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"FABRICATION OF ELECTRICAL CONDUCTOR BY AUGMENTATION
REPLACEMENT PROCESS"

Background of the Invention

5 The present invention relates to the fabrication of
electrical conductors by replacement of metallic powder in a
polymer with a more noble or electropositive metal. More
particularly, the present invention relates to fabrication of a
10 printed circuit by applying a mixture of a metallic powder and
polymer on a substrate and curing the polymer, followed by an
augmentation replacement reaction wherein some of the metallic
powder is replaced with a more noble metal in such a way that
the total volume of deposited metal on the surface exceeds that
of the original metal powder at the surface, and thereafter
15 increasing the thickness of more noble metal by immersing the
thin coated circuit in an electroless plating bath.

 Many types of electronic apparatus are known in which the
various electrical components are interconnected by conductors.
The interconnecting conductors are fabricated by a wide variety
20 of processes such as, for example, thick-film fired conductor
systems, polymer conductors and printed circuit boards.

 In thick-film fired conductors, a mixture of a conducting
metal powder, a ceramic or glass binder, and an appropriate
vehicle is screen printed on a substrate. The conductor
25 pattern on the substrate is then fired at a relatively high
temperature, typically between 650°C and 900°C. As the
temperature rises to the firing temperature, the vehicle is

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volatilized, leaving the metal and binder behind. At the firing temperature, sintering of the metal takes place to a greater or lesser extent with the binder providing adhesion between the metal film formed and the substrate.

5 Thick-film fired conductors have classically employed
precious metals such as gold, silver, platinum and palladium.
Due to the high cost of these metals, new conductor systems
using copper, nickel, and aluminum are being made commercially
available. Many of the newer systems are not significantly
10 less expensive than thick-film fired systems because of the
special chemistry which is required to prevent oxidation of the
metal during the firing process. Moreover, these systems are
very difficult to solder using conventional tin/lead solder and
the high firing temperatures required during fabrication
15 preclude the use of low cost substrate materials.

In polymer conductor systems the polymer is heavily loaded
with a conducting metal and screened onto a substrate. The
advantage of such a system is that the polymer can be cured
either catalytically or thermally at temperatures which range
20 from room temperature to about 125°C. As a result of this
so-called "cold processing" it is possible to use very
inexpensive substrates such as films of Mylar (R) (polyethylene
terephthalate). The mechanism by which conductivity is
achieved is supplied entirely by contact between individual
25 metallic particles. It has been found that the only metals
which can be loaded into the polymer to give acceptable
conductivity are the precious metals such as gold and silver.
All of the other standard conducting metals oxidize over a
period of time, reducing conductivity between the particles.
30 Silver has been the predominant choice in polymer conductor

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5 systems, but the silver systems are generally not solderable because the silver is leached by the tin/lead solder. When the price of silver is about \$10 per ounce these conductor systems are competitive with other systems if used on very low cost substrates. However, when the price of silver is higher, these systems are not very competitive with printed circuit boards.

10 The techniques used to prepare printed circuit boards can be divided into additive and subtractive technologies. In both the additive and subtractive techniques, the starting point is a substrate, which can vary widely from phenolics to glass-filled epoxies, on which a copper foil is bonded. In the traditional additive preparatory system the copper foil is very thin, usually on the order of 200 microinches. A resist is
15 patterned such that the copper is exposed only where the conductors are desired and the board is then electroplated to form copper conductors of about 1 mil thickness. The plating resist is stripped and the copper is etched. In areas where the conductor is not desired, the copper is only about 200
20 microinches thick so that etching quickly removes this copper while leaving a 1 mil thick conductor. In the subtractive process the starting thickness of the copper foil is usually between 1 and 2 mils. An etch resist is deposited wherever conductors are desired, the board is etched, and the resist is
25 then removed. The resist prevents etching where the conductors are desired.

30 Both the additive and subtractive printed circuit board procedures require the application of a copper foil over the entire substrate, deposition and removal of a resist, etching of the printed circuit board, drilling holes for component

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insertion and, in one case, the additional step of electroplating. An advantage of this technology is that the resulting circuit boards can be relatively easily soldered.

