

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
18 May 2006 (18.05.2006)

PCT

(10) International Publication Number
WO 2006/050792 A1

(51) International Patent Classification:

C23C 18/22 (2006.01) H05K 3/00 (2006.01)
H05K 3/38 (2006.01)

(21) International Application Number:

PCT/EP2005/011231

(22) International Filing Date: 19 October 2005 (19.10.2005)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

04026653.8 10 November 2004 (10.11.2004) EP

(71) Applicant (for all designated States except US):

ATOTECH DEUTSCHLAND GMBH [DE/DE];
Erasmusstrasse 20, 10553 Berlin (DE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **PIEL, Merten**
[DE/DE]; Bochumer Strasse 18, 10555 Berlin (DE).
STAMP, Lutz [DE/DE]; Räuschstr. 52, 13509 Berlin 52
(DE). **MOEPERT, Christiane** [DE/DE]; Schwalbacher
Strasse 7, 12161 Berlin