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(54) Title: COATING COMPOSITIONS			
(57) Abstract			
A coating composition for the production of photopolymerizable coatings comprises: a) an ethylenically unsaturated polymerizable reaction product of a polyepoxide and an ethylenically unsaturated carboxylic acid, further modified by reaction with an anhydride of a dicarboxylic acid so as to have an acid value of from 30 to 80 mgKOH/g, the final product being solid or semi-solid in nature; b) an inert inorganic filler, the said filler and the said reaction product being present in a ratio of from 20 to 65 parts by weight of filler to from 80 to 35 parts by weight of modified reaction product (a); c) a photopolymerization initiator for the said polymerizable reaction product; and d) a volatile organic solvent for the said polymerizable reaction product. The composition may be used as an etch resist, plating resist or, especially, a solder resist in the fabrication of printed circuit boards.			

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COATING COMPOSITIONS

This invention is concerned with improvements in and relating to coating compositions and more particularly is concerned with coating compositions for the production of photopolymerizable coatings upon substrates.

In order to provide for the attachment of electrical components to a printed circuit board of the type comprising a patterned layer of an electroconductive metal (generally copper) on an electrically non-conductive substrate (generally a plastics impregnated substrate) a patterned layer of a solder resist is applied to the board so as to expose parts of the patterned metal layer and the so-coated board is contacted with molten solder so that the solder adheres to the patterned metal layer at the exposed portions thereof. Generally, before the board is contacted with the solder, the electrical components are placed on the other side of the board (although, of course, not in the case of surface-mounted boards) with conducting elements extending therefrom passing through holes in the board into the exposed portions of the patterned metal layer.

It has now been found, in accordance with the present invention, that a patterned solder resist may be formed from a photopolymerizable composition as hereinafter defined by exposing a layer of the composition to actinic radiation through a suitable transparent substrate bearing an opaque image, and subsequently, in a "development" step, removing unexposed composition with a solvent therefor, namely water.

According to one embodiment of the invention, therefore, there is provided a coating composition, for the production of photopolymerizable coatings, comprising:-

- (a) an ethylenically unsaturated polymerizable reaction product of a polyepoxide and an ethylenically unsaturated carboxylic acid, further modified by reaction with an anhydride of a dicarboxylic acid so as to have an acid value of from 30 to 80 mgKOH/g, the final product being solid or semi-solid in nature;
- (b) an inert inorganic filler, the said filler and the said reaction product being present in a ratio of from 20 to 65 parts by weight of filler to from 80 to 35 parts by weight of modified reaction product (a);

- (c) a photopolymerization initiator for the said polymerizable reaction product; and
- (d) a volatile organic solvent for the said polymerizable reaction product.

The invention also provides a method of forming a photopolymerizable coating upon a substrate which comprises applying a coating of a coating composition as defined above to the substrate and allowing it to dry by evaporation of volatile organic solvent.

A principal ingredient of the coating compositions of the invention is the modified reaction product of a polyepoxide and an ethylenically unsaturated carboxylic acid, generally acrylic acid or methacrylic acid, and which will hereinafter simply be referred to as "modified epoxy acrylate". The modified epoxy acrylate should be solid or semi-solid at ambient temperature, e.g. should have a ring and ball softening point (determined according to British Standard Specification No. 4692 of 1971) of at least 5°C, preferably at least 30°C. The unmodified epoxy acrylate is one derived from the reaction of a polyepoxide and an ethylenically unsaturated carboxylic acid or reactive derivative thereof. The polyepoxide should be an aromatic polyepoxide and any such polyepoxide may be employed

provided that the final modified reaction product is a solid or semi-solid at ambient temperatures. Aromatic polyepoxides are polyepoxides containing phenyl groups (polyphenyl polyepoxides) such as polyepoxides derived from the reaction of bisphenols, especially polynuclear bisphenols such as bisphenol-A, with epichlorohydrin, or epoxidised phenyl novolacs, the latter being generally preferred. Aromatic polyepoxides are well known materials and are described, for example in "Chemistry of Organic Film Formers", Solomon D.H., 2nd Edition, Krieger Publishing, 1977, at page 188, 189 and 192.

