PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 **:**
C01B 31/00

A1

(11) International Publication Number: **WO 97/27142**

(43) International Publication Date: 31 July 1997 (31.07.97)

(21) International Application Number: PCT/US97/01498

(22) International Filing Date: 29 January 1997 (29.01.97)

(30) Priority Data:
08/593,232 29 January 1996 (29.01.96) US

(71) Applicant: ELECTROCHEMICALS INC. [US/US]; 5630 Pioneer Creek Drive, Maple Plain, MN 55359 (US).

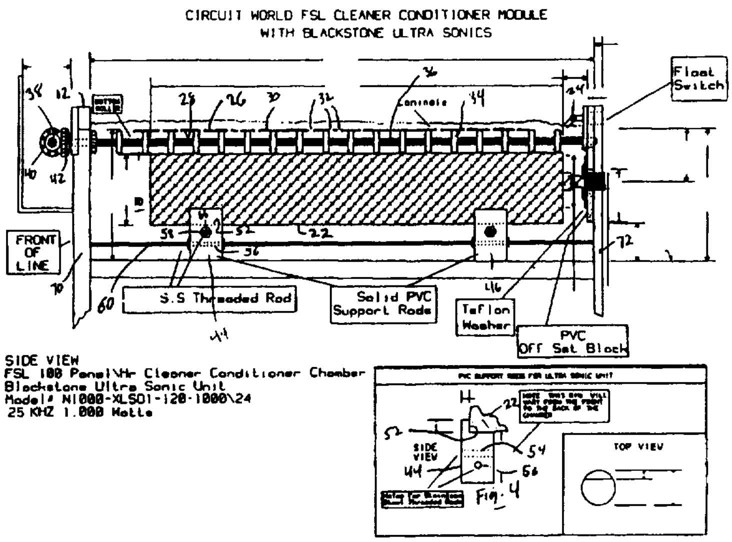
(72) Inventors: GARLOUGH, Gregory, Dean; 9509 Nesbitt Avenue S., Bloomington, MN 55437 (US). CARROLL, Benjamin, Todd; 7633 Lee Avenue N., Brooklyn Park, MN 55443 (US). CARANO, Michael, Val; 3305 Olive Lane North, Plymouth, MN 55447 (US). POLAKOVIC, Frank; 243 Buena Vista Drive, Ringwood, NJ 07456 (US).

(74) Agents: WHEELER, George, F. et al.; McAndrews, Held & Malloy, Ltd., Suite 3400, 500 West Madison, Chicago, IL 60661 (US).

(81) Designated States: CA, CN, JP, KR, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: ULTRASONIC MIXING OF THROUGH HOLE TREATING COMPOSITIONS



(57) Abstract

A method for treating a non-conductive through hole surface of a printed wiring board is disclosed. A printed wiring board (26) including through holes (32) is cleaned, conditioned, and a conductive coating is applied to the initially-nonconductive through hole (32) by contacting it with a series of baths. The conductive coating, for example a graphite dispersion coating, facilitates later electroplating of the conductive surface. While at least partially immersing the through hole in one or more of these baths, ultrasonic energy is introduced in the bath in the vicinity of the through hole (32). The ultrasonic energy reduces the formation of blowholes during later processing (and especially soldering) of the printed wiring board (26). The ultrasonic treatment can also improve the dispersion of the conductive particles in a conductive carbon dispersion, reduce or eliminate the formation of pinhole defects, and provide other advantages.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic			SE	Sweden
CG	Congo	KR	Republic of Korea	SG	Singapore
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LR	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	TT	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	France	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

ULTRASONIC MIXING OF THROUGH HOLE TREATING COMPOSITIONS

The present invention generally relates to a method for making an initially electrically nonconductive surface electrically conductive by cleaning and conditioning the surface and then applying an electrically conductive coating. The present invention relates more particularly to such a method for making the initially-nonconductive through hole and via walls of printed wiring boards electrically conductive, so they can be electroplated. ("Through holes" as used herein refers both to through holes and to vias.)

Conductive graphite and carbon black dispersions are used to provide a superior conductive coating on through hole walls and other nonconductive surfaces. Such dispersions, methods for using such dispersions to coat through holes, and improved printed wiring boards fabricated by using such dispersions are defined in U.S. Patent Nos. 5,476,580 and 5,389,270. A graphite composition, cleaners, conditioners, and other materials and directions needed to practice these patents are available under the trademark SHADOW® from Electrochemicals Inc., Maple Plain, Minnesota, USA and its foreign affiliates. Other carbon dispersions containing carbon black or graphite are described, for example, in U.S. Patent No. 5,139,642.

A problem with "blowholes" occasionally develops after the through hole wall has received a conductive coating, has been electroplated, and is then suddenly heated. Soldering heats the plated through hole walls very quickly. If there are any gaps or voids in the plated copper, moisture in the substrate is vaporized by the hot solder, which can blow some or all of the solder out of the hole and breach the copper layer. The result is a blowhole or a partially-filled or empty hole, any of which is counted as a soldering defect.

The problem of blowholes in through holes made electrically conductive by electroless plating, and the solution to blowholes when that technology is used, are described in a series of articles published in CIRCUIT WORLD, Vol. 12 No. 4 (1986), Vol. 13 No. 1 (1986), and Vol. 13 Nos. 2-3 (1987), under the common title, *Blowholing in PTH Solder Fillets*. A related article is C.Lea, *The Harmfulness of Blowholes in PTH Soldered Assemblies*, CIRCUIT WORLD, Vol.16, No.4, (1990).