5 Another advantage of such printed circuit board technology is that plated-through holes can be fabricated. This process involves the addition of several steps to the additive fabrication process. Holes are drilled in the substrate and thereafter the resist is applied over all areas except where the conductors are desired. The board is then soaked in a stannous chloride sensitizer which forms a coating over the exposed
10 parts of the substrate, namely inside the holes. The board is then sequentially dipped in a bath of palladium chloride, acid to dissolve the stannous chloride, and an electroless copper bath. The last step, i.e. immersion in an electroless copper bath, deposits a very thin film of copper inside the activated hole. This "electroless copper" is plated out by a catalytic
15 reaction in which the catalyst is copper such that a continuous plating reaction can occur. Typically, thickness on the order of 24 to 50 microinches can be achieved in half an hour. At this point, a thin film of copper is adhered to the inside
20 edges of the holes. The subsequent electroplating will build up the thickness of the copper within the holes as well as along all of the conductor runs. At this point, the various processes employed differ. The simplest process merely strips the resist and then etches, eliminating the much thinner copper where the conductor runs are not desired. In more complex
25 processes, electroplating of tin/lead solder inside the hole and along the conductor runs, followed by stripping the plating resist and etching with chromic acid, which does not attack the tin/lead solder so that the solder acts as an etch resist.
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5 The most significant drawbacks of the printed circuit board technology are that a substantial number of processing steps are necessary and this requires a large amount of associated equipment. In addition, the choice of substrate materials is limited to one of those available for circuit board materials. The number of processing steps and equipment results in relatively high processing costs and the limitation of the substrate material eliminates the opportunity to use a decorative or structural member which may already be required in the apparatus as a substrate material.

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In U.S. Patent No. 4,404,237 to Eichelberger et al., assigned to the same assignee as the present invention, and incorporated herein in its entirety, the formation of an electrical conductor by an augmentation replacement reaction technique is described. Briefly, Eichelberger et al. disclose a process wherein the desired conductive design is applied to the substrate with an ink composition which contains a finely divided metal powder, a curable polymer, and a solvent. The curable polymer is at least partially cured and then the resulting ink composition pattern is contacted with a metal salt solution in which the metal cation is more noble (electropositive) than the metal of the finely divided powder, and the anion forms a salt with the metal of the salt and the powder which is soluble in the solution. The system can be applied to a multiplicity of low-cost substrate materials such as soda-lime glass, plastic and even paper.

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While the augmentation replacement process of Eichelberger et al. provides a very low cost means for providing a conductor pattern on a substrate surface, it is often desirable to build up conductor pathways having a thickness greater than can be achieved by the augmentation replacement process alone.

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Summary of the Invention

5 It is an object of the present invention to provide a means for providing conductor pathways on a substrate surface which have a greater thickness than can be obtained solely by an augmentation replacement process.

It is another object of the present invention to provide conductor systems wherein the conductor paths have increased thickness.

10 In accordance with one aspect of the present invention there is provided an improved process for providing printed circuits and other conductive patterns or designs, comprising
15 (a) applying the desired design on a substrate with an ink composition comprising at least one finely divided metal powder composition, at least one curable polymer and, optionally, a solvent, (b) at least partially curing the curable polymer, and
20 (c) contacting the resulting designed substrate with a metal salt solution in which the metal cation is more noble than the metal of the finely divided powder so that the anion forms a salt with a portion of the metal powder composition and the cation metal plates out on the surface of the at least partially cured polymer; the improvement comprising further increasing the thickness of the more noble metal plated on the surface of the at least partially cured polymer by immersing the coated substrate of step (c) in an electroless plating bath.

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Description of the Invention

5 In its broadest form, the present invention involves the establishment of a desired conductive pattern on a substrate by means of a metal-containing, at least partially cured polymer which is subjected to an augmentation replacement reaction and thereafter further increasing the thickness of said conductive pattern by means of an electroless plating bath. The preferred method for carrying out the augmentation replacement reaction is described in U.S. Patent No. 4,404,237, assigned to the same assignee as the present invention and incorporated herein by reference.

10 The substrates on which the conductive patterns are formed are not restricted and any insulator to which the metal ink can be adhered is employable. Thus, the usual printed circuit substrates can be used as well as glass-filled polyesters, phenolic boards, polystyrene and the like. Of particular interest as a substrate for use in the present invention is silicone impregnated glass. The use of such a substrate will enable the artisan to fabricate flexible circuit boards capable of withstanding high temperatures, for example, on the order of about 150°C to about 300°C.