The unmodified epoxy acrylate is subsequently modified by reaction with an anhydride of a dicarboxylic acid to give a product having an acid value of from 30 to 80 mgKOH/g, preferably from 45 to 55 mgKOH/g. A wide variety of anhydrides may be employed to the purpose of modification and examples of these include succinic, didodecylsuccinic itaconic, citraconic, maleic, phthalic, hexahydrophthalic, tetrahydrophthalic, methylnadic and trimellitic anhydrides.

The second principal ingredient of the compositions of the invention is an inert inorganic filler. The filler, which will be in powdered or finely divided form, serves to improve the resistance of the composition, when used as a solder resist, to heat or

thermal shock such as is experienced when the cured composition is brought into contact with molten solder. The filler should, when the coating composition is employed in the production of a solder resist, not be one which undergoes thermal decomposition when heated by contact with molten solder and examples of suitable fillers include blanc fixe, aluminium hydrate, china clay, calcium carbonate (coated or uncoated) and micronised talc, or mixtures thereof. The weight ratio of filler to modified epoxy acrylate is from 20 - 65 : 80 - 35, preferably from 25 - 55 : 75 - 45, more preferably from 30 - 45 : 70 - 55.

In general, in order to provide a generally tack-free coating from the composition (as is described below), it is preferable, when using less solid modified epoxy acrylates (i.e. those having lower softening temperatures), to employ higher levels of inorganic fillers, but, of course, within the broad range noted above.

The photopolymerization initiator used in the compositions of the invention serve to induce polymerization of the epoxy acrylate when the composition, after application to a substrate, is subjected to actinic radiation. A wide variety of such photopolymerization initiators are known in the art, such as benzoin ethers and anthraquinone derivatives.

Preferred initiators for use in the compositions of the invention are phenyl ketone initiators such as benzophenone, acetophenone or Mischlers ketone or mixtures thereof.

The initiator is suitably present in the composition in an amount of from 1 to 20% by weight, preferably from 5 to 15% by weight, based on the weight of the epoxy acrylate.

The compositions of the invention also contain a volatile organic solvent for the modified epoxy acrylate, with the modified epoxy acrylate dissolved therein, and examples of such solvents include lower carboxylic acid ester of lower alcohols (e.g. isopropyl acetate), lower dialkyl ethers (such as diethyl ether), ketones (such as acetone or methyl ethyl ketone), or, preferably, hydroxyalkyl ethers such as glycol monoethyl ether and ethylene glycol monobutyl ether.

The amount of organic solvent present in a coating composition of the invention as applied to a substrate (e.g. a printed circuit board) will, to some extent, depend upon the nature of the method by which the composition is to be applied to the substrate. Thus, where the composition is to be applied to a substrate by, for example, a screen printing process, it may contain up to 50% by weight of volatile organic solvent whereas if it is to be applied to the substrate by a

curtain coating process it may contain up to 85% by weight of volatile organic solvent. The compositions of the invention may conveniently be formulated containing a lower amount of solvent than is required in the actual application process, the additional solvent required being added to the composition to dilute it prior to the application process. In any case the composition should contain sufficient volatile organic solvent to dissolve the epoxy acrylate and, before dilution as described above, suitably contains up to 35% by weight of volatile organic solvent.

The coating compositions of the invention also suitably contain a colorant, for example an organic pigment such as a chlorinated phthalocyanine pigment, in order that the application of the composition to a substrate provides a visible image. Suitably such colorants will be present in amounts of up to 5% by weight, based on the weight of epoxy acrylate, filler and initiator, preferably from 0.5 - 2% by weight thereof. The coating compositions of the invention may also contain antifoaming agents, such as silicone oils, in order to improve their application properties and such antifoaming agents may be present in amounts similar to those given above for the coloring agents.