Recently, the present inventors have discovered that blowholes can occasionally be a problem for electroplated through holes which have been made conductive by applying certain aqueous conductive-carbon-based conductive compositions. Thus, a need has arisen to solve the problem of blowholes when a carbon-based conductive coating is used to make through hole walls electrically conductive to facilitate electroplating.

Separately, printed wiring boards have been exposed to ultrasonic energy to facilitate cleaning through holes. See *New Process Forces a Solution*, CIRCUITS MANUFACTURING, June 1987, p. 18; F. John Fuchs, *Ultrasonic Cleaning*, p.145. These articles do not discuss blowholes.

SUMMARY OF THE INVENTION

The invention is a method for treating a non-conductive through hole surface of a printed wiring board. The method can be used while or before making the through hole surface electrically conductive.

A printed wiring board including at least one through hole is supplied. Generally, the printed wiring board will include many through holes. At least one bath is provided to carry out at least one of the steps of conditioning and applying a conductive coating to the through hole.

The method is carried out by at least partially immersing the through hole in the bath and introducing ultrasonic energy in the bath in the vicinity of the through hole. The ultrasonic energy is introduced before the end of the immersing step. Optionally, the ultrasonic energy can be introduced during part or all of the immersing step, before the immersing step, or both.

Surprisingly, the ultrasonic treatment according to the present invention has been found effective for reducing, and in some instances substantially eliminating, the formation of blowholes. The ultrasonic treatment can also improve the dispersion of the carbon particles in the conductive carbon dispersion, reduce or eliminate the formation of pinhole defects, and provide other advantages.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic view of a recirculating bath of an aqueous carbon dispersion which is treated with ultrasonic energy.

Figure 2 is a front elevation, looking in the direction of travel of the printed wiring board, of a conveyorized process bath vessel containing an ultrasonic generator. The intervening wall of the vessel is cut away to reveal internal structure.

Figure 3 is a plan view of the embodiment of Figure 2, with the ultrasonic transducer reduced to its footprint and the overlying rollers cut away to better reveal underlying structure.

Figure 4 is an isolated side elevation of one of the feet of Figure 2, showing its details.

Like reference characters in the several views indicate like or corresponding parts.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is carried out by exposing a printed wiring board having at least one through hole to ultrasonic energy when conditioning or applying a conductive coating to the through hole. The process can be carried out during either or both of these steps.

The present process can be carried out in a variety of equipment. Two common types of equipment are vertical or dip process equipment, in which the cleaners, conditioners, combined cleaner/conditioners, conductive dispersions, rinses, and other chemicals are provided in stationary baths into which the vertically-disposed boards are sequentially dipped, and conveyorized or horizontal equipment in which the boards are flooded or sprayed with the respective reagents while disposed and travelling substantially horizontally. Either type of equipment, or any combination of the two types of equipment, may be used within the scope of the present invention.

A board to be processed commonly is dip-processed in the cleaning solution for 4-6 minutes at 54° to 60°C. A board is commonly cleaned in a conveyorized process by flooding it at a similar temperature for a (usually) much shorter time such as 20 to 60 seconds. These conditions may need to be modified to suit a given situation.

A board to be processed commonly is dip-processed in the conditioning solution under conditions as given above for the cleaning solution. The conditions of use of the cleaning and conditioning solutions can be independently optimized.

As an alternative to separate cleaning and/or conditioning steps, these two steps can be combined into one by consolidating their respective ingredients into a single formulation which both cleans and conditions the substrates. A typical cleaner/conditioner is used in about the same manner, for about the same treatment time, at about the same treatment temperature, as an independent cleaner or conditioner.

Other steps, such as rinsing, may be interposed between the previously-described steps at appropriate times.

Before or while the cleaning, conditioning, and conductive-material-depositing baths are used, at least one of them is subjected to ultrasonic energy. Ultrasonic energy is applied in various ways, within the scope of the present invention. The process is illustrated by Figure 1, which is a schematic view of a bath of the present dispersion which is both mixed and subjected to ultrasonic energy while in use.

Referring to Figure 1, a bath 10 of a carbon dispersion is supported in a tank 12 which has a sump 14. The bath 10 is recirculated by periodically or (preferably) continuously withdrawing the bath 10 from the sump 14 through a conduit 16, using a pump 18, which may be either a conventional low-shear pump or a high-shear pump. The pump 18 returns the recirculation stream through the conduit 20 to the bath 10. Tanks for other treatment baths, such as a cleaner/conditioner bath, can be similarly configured.

Still referring to Figure 1, in this embodiment, an ultrasonic transducer 22 is operatively coupled with the bath 10 to transmit ultrasonic waves into the bath 10. Depending on the arrangement and volume of the tank 12, the choice of ultrasonic conditions, the nature and composition of the bath 10, the choice (or presence or absence) of a pump 18, the presence or absence of other stirring apparatus, and other factors, one or more transducers 22 may desirably be located in the vicinity of the sump 14 or elsewhere on or in the tank 12, the conduits 16 or 20, or the pump 18.