15 The inks used in the present invention are a combination of finely divided metal powder and a polymer whose viscosity and flow characteristics can be controlled by incorporating a solvent therein. The metal can be any metal which is stable in the ink and cured polymer; can be obtained in finely divided form; and is placed above the metal used in the augmentation replacement reaction in the activity series of the metals. Because of their availability and low cost, the most preferred

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5 metals are iron, nickel or zinc or a mixture thereof. The metal powder generally has a particle size less than about 50 microns, preferably less than about 25 microns, and most preferably less than about 10 microns. When the ink is deposited by screen printing, the metal particles must be of a size to pass through the screen. It should be noted that although screen printing is preferred, other types of application techniques can be used, including without limitation, pad flexographic printing, stencil, rotogravure and offset printing.

10 The polymer employed in the ink is any material or mixture of materials which exhibits a degree of adhesion to the substrate being employed and to the finely divided metal powder which is dispersed therein. Typical polymers are described in the aforesaid U.S. Patent No. 4,404,237.

15 The polymers and inks employed in the present invention can contain various other materials such as fillers, dyes, pigments, waxes, stabilizers, lubricants, curing catalysts, polymerization inhibitors, wetting agents, adhesion promoters, and the like.

20 The amounts of finely divided metal powder and polymer are such that a significant amount of metal particles are on the surface of the at least partially cured ink so as to facilitate the subsequent augmentation replacement reaction. Generally, the metal should constitute from about 60% to about 80% by
25 volume of the mixture, after curing, to achieve the best results.

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5 A solvent is used in the ink formulation in order to adjust
the viscosity and flow characteristics for the type of printing
desired. In general, the solvent should be employed in an
amount sufficient to adjust the ink's viscosity from about
15,000 centipoise to about 200,000 centipoise at 25°C. Prefer-
ably, the viscosity will range from about 50,000 centipoise to
about 150,000 centipoise for screen printing usage. Suitable
solvents or diluents can be aliphatic or aromatic and can
contain up to about 30 carbon atoms. Representative solvents
10 are disclosed in U.S. Patent No. 4,404,237. It is preferred to
employ a solvent which is relatively nonvolatile at room
temperature so that the viscosity and flow of the ink is
appropriate during application to the substrate, and highly
volatile at the curing temperature of the polymer or at other
15 temperatures above the application temperature.

The ink is applied to the substrate to achieve the desired
conductor patterns thereon. For example, standard printed
circuit application technology can be employed. Any tempera-
ture which will not cause premature curing of the ink and at
20 which the viscosity and flow characteristics of the ink are
appropriate to the application technique can be employed. It
is preferred, but not necessary, to permit at least a portion
of the solvent to evaporate after application of the ink to the
substrate but before curing. Evaporation tends to expose
25 additional metal powder and increase the ratio of metal powder
to polymer so as to achieve a balance between sufficient metal
to provide a base for the conductive film to be formed thereon
and too little polymer to act as a binder to hold the metal
particles together. Preferably, the drying is effected for
30 about 0.1 to about 1 hour and, more preferably, for about 0.25
to about 0.5 hour at a temperature of about 70°C to about
150°C, preferably from about 110°C to about 130°C.

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Following application, the ink polymer is cured by the most convenient method. If an autocatalyst has been added the polymer will cure by itself with no additional initiation. In the case of ultraviolet light initiators, the substrates carrying the conductor patterns can be passed under a high intensity ultraviolet source which causes the initiators to begin the curing reaction. It is presently preferred to employ a thermal curing system which is activated by exposure to temperatures above 100°C, preferably from about 140°C to about 200°C, for a time of about 0.1 to about 1 hour, preferably about 0.15 to about 0.5 hour. As a result of this step, a closely compacted metal powder bound to the substrate by the cured polymer is achieved. Because of the high percentage of metal and shrinkage of the polymer chosen, the conductive pattern thus obtained may have some conductivity due to physical contact between the metal particles.

In some instances it may be desirable to only partially cure the polymer. For example, occasions arise where it is desirable to mount components by inserting the leads thereof in the polymer ink. In such instances it may be desirable to partially cure the polymer, or only gel the polymer in situations where the polymer employed is gelable, so as to provide an adhesive for the lead wire.

The ink-designed substrate is then subjected to an augmentation replacement reaction in which some of the metal powder is replaced by a metal further down in the activity series, i.e., which is more noble. This step takes advantage of the known chemical behavior of metals, i.e., that any metal will displace any succeeding, less active metal from a water solution of one of its salts. Eichelberger et al., in U.S.