Whilst the compositions of the invention contain the

modified epoxy acrylate as principal photopolymerizable ingredient, other photopolymerizable materials may be present and examples of such include esters of mono- or polyhydric alcohols with ethylenically unsaturated carboxylic acids such as acrylic or methacrylic acid, and liquid epoxy acrylates. Such other photopolymerizable materials are not, however, essential and when used it is preferred that they be employed in minor amounts as compared with the modified epoxy acrylate, e.g. in amounts of less than 25%, preferably less than 10%, of the weight of the modified epoxy acrylate.

A coating composition of the invention is used to form a photopolymerizable coating upon a substrate by applying it to the substrate by a convenient method, such as screen printing, curtain coating, roller coating or spray coating, and then allowing the applied coating to dry to a tack-free condition (i.e. to a condition such that it does not adhere to a surface with which it may come into contact) and generally this drying will be accelerated by heating the applied coating.

The resultant coating may be polymerized by exposure to actinic radiation, for example from a source such as a mercury vapour lamp.

As indicated above, a polymerizable coating obtained from a coating composition of the invention is particularly suitable for use in the production of a solder resist in a process for the manufacture of a printed circuit board. It should, however, be noted that such a polymerizable coating may also be used as to form a patterned etch or plating resist since the coating is acid resistant (it being possible to later wholly remove the coating by treatment with a dilute aqueous alkaline solution such as 3% aqueous sodium hydroxide solution, although such removal may not be necessary when the coating is used in the definition of inner layers in a multilayer construction since it is chemically compatible with adhesives used to bond multilayer constructions).

A further embodiment of the invention provides a method of forming a pattern of solder upon a layer of an electrically conductive metal supported on an electrically non-conductive substrate by providing the metal layer with a patterned resist coating, whereby portions of the metal layer are coated with the solder resist coating and other portions of the metal layer are not so coated, and contacting the metal layer provided with the solder resist coating with molten solder whereby solder adheres to the portions of the metal layer not coated with the solder resist coating, in which the solder resist coating is formed by

polymerizing, by exposure to actinic radiation, a photopolymerizable coating obtained by applying a coating composition in accordance with the invention to the metal layer and allowing it to dry.

One such process comprises the steps of:

- (a) providing a circuit board having a patterned layer of a conductive metal (hereinafter simply referred to as copper) with a coating of a coating composition of the invention, at least over the copper layer, for example by screen printing process, by a curtain coating process or by electrostatic spray deposition, in which latter two cases the coating of the composition will extend over the whole of the surface of the board;
- (b) allowing the coated composition to dry to a tack-free, i.e. by evaporation of volatile organic solvent therefrom.
- (c) exposing the coated board to actinic radiation through a positive for the desired solder pattern (i.e. a transparency, generally a photographic transparency, having light transmitting portions corresponding to the

non-solderable portion of the desired solder pattern and non-transmitting portions corresponding to the solderable portions of the desired solder pattern) to cure the exposed portions of the coating, i.e. to photopolymerize the photomerizable material therein;

- (d) removing the non-exposed portions of the coating by means of aqueous alkaline solution (e.g. sodium carbonate solution); and
- (e) contacting the board having a patterned coating image with molten solder, e.g. in the form of a so-called "standing wave" of solder, to apply solder to the board in the desired pattern.

This process makes it possible to provide circuit boards with a patterned solder resist of high definition and accuracy since, in general, exposure through a positive to actinic radiation provides for good accuracy and definition which is of importance as the overall size of circuit boards, and hence the size of individual parts of the solder resist pattern, decrease, a tendency which has been noted recently. It is to be noted that in the above process, step (e) follows directly from step (d), that is there is no heat-curing step after radiation curing.

The circuit board having a patterned layer of copper thereon used as starting material in step (a) of the process described above may be produced in a number of ways, either by the so-called "subtractive" method or by the so-called "additive" method.