The ultrasonic transducer 22 can be operatively coupled with the bath 10 by locating one or more transducers 22 anywhere, relative to the bath 10, which is effective to introduce ultrasonic energy into the bath 10 while it is used or before it is used for coating a non-conductive substrate. In one embodiment, the transducer can be the wall of the tank 12 itself, or can be located outside the wall and transmit energy through the wall. This arrangement has the advantage of avoiding the need for an immersible transducer. In another embodiment, the transducer 22 can be suspended directly in the bath 10.

The ultrasonic transducer 22 generates ultrasonic waves having any desired frequency, such as a frequency between about 16 kHz and about 100 kHz, alternatively between about 20 kHz and 50 kHz, alternatively between about 25-40 kHz, alternatively on the order of 28 kHz. The frequency and the amplitude or power of any ultrasonic waves produced in the carbon dispersion bath should be sufficient, under the conditions employed, to break up agglomerates or gel particles of the bath to a measurable or noticeable degree which provides at least some practical benefit. For one example, ultrasonic treatment according to the present invention is occurring if turning on the ultrasonic generator provides a coating with fewer pinholes than the same apparatus provides when operated with the ultrasonic generator turned off.

While the inventors presently contemplate that a recirculation pump 18 and an ultrasonic transducer 22 will normally be used together, the inventors further contemplate that the bath 10 can be treated to keep the solid particles finely dispersed by operating an ultrasonic transducer 22 without operating a recirculation pump 18.

Some benefit can also be gained by subjecting the dispersion to high-shear mixing, whether or not an ultrasonic transducer is used too. Referring to Figure 1, the pump 18 can be a high-shear in-line pump or mixer which is capable in itself of treatment the bath 10.

Figures 2 and 3 show conveyorized equipment for carrying out any of the cleaning, conditioning, and carbon dispersion coating steps according to the present invention. Again, a bath 10, a tank 12, flood conduits for recirculating the process bath, and a transducer 22 are shown. Like Figure 1, the embodiment of Figures 2 and 3 also has a recirculation pump (not shown).

Figures 2 and 3 show more details of the process equipment. The level of the bath 10 is controlled by a float switch 24. Printed wiring boards such as the board 26 are provided which have first and second major surfaces 28 and 30 which are perforated by a multiplicity of through holes 32. The boards are supported in a generally horizontal position and conveyed along a path extending at least substantially parallel to their major surfaces by a series of rollers such as 34 carried on axles such as 36. The axles such as 36 are driven by a drive shaft 38 via a pair of meshed crown gears 40 and 42, respectively connected to the drive shaft 38 and the axle 36. This drive arrangement turns all of the rollers 34 at the same rate, thus smoothly immersing a series of the printed wiring boards 26 in the bath 10 and conveying them through the bath 10 just beneath its surface. Dam rollers 40 and 42 are provided near the entrance and exit to the tank 12.

The transducer 22 is supported on polyvinyl chloride or other suitable feet 44, 46, 48, and 50 which are short cylindrical rod sections. Figure 4 shows that each foot such as 44 has a notch 52 receiving the lower edge of the transducer 22. Figures 2 and 4 show that each foot such as 44 has crossed bores 54 and 56 which respectively receive a machine-direction threaded rod 58 and a transverse threaded rod 60. Figure 3 best shows that there are two machine-direction threaded rods 58 and 62 and two transverse threaded rods 60 and 64. The threaded rods may conveniently be made of stainless steel or any other material which is compatible with the bath 10. The feet 44-50 and rods 58-64 are joined by nuts 66 threaded on the rods 58-64 and abutting the feet 44-50 to form a frame 68. Figure 2 illustrates that the ends of the rods such as 60 may abut the side walls such as 70 and 72 to locate the frame 68 in the tank 12.

In this embodiment, the ultrasonic transducer 22 is normally completely immersed in the bath 10 during the process. The transducer 22 is located beneath the path of the printed wiring boards 26 and adjacent to the first major surfaces 28.

In this embodiment, the ultrasonic generator 22 is positioned with its exterior transducer surface (its upper surface) less than about 5 cm from the path of the printed wiring boards 26. Alternative values for this dimension are about 3 cm from the path, about 3.3 cm from the path, or about 3.18 cm from the path.

Alternatively, the transducer may be partially immersed, or the transducer 22 may be positioned above the path of the printed wiring boards 26, adjacent to their second major surfaces 30. The ultrasonic transducer 22 can be an immersible transducer operated at a frequency of 25 kHz and a power of about 1 watt. Any other suitable transducer can instead be used.

The conveyorized horizontal apparatus of Figures 2-4 can also include multiple tanks 12 or other apparatus in sequence for carrying out a series of bath treatment steps on a printed wiring board 26. In this example, the indicated apparatus can be used for a cleaning/conditioning step (carried out in one bath), for a conductive colloid application step (carried out in another bath), or both. Conventionally, a rinsing step is interposed between these two process steps. Conveniently, the rinsing step may be a spray rinsing step.

Ultrasonic energy used in other cleaning baths, such as a deburring bath for removing drilling debris from through holes, may also reduce the amount of blowholing in a given installation.

Examples 1-4

A copper-clad printed wiring board coupon having a variety of through holes was desmeared, cleaned, and conditioned. A 500 ml working bath of Electrochemicals Inc. SHADOW® II conductive graphite aqueous dispersion was made by diluting the dispersion as sold with water to 5% solids. Example 1 was a comparative example, for which the graphite dispersion was not exposed to ultrasonic energy. The dilute graphite dispersion was coated on the printed wiring board coupon and fixed, dried, and micro-etched as recommended by Electrochemicals Inc. to prepare the coupon for electroplating. The coupon was electroplated with copper at 270 amperes per square meter for ten minutes.