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Patent No. 4,404,237, found that while the powder metal enters into solution from the surface and somewhat below the surface of the polymer, the plating out of the more noble metal takes place, to a large extent, on the surface. Thus, an additional amount of noble metal is deposited on the surface than that which would form a one-to-one exchange with the powder metal at the surface. The additional metal from the solution plates to both the original and replacement metal particles which are adhered to the substrate by the polymer, to interconnect all metal particles at the surface and thus form a contiguous film of conductive metal over the printed conductor pattern. Eichelberger et al. found that several hundred microinches of conductor material can be built up from a solution in a period of about five minutes. Preferably, the more noble metal is copper.

Those skilled in the art will appreciate that the thickness of conductor material which can be built up is limited by the rate and ability to exchange original metal particles in the polymer for more noble metal particles contained in the augmentation reaction solution. Thus, although conductor pathways having a thickness of about 300 microinches are obtainable by such augmentation replacement process, it is often desirable to employ conductor pathways having a thickness ranging from about three to about ten times that obtained by the augmentation replacement reaction.

It has now been found that additional more noble metal can be deposited over the conductor pathways prepared by an augmentation replacement process by immersing the substrate in a conventional electroless plating bath. The more noble metal deposited by the electroless plating bath can be the same as or

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different from the more noble metal applied by the augmentation replacement process.

Electroless plating is well known in the art and is described generally in "Encyclopedia of Chemical Technology", Third Edition, Vol. 8, pages 738-750, John Wiley and Sons, 1979. Briefly, electroless plating solutions contain a metal salt of the metal to be plated, a reducing agent, a pH adjuster or buffer, a complexing agent and one or more additives to control stability, film properties, deposition rates and the like. Of course, the metal salt and reducing agent must be replenished at periodic intervals because they are consumed during the plating process. Preferred plating baths utilize copper salts and are described in U.S. Patent Nos. 2,874,072; 2,938,805; 2,996,408; 3,075,855; 3,075,856 and 3,649,350, all of which are incorporated by reference into the present disclosure. Especially preferred is the stabilized copper plating bath of Agens, U.S. Patent No. 3,649,350, assigned to the same assignee as the present invention. Additional patents describing bath stabilizers as well as physical property improvers and deposition aids are compiled in "Plating of Plastics with Metals", John McDermott, pages 62-93, Noyes Data Corporation, 1974. Patents directed to the preparation of printed circuits by electroless plating are compiled at pages 227-271 of the aforesaid McDermott reference.

In order that those skilled in the art may better understand my invention, the following example is given by way of illustration and not by way of limitation. All parts and percentages are by weight unless otherwise stated.

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Example

A printing ink was prepared by mixing 12 grams RTV 615A and 1.2 grams RTV 615B (available from General Electric Company), 90 grams of a blend of finely divided iron and nickel and 10.5 grams Solvesso 100. The thus prepared ink was screen printed onto a silicone impregnated glass cloth (available from Laur Company) and cured by heating for 15 minutes at 150°C. An augmentation replacement reaction was then conducted in accordance with U.S. Patent No. 4,404,237 to Eichelberger by immersing the printed substrate in an aqueous bath containing a copper salt. The resulting printed circuit, having conductive copper pathways about 200 microinches in thickness, was then immersed in a MacDermid Macuplex electroless copper coating bath comprising:

1710 ml deionized water
200 ml Macuplex 7921 copper complexor solution
60 ml Macuplex 7920 copper/formaldehyde solution
28 ml Macuplex 7922 caustic solution
2 ml Macuplex 7924 cyanide solution
9 grams Macuplex 7923 formaldehyde solution.

The copper of the electroless plating bath deposited on the copper of the augmentation replacement reaction to provide conductive copper pathways about 1.5 mils in thickness.

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I Claim:

1. A method for applying metal to a substrate, comprising:
 - (a) effecting an augmentation replacement reaction, and thereafter
 - (b) increasing the thickness of metal by an electroless plating process, wherein the metal applied by the electroless plating process is the same as or different from the metal applied by the augmentation replacement reaction.
2. A method as in Claim 1, wherein the metals applied by the augmentation replacement reaction and the electroless plating process are the same.
3. A method as in Claim 2, wherein the metal is copper.
4. An article made by the method of Claim 1.
5. An article as in Claim 4, wherein said article is a printed circuit.
6. In a method for making a design on a substrate, comprising (a) applying the desired design on said substrate with an ink composition comprising at least one finely divided metal powder composition and at least one curable polymer; (b) at least partially curing said curable polymer; and (c) contacting the resulting designed substrate with a metal salt solution in which the metal cation is more noble than the metal of said finely divided metal powder so as to cause the more

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noble metal to plate out on the surface of the at least partially cured polymer; the improvement which comprises increasing the thickness of more noble metal plated on the surface of the at least partially cured polymer by immersing the designed substrate obtained in (c) in an electroless plating bath.