In the subtractive method a laminate comprising a layer of copper on a non-conducting substrate is first provided with a positive patterned image of an acid-resisting coating and the exposed copper is then etched away with a suitable acid (e.g. hydrochloric acid), the remaining copper then being exposed by removal of the acid-resisting coating. A coating of acid-resistant material may, as is wellknown, be applied by a patterned coating method, such as a screen printing method, or by coating the copper with a layer of a photosensitive composition and subsequently exposing this to light through a positive or negative image of the desired copper layer, depending on whether the resist coating is a so-called positive or negative working resist and subsequently removing the developable (i.e. solvent-soluble) portions of the image with a suitable solvent.

The compositions of the invention are, themselves, perfectly suitable for use as negative working resists, i.e. resists the exposed portions of which are cured to give an insoluble coating. Thus, the circuit boards

having a patterned layer of copper on the surface thereof may be provided by firstly coating a copper-clad substrate with a coating composition of the invention, allowing the coating to dry, exposing the dried coating to actinic radiation through a positive of the desired copper layer pattern to cure the portion of the coating exposed to radiation, removing the uncured portion of the coating with a solvent therefor and subsequently etching the coated board. The cured coating may then be removed by washing with a solvent therefor, e.g. aqueous sodium hydroxide solution. The board may then be provided with a patterned solder coating as described above.

Dried but uncured coatings of the composition of the invention are resistant to the acid etches used to remove the copper and hence the circuit board having a patterned image of copper thereon may be produced by printing (e.g. by a screen printing process) a patterned coating of a composition of the invention on to a copper clad non-conducting substrate, allowing the coating to dry, and then etching exposed copper from the board. In order to provide a patterned solder coating on the resultant board it is then merely necessary to expose the board to actinic radiation through a positive of the solder pattern [as described in step (c) above] without applying a further coating of a composition of the

invention and then proceeding as described in steps (d) and (e) above. However, if desired a further coating of a composition of the invention may be applied to the board before exposure to actinic radiation in the manner described in step (c) above.

In the additive method for the preparation of the board having a patterned layer of copper, a non-conductive substrate is first coated with an activating material for a so-called electroless copper plating solution, the board is then provided with a negative patterned image of a resist coating, and the board is then immersed in an electroless copper plating solution to form a layer of copper on the exposed portions of the board, i.e. those not covered with the resist. Here again the composition of the invention may be used to form the resist layer, for example by coating the activated board with a layer of the coating composition, allowing it to dry and exposing it to actinic radiation through an appropriate positive of the circuit pattern so that the exposed portion of the coating is photohardened, the non-exposed portion subsequently being removed with a suitable solvent.

Whilst the compositions of the invention are photosensitive, they are not effectively sensitive to subdued light or light having a wavelength above 420 nanometers. Thus the initial application of the coating

composition to a substrate can be carried out in the light (although of course not light having a high amount of actinic radiation).

In order that the invention may be well understood the following examples are given by way of illustration only. In the examples all parts are by weight unless otherwise stated.

Preparative Example A

210 Parts of a commercially available epoxy novolak resin (Dow Epoxy Novolak DEN 444) were placed in a reaction vessel fitted with a stirrer and heated therein to 50°C to dissolve the resin in propylene glycol methyl ether acetate. Then, 72 parts of glacial acrylic acid (in admixture with a small amount of catalyst, were added to the vessel.

The reaction mixture was stirred at about 110°C until the acid value of the mixture had fallen less than 5 KOH/gm. The reaction mixture was cooled to 80°C and 26.5 parts of maleic anhydride were added thereto. The mixture was held at about 80°C until the acid value fell to below 38 mg KOH/g. The mixture was then cooled and discharged after the addition of sufficient propylene glycol methyl to give a final solids content of 72%.

Preparative Example B

The procedure of Preparative Example A was repeated except that 41.6 parts of tetrahydrophthalic anhydride were used in place of the maleic anhydride and reaction with the anhydride was effected at 90°C.