The coupon of Example 1 was examined by back-light testing the coupon through holes for plating defects. The plating sample was given an overall score on a scale of 1-10, with 10 representing through hole plating with no discernable defects. At the same time, the sample was evaluated directly for pinhole, small patch, and medium patch plating defects. For these evaluations, fewer defects of each kind represent better plating uniformity. The results are set out in Example 1 of Table 1.

Example 2 was carried out like Example 1, except that the diluted SHADOW® II graphite dispersion was placed in the treatment tank of a SONICOR SC-40 ultrasonic generator (obtained from Sonicor Instrument Corp., Copiague, New York) and exposed to ultrasonic energy at 60 kHz, 55 watts, for five minutes. The treated dispersion was immediately applied to the coupon and the remaining steps defined in Example 1 were carried out. Example 3 was carried out like Example 2, except that the ultrasonic treatment time was increased to 15 minutes.

Example 4 was carried out in a slightly different manner. Instead of using a SHADOW® II graphite dispersion, another commercially available graphite dispersion was employed. The dispersion at 22% solids was treated with ultrasonic energy for 15 minutes in the manner described previously. After the ultrasonic treatment, the dispersion was diluted to 5% solids and then used and evaluated as described in Examples 1-3.

The results of Examples 1-4 are presented in Table 1. Looking first at Examples 1 (control -- no ultrasonic treatment), 2 (5-minute ultrasonic treatment), and 3 (15-minute ultrasonic treatment), the backlight score progressively improved from 6.5 for Example 1 to 9.5 for Example 2 to 10.0 -- the best score -- for Example 3. Similarly, from Example 1 to Example 3 the number of pinholes decreased dramatically, as did the numbers of small and medium patches. These results confirm the unexpected benefit, to coating uniformity, of pretreating the graphite dispersion with ultrasonic energy before using the dispersion to render through holes conductive.

The benefit of ultrasonic treatment is not lost if, after the graphite dispersions are prepared and ultrasonic energy is applied to them, the dispersions are allowed to stand for from one day up to four days or more, then retested. The disclosed ultrasonic treatment also can be used more than once to improve the coating performance of the dispersion. Repeated ultrasound treatments provide some benefit over a single treatment, particularly for reducing the number of pinholes.

Examples 5-10

Table 2 illustrates the use of ultrasonic energy in a cleaner/conditioner bath, and its effect on the number of blowholes and total defects on printed wiring board panels. The boards in question were cleaned and conditioned in one bath, coated with SHADOW® colloidal graphite, microetched, electroplated, wave soldered, and then evaluated visually for instances of solder shock and for all defects. The incidence of defects was calculated in "ppm" -- the number of defective holes per million holes in all the boards in one example.

Examples 6, 7, and 10 are most directly comparable, as the same type of circuit board was used in each instance. These examples illustrate that the use of ultrasonic energy reduced both the frequency of blowholes and the frequency of total defects. Examples 5, 8, and 9 performed on other boards illustrate the elimination of blowholes and other defects by carrying out an ultrasonic treatment.

Examples 11-14

Soldering defects were measured on a series of identical test panels processed in conveyorized horizontal process apparatus. "Cleaner/conditioner type" in Table 3 represents the SHADOW® cleaner/conditioner used for a particular test. Cleaner/conditioner I and Cleaner/Conditioner IV are two different commercially available formulations. The "%" figures in Table 3 indicate the proportion of the as-sold cleaner/conditioner used in the bath. The cleaner/conditioner bath was provided with two immersible ultrasonic units; a 25 kHz and a 40 kHz unit. Both units operated at 1000 watts. The ultrasonic transducers were placed 32 mm. from the bottom of the panel.

The results, tabulated in Table 3, are measured in terms of Total Solder Defects, which include blowholes, partial-fills and no-fills. Table 3 illustrates that a substantial improvement in soldering defects was made by switching to Cleaner/Conditioner IV. However, an additional improvement was made by generating ultrasonic energy in the Cleaner/Conditioner bath during processing. (Compare Example 12 to Examples 13 and 14).

Examples 15-21

In these Examples the effects of putting ultrasonic generators in either or both of the cleaner/conditioner IV bath and the SHADOW® graphite dispersion bath were determined. In these tests SHADOW® cleaner/conditioner IV was used at the recommended dilution as the cleaner/conditioner. Shadow® II graphite dispersion was used at the recommended 1:1 dilution. The test apparatus is the dual-frequency arrangement used in Examples 11-14.

The incidence of defects was measured for these examples by using the Hot Oil Test to measure the proportion of through holes which release visible gas when immersed in a body of essentially non-volatile liquid held at an elevated temperature substantially exceeding the boiling temperature of water. The gas may be water vapor, air or other gases.

5 cm square coupons, each having 70 through holes, were prepared according to the present invention or a control, then electroplated. Each coupon was immersed in a hot oil bath and viewed via a video camera which provided an enlarged image of the coupon on a monitor. The presence or absence of gas bubbles under the test conditions was noted for each through hole. The test was scored by counting the number of outgassing through holes, multiplying that number by (100%/70 holes), and reporting the total as a percent. In the Hot Oil Test, the percentage result reported represents the incidence of defects; a lower result indicates fewer defects, thus better performance.

