supplemental sheet (2)) (January 1985)
This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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INTERNATIONAL APPLICATION NO. PCT/AU 86/00027 (CONTINUED)

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