7. A method as in Claim 6, wherein the substrate is selected from the group consisting of glass-filled polyesters, phenolic boards, polystyrene and silicone impregnated glass.

8. A method as in Claim 6, wherein the ink composition further comprises an effective amount of solvent.

9. A method as in Claim 6, wherein the finely divided metal powder is selected from the group consisting of iron, nickel and zinc or mixtures thereof.

10. A method as in Claim 6, wherein the metal powder composition has a particle size less than about 50 microns.

11. A method as in Claim 6, wherein the metal powder composition has a particle size less than about 25 microns.

12. A method as in Claim 6, wherein the metal powder composition has a particle size less than about 10 microns.

13. A method as in Claim 6, wherein said ink composition is applied by screen printing.

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14. A method as in Claim 6, wherein the finely divided metal powder composition comprises from about 60% to about 80% by volume of the ink composition after curing.

15. A method as in Claim 6, wherein the viscosity of the ink composition is from about 15,000 centipoise to about 200,000 centipoise at 25°C.

16. A method as in Claim 8, wherein the viscosity of the ink composition is from about 15,000 centipoise to about 200,000 centipoise at 25°C.

17. A method as in Claim 6, wherein the viscosity of the ink composition is from about 50,000 centipoise to about 150,000 centipoise at 25°C.

18. A method as in Claim 8, wherein the viscosity of the ink composition is from about 50,000 centipoise to about 150,000 centipoise at 25°C.

19. A method as in Claim 8, wherein a portion of the solvent is evaporated after application of the ink to the substrate but before curing.

20. A method as in Claim 19, wherein evaporation of solvent is effected by heating at a temperature of from about 70°C to about 150°C for about 0.1 to about 1 hour.

21. A method as in Claim 6, wherein the metal which is more noble than the metal of the finely divided metal powder is copper.

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22. A method as in Claim 9, wherein the metal which is more noble than the metal of the finely divided metal powder is copper.

23. A method as in Claim 6, wherein the metals applied by step (c) and the electroless plating process are the same.

24. A method as in Claim 23, wherein the metal is copper.

25. An article of manufacture prepared by a method, comprising:

- (a) applying a desired design on a substrate with an ink composition comprising at least one finely divided metal powder composition and at least one curable polymer;
- (b) at least partially curing said curable polymer;
- (c) contacting the resulting designed substrate with a metal salt solution in which the metal cation is more noble than the metal of said finely divided metal powder; and
- (d) immersing the designed substrate obtained in (c) in an electroless plating bath.

26. An article as in Claim 25, wherein said article is an electrical conductor.

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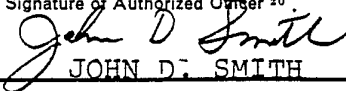
27. An electrical conductor as in Claim 26, wherein the finely divided metal powder is selected from the group consisting of iron, nickel and zinc and mixtures thereof.

28. An electrical conductor as in Claim 27, wherein the metal which is more noble than the metal of the finely divided metal powder is copper.

29. An electrical conductor as in Claim 28, wherein the metal applied by immersing the substrate in an electroless plating bath is copper.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/02675

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC(4): C23C 18/54; H05K 3/18		
US CL. 427/98, 436; 428/209, 901		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	427/98, 436; 428/209, 901	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
Y	US,A, 4,470,883 (EICHELBERGER) 11 SEPTEMBER 1983. See the entire document.	1-29
Y	US,A, 4,404,237 (EICHELBERGER) 13 SEPTEMBER 1983. See the entire document.	1-29
Y	US,A, 3,332,860 (DIEBOLD) 25 JULY 1967. See column 2, lines 33-37 and 60-65.	1-29
Y	US,A, 3,764,280 (LUPINSKI) 09 OCTOBER 1973. See column 5, lines 59-72.	1-29
A	US,A, 4,284,665 (HEIMALA) 18 AUGUST 1981.	
A	US,A, 4,454,168 (FRITZ) 12 JUNE 1984.	
<p>* Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²	Date of Mailing of this International Search Report ²	
02 FEBRUARY 1987	10 MAR 1987	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
ISA/US	 JOHN D. SMITH	