The results of Examples 15-21 are tabulated in Table 4. First, compare Example 15, where the ultrasonic generator was turned off in the SHADOW® bath, with Examples 16-20, where the ultrasonic generator in the SHADOW® bath was turned on for the indicated periods. Because the ultrasonic generator was on in the cleaner/conditioner bath in Examples 16-20, the hot oil test result yielded few defects, with or without ultrasonic energy in the graphite dispersion. Next, compare Examples 20 and 21, in which the same ultrasonic conditions were maintained in the graphite dispersion bath, while the ultrasonic generator in the cleaner/conditioner was on in Example 20 and off in Example 21. Turning on the ultrasonic energy in the cleaner/conditioner reduced the incidence of defects from 73% to 0%.

Examples 22-27

Examples 22-27 were carried out to evaluate the effect of the amount of time the panels were exposed to ultrasonic energy in a SHADOW® Cleaner/Conditioner IV bath. For this study 5 cm by 5 cm hot oil test coupons were used. For each example, two coupons supported on wire hooks were processed vertically through a SHADOW® beaker line. The results of the two coupons were separately reported for each example. The cleaner/conditioner bath was SHADOW® cleaner/conditioner IV, at the recommended dilution, in a 1 liter ultrasonic unit model #BL-12, operated at 80 Watts and 40 kHz, at 57°C.

Table 5 shows that the 40 kHz ultrasonic unit was able to improve the hot oil test results. Applying ultrasonic energy for a period between about 30 seconds and one minute during the cleaning/conditioning step improved the hot oil test result; the result was not further improved by applying the ultrasonic energy for a longer time.

Examples 28-30

In Examples 28-30, the concentration of the cleaner/conditioner was varied to determine what effect that might have on the results. SHADOW® Cleaner/Conditioner IV was used except in Example 28, where SHADOW® cleaner/conditioner III was used, as noted in Table 6. The table shows that cleaner/conditioner concentrations of 1% to 10% of the as-sold composition all performed well in the hot oil test.

Examples 31-32

Two sets of panels consisting of five laminate types were drilled at three different locations. One set was processed at by one shop without ultrasound in the cleaner. A few months later, after an ultrasound unit was placed in the cleaner, the second set was processed in the same shop. The frequency of the ultrasound used was 25 kHz.

Table 7 demonstrates that the addition of ultrasonic energy dramatically reduced the incidence of blowholes -- from 12,069 ppm to 319 ppm.

Examples 33-36

In these Examples, dual frequency ultrasonic process equipment substantially like that of Examples 11-14 was used. Two different commercial SHADOW® cleaner/conditioner formulations (I and IV), each diluted to 20%, were evaluated. Table 8 tabulates the results. Examples 33 and 34 demonstrate that SHADOW® cleaner/conditioner IV itself provided many fewer blowholes and other defects than SHADOW® cleaner/conditioner I. Examples 34 and 35-36 again show that the introduction of ultrasonic energy in the cleaner/conditioner makes a further, substantial reduction in the incidence of blowholes and other defects, with a dual frequency ultrasonic arrangement providing the best results.

Examples 37-39

Table 9 shows further results of carrying out the present process using 25 kHz ultrasonic generators in the SHADOW® Cleaner/conditioner and graphite dispersion baths.

First, compare Examples 37 and 38. Employing ultrasound in the SHADOW graphite dispersion in Example 38 reduced both the incidence of blowholes and other defects, versus Example 37 which was carried out without ultrasound in the graphite dispersion.

Now compare Examples 37 and 39, which differ in that ultrasound is used in the cleaner/conditioner in Example 37, but not in Example 39. Here, no benefit was observed in the number of blowholes, but some benefit was observed in the number of other defects. In this particular experiment, therefore, ultrasonic energy in the graphite dispersion was the more decisive factor reducing the number of blowholes and other defects.

In summary, the present invention is practiced by treating any one or more of a conditioner, a cleaner/conditioner, and a conductive carbon coating composition, using an ultrasonic generator or equivalent means, when or shortly before the composition is applied to a non-conductive substrate.

The present invention allows one to deposit a more controlled and uniform coating of conductive carbon particles than before on the non-conductive surface of a through hole. This carbon coating can be electroplated, and the resulting electroplating will be unexpectedly better than the electroplating deposited on a carbon coating which is not subjected to ultrasonic energy before or while it is applied. The present invention also allows one to avoid the formation of blowholes and other soldering defects later in the processing of the printed wiring boards when they are exposed to solder.

TABLE 1

Example:	1	2	3	4
Original Ultrasonic time (minutes)	0	5	15	15[1]
Delay After Original Ultrasound (days)	0	0	0	0
Plating time (minutes)	10	10	10	10
Backlight score (scale: 1-10)	6.5	9.5	10.0	9.5
# of pinholes/hole (average)	40	5.6	0	2.8
# of small patches/hole (average)	7	0	0	0.2
# of medium patches/hole (average)	0	0	0	0

1. For example 4 the graphite dispersion was treated with ultrasonic waves at its as-sold concentration, then diluted to its working concentration.