Example 1

A resist ink was made up from the following:

Phthalo green pigment	0.5 parts
Micronised talc	20.0 parts
Product of Preparative Example A	73.5 parts
Irgacure 651	73.5 parts
(A photopolymerization initiator manufactured by Ciba-Geigy; dimethoxyphenyl acetophenone)	
Modaflow	1.0 parts

The ink was diluted with upto 50% of Butyl Cellosolve and applied, by curtain coating, over the whole surface of a clean copper clad epoxy laminate on which the copper was already in the form of a circuit

pattern. The coated laminate was placed in an infrared drier for 5 minutes (at 120°C) in order to render the coating tack free. Once dried, a positive of the required solder pattern was placed over the coating and the resultant combination was exposed to ultraviolet radiation in order to harden the coating by passing it under two 80 watt/cm medium pressure mercury vapour lamps at a rate of 160 cm/min. Once hardened, the positive was removed and the solder pattern was developed by washing with aqueous sodium carbonate solution. Finally the board was fluxed (using CECM Solders 'Superspeed 17' flux) and dried. The fluxed board was then passed over a standing wave of molten solder at about 260°C.

EXAMPLE 2

An ink was made up from the following:

Product of Preparative Example B	73.5%
Phthalo green pigment	0.5%
Micronised talc	20.0%
Isopropyl thioxanthane	5.0%
Silica	5.0
Modaflow	1.0%.

The ink was used as described in Example 1.

EXAMPLE 3

A plain copper board, with copper thickness 25 microns on FR4 laminate, was curtain-coated with a diluted ink of Example 2. The board was coated so as to yield a 14 micron dry-film thickness. The coated board was dried at 90°C for half an hour to remove solvent from the resist to give a tack-free dry film on its surface. The board was then exposed through art work to UV light. Uncured areas of the film were then developed away using 0.6% w/w aqueous sodium carbonate solution. The areas of metal uncovered by the development of the resist were then removed using an etch solution based on an acidified solution of cupric chloride, stabilised with peroxide, at 40°C in a Kepro BTE202E bench etch bath. An etch time of 20 minutes was necessary for the total etch of the unprotected metal. The cured resist was then removed from the metal remaining on the board by immersion in 3% w/w aqueous sodium hydroxide solution at 40°C. The circuit pattern faithfully reproduced the artwork, with no signs of resist failure being apparent.

EXAMPLE 4

A plain copper board, as used in Example 3, was coated with the ink of Example 1, by a screen printing press to give was used with a dry film thickness of 20 microns. The film was processed and the board etched as discussed in Example 3 and gave the same results.

EXAMPLE 5

A board was coated as is Example 3 but this time to a dry film thickness of 35 microns. The resist was processed as in Example 3 but this time the film was UV-exposed through art work suitable for a plating resist application. Once the resist had been developed, the exposed copper was cleaned and degreased using, McDermid's Metex acid Cleaner 9771, water rinsed, microetched with McDermid's Metex G2, water rinsed again and dipped in a 5% sulphuric acid predip before plating copper electrolytically onto the bare copper surfaces. The plating solution was McDermid's Macuspec 9241. The board was then water rinsed and dipped in a 5% w/w fluroboric acid bath before electrolytically plating a layer of tin/lead alloy onto the bare copper using Schloetter tin/lead LA as the plating solution. The resist was then stripped by dipping in 3% w/w aqueous sodium hydroxide solution at 40°C. The copper uncovered

by this operation was then etched away using the Kepro etch bath described in Example 3 using the tin/lead deposit as the etch resist. The tin/lead-covered copper tracks produced by this method were faithful to the art work used and displayed none of the blemishes associated with resist failure.

EXAMPLE 6

The procedure of Example 5 was repeated except that the resist was applied by screen printing. A board of the same good quality as in Example 5, was obtained.

EXAMPLE 7

A plain copper board was coated by screen printing an ink of Example 2 through 48T mesh screen to give a dry film thickness of 20 microns. The board was processed as in Example 3 but etching was carried out using an alkaline etch solution, McDermid's Metex Ultra Etch 9151 at 40°C on an SSO 22 etch line. The resist was tripped as in Example 3 to yield a circuit pattern free of faults and true to the art work pattern used.