TABLE 2

Ex.	# of panels	Holes/ Panel	Ultra - sound	Blowholes (ppm)	Total defects (ppm)
5	4	600	yes	0	-
6	11	2400	yes	0	0
7	6	2400	no	1042	high
8	5	200	yes	0	0
9	2	700	yes	0	0
10	5	2400	yes	0	0

TABLE 3

#	Cleaner/ Conditioner Type	Ultrasonics	Total Solder Defects
11	I at 20%	None	43,358 ppm
12	IV at 20%	None	6,146 ppm
13	IV at 20%	25 and 40 kHz	660 ppm
14	IV at 20%	25 kHz	1,075 ppm

TABLE 4

#	Ultrasonic in Cleaner/Conditioner IV	Ultrasonic in Shadow® On/Off	Hot Oil Test
15	1.5 minutes	Off	4% 3%
16	1.5 minutes	30 seconds on 3 minutes off	1.5% 4%
17	1.5 minutes	1 hour on before test, 30 seconds on during the test, 3 minutes off	0% 0%
18	1.5 minutes	5 hours on before test, 30 seconds on during the test, 3 minutes off	1.5% 3%
19	1.5 minutes	5 hours on before test, 3 minutes on during the test	1.5% 1.5%
20	1.5 minutes	5 hours on before test, off during the test	0% 0%
21	Off	5 hours on before test, Off during the test	70% 73%

TABLE 5

Test Number	Ultrasonic Time in Cleaner/Conditioner IV	Hot Oil Test
22	0	20% 15%
23	30 seconds	6% 8%
24	1 minute	1.5% 0%
25	2 minutes	3% 1.5%
26	3 minutes	0% 3%
27	6 minutes	1.5% 0%

TABLE 6

Test No.	Formula	Hot Oil Test
28	1%*	0% 0%
29	5%	0% 0%
30	10%	0% 0%

* SHADOW® cleaner/conditioner III was used in this instance

TABLE 7

Ex.	Ultrasound?	Blowholes (ppm)	Other Defects (ppm)
31	no	12069	56944
32	yes	319	20444

TABLE 8

Ex.	Cleaner	Ultra-sound	Blowholes (ppm)	Other Defects (ppm)
33	C/C I	none	32879	10479
34	C/C IV	none	3960	2186
35	C/C IV	25 kHz and 40 kHz	495	165
36	C/C IV	25 kHz	907	168

TABLE 9

Ex.	Ultrasound in Cleaner?	Ultrasound in Shadow®	Blowholes (ppm)	Other Defects (ppm)
37	yes	no	625	5000
38	yes	yes	156	2812
39	no	no	625	8125

CLAIMS:

1. In a method for treating a non-conductive through hole surface of a printed wiring board, including the steps of:

A. providing a printed wiring board including at least one through hole;

B. providing at least one bath which is useful for at least one of the steps of conditioning and applying a conductive coating to said through hole; and

C. at least partially immersing said through hole in said at least one bath;

the improvement characterized by the step of introducing ultrasonic energy in said at least one bath, beginning not later than at the end of said immersing step, under conditions effective to at least reduce the formation of blowholes during later processing of the printed wiring board.

2. The method of claim 1, wherein said at least one bath is a through hole conditioning composition.

3. The method of claim 1, wherein said at least one bath is an aqueous conductive carbon dispersion.

4. The method of claim 1, wherein said at least one bath is an aqueous conductive graphite dispersion.

5. The method of claim 1, wherein said ultrasonic transducer generates ultrasonic waves having a frequency between 16 kHz and 100 kHz.

6. The method of claim 1, wherein said ultrasonic transducer generates ultrasonic waves having a frequency between 20 kHz and 50 kHz.

7. The method of claim 1, wherein the step of introducing ultrasonic energy is carried out by placing an ultrasonic generator in said at least one bath.

8. The method of claim 7, wherein said ultrasonic generator is positioned less than 5 cm. from said printed wiring board.

9. The method of claim 1, comprising the further steps of:

A. providing at least one other bath which is useful for at least one of the steps of cleaning, conditioning, and applying a conductive coating to said through hole;

B. at least partially immersing said through hole in said at least one other bath; and

C. beginning not later than at the end of said immersing step in said at least one other bath, introducing ultrasonic energy in said at least one other bath in the vicinity of said through hole under conditions effective to at least reduce the formation of blowholes during soldering of the printed wiring board.

10. A conductive coating on a substrate, made by the method of claim 1.

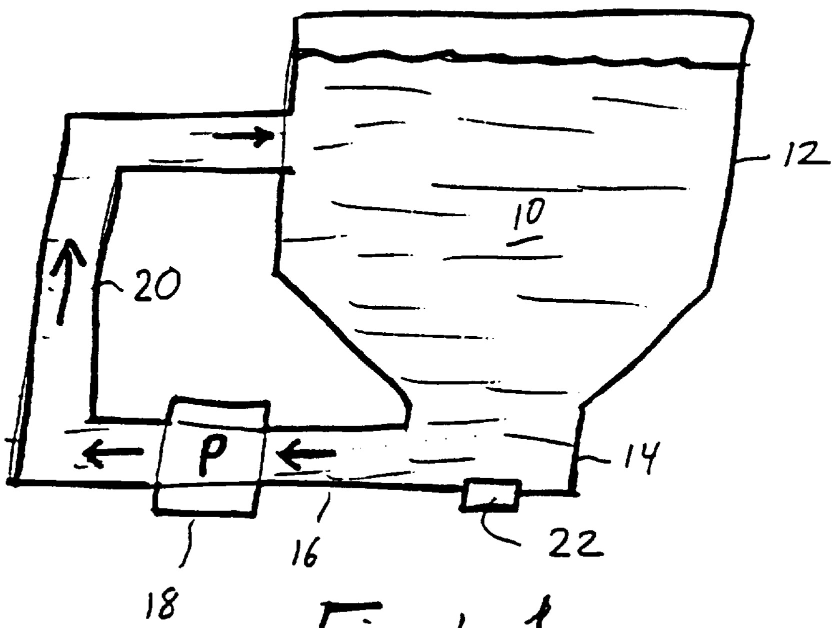


Figure 1

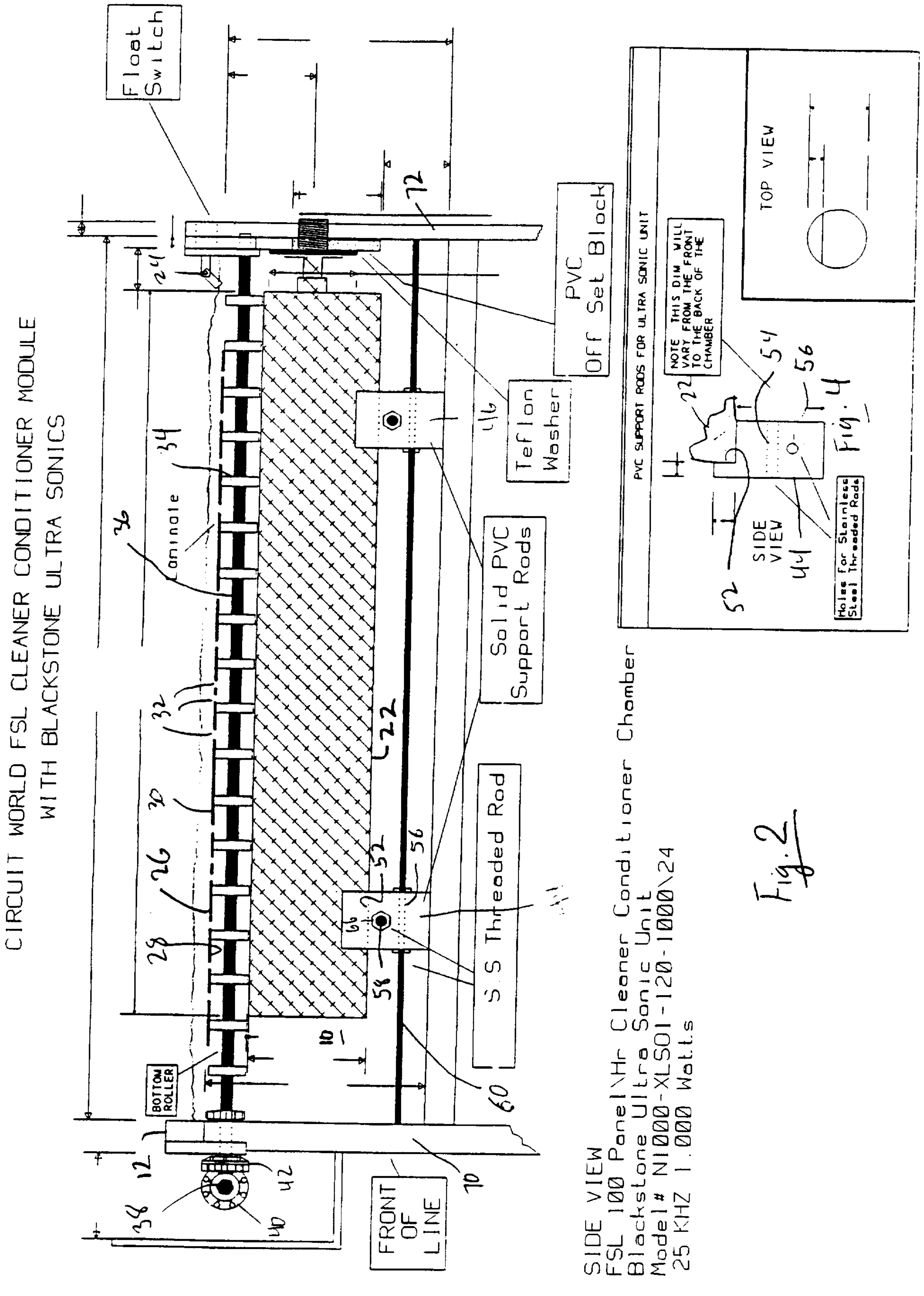

CIRCUIT WORLD FSL CLEANER CONDITIONER MODULE
WITH BLACKSTONE ULTRA SONICS
Float Switch
PVC Off Set Block
Teflon Washer
Solid PVC Support Rods
S.S Threaded Rod
Laminate
BOTTOM ROLLER
FRONT OF LINE
SIDE VIEW
FSL 100 Panel\Hr Cleaner Conditioner Chamber
Blackstone Ultra Sonic Unit
Model# N1000-XLS01-120-1000\24
25 KHZ 1.000 Watts
PVC SUPPORT RODS FOR ULTRA SONIC UNIT
NOTE THIS DIM WILL VARY FROM THE FRONT TO THE BACK OF THE CHAMBER
TOP VIEW
SIDE VIEW
Holes For Stainless Steel Threaded Rods
Fig. 4
10
12
22
24
26
28
30
32
34
36
38
40
42
44
46
52
54
56
58
60
66
70
72