CLAIMS:

A coating composition, for the production of photopolymerizable coatings, comprising:-

- (a) an ethylenically unsaturated polymerizable reaction product of a polyepoxide and an ethylenically unsaturated carboxylic acid, further modified by reaction with an anhydride of a dicarboxylic acid so as to have an acid value of from 30 to 80 mgKOH/g, the final product being solid or semi-solid in nature;
- (b) an inert inorganic filler, the said filler and the said reaction product being present in a ratio of from 20 to 65 parts by weight of filler to from 80 to 35 parts by weight of modified reaction product (a);
- (c) a photopolymerization initiator for the said polymerizable reaction product; and
- (d) a volatile organic solvent for the said polymerizable reaction product.

2. A method of forming a photopolymerizable coating upon a substrate which comprises applying a coating of a coating composition as defined in claim 1 to the substrate and allowing it to dry by evaporation of volatile organic solvent.

3. A method of forming a pattern of solder upon a layer of an electrically conductive metal supported on an electrically non-conductive substrate by providing the metal layer with a patterned resist coating, whereby portions of the metal layer are coated with the solder resist coating and other portions of the metal layer are not so coated, and contacting the metal layer provided with the solder resist coating with molten solder whereby solder adheres to the portions of the metal layer not coated with the solder resist coating, in which the solder resist coating is formed by polymerizing, by exposure to actinic radiation, a photopolymerizable coating obtained by applying a coating composition as claimed in claim 1 to the metal layer and allowing it to dry.

A method as claimed in claim 3 comprising the steps of:

- (a) providing a circuit board having a patterned layer of a conductive metal with a coating of a coating composition as claimed in claim 1, at least over the conductive metal layer;
- (b) allowing the coated composition to dry to a tack-free condition by evaporation of volatile organic solvent therefrom;
- (c) exposing the coated board to actinic radiation through a positive for the desired solder pattern to cure the exposed portions of the coating;
- (d) removing the non-exposed portions of the coating by means of aqueous alkaline solution; and
- (e) contacting the board having a patterned coating image with molten solder, to apply solder to the board in the desired pattern.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 89/00167

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : G 03 C 1/68; G 03 F 7/10		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	G 03 C 1/00; G 03 F 7/00	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X,Y	Patent Abstracts of Japan, vol. 12, no. 59 (C-478)(2906), 23 February 1988, & JP, A, 62205113 (MITSUBISHI RAYON CO.) 9 September 1987 see abstract --	1-4
Y	FR, A, 2242702 (KANSAI PAINT CO.) 28 March 1975 see page 2, line 40 - page 12, line 26; page 13, line 30 - page 20, line 21 --	1-4
A	Patent Abstracts of Japan, vol. 8, no. 129 (P-280)(1566), 15 June 1984, & JP, A, 5931947 (MITSUI TOATSU KAGAKU K.K.) 21 February 1984 see abstract --	1-4
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¹⁰ 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. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
23rd May 1989	12. 07. 89	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	P.C.G. VAN DER PUTTEN	

International Application No. PCT/GB 89/00167

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	Patent Abstracts of Japan, vol. 8, no. 125 (P-279)(1562), 12 June 1984, & JP, A, 5929246 (MITSUI TOATSU KAGAKU K.K.) 16 February 1984 see abstract --	1-4
A	Patent Abstracts of Japan, vol. 7, no. 274 (P-241)(1419), 7 December 1983, & JP, A, 58153930 (MITSUI TOATSU KAGAKU K.K.) 13 September 1983 see abstract --	1-4
A	Patent Abstracts of Japan, vol. 6, no. 168 (P-139)(1046), 2 September 1982, & JP, A, 5785050 (MITSUI TOATSU KAGAKU K.K.) 27 May 1982 see abstract --	1-4
P,X	EP, A, 0292219 (AMERICAN TELEPHONE AND TELEGRAPH) 23 November 1988 see the whole document -----	1-4

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 8900167

SA 27589

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 28/06/89
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A- 2242702	28-03-75	JP-A- 50050106	06-05-75
		DE-A, C 2442527	03-04-75
		GB-A- 1489425	19-10-77
EP-A- 0292219	23-11-88	None	