Fig. 2

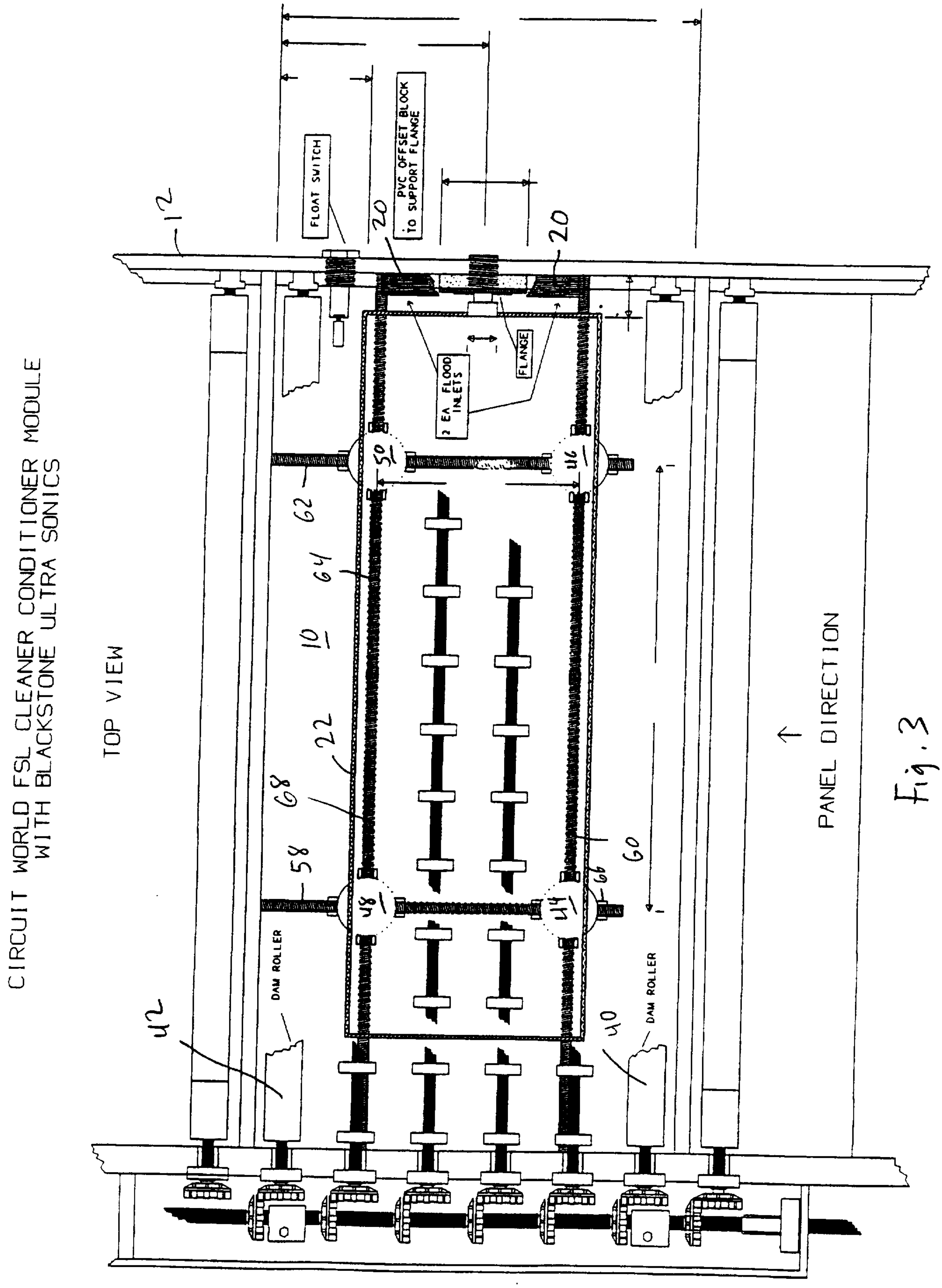

CIRCUIT WORLD FSL CLEANER CONDITIONER MODULE
WITH BLACKSTONE ULTRA SONICS
TOP VIEW
FLOAT SWITCH
PVC OFFSET BLOCK
TO SUPPORT FLANGE
2 EA FLOOD
INLETS
FLANGE
DAM ROLLER
DAM ROLLER
PANEL DIRECTION
12
20
20
50
46
62
64
10
22
68
58
48
44
66
60
42
40

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/01498

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :C01B 31/00.
US CL :204/157.15, 157.42; 205/125, 166.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
U.S. : 204/157.15, 157.42; 205/125, 166.

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 practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,351,539 A (BRANSON) 07 NOVEMBER 1967, see Figure 1 and col. 3, lines 17-22.	1-9.
Y	US 3,807,704 A (JANZEN ET AL) 30 APRIL 1974, see abstract and col. 1, line 64 through col. 2, line 37.	1-9.
X/Y	US 5,139,642 A (RANDOLPH ET AL) 18 AUGUST 1992, see abstract; col. 4, lines 31-35 ;col. 7, lines 41-68; col. 10, lines 22-38; col. 11 lines 15-37; and col. 13, lines 52-65.	1-4 and 9-10/7-8

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* 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 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 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
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 MARCH 1997	08 MAY 1997

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230

Authorized officer
KATHRYN GORGOS
Telephone No. (703) 308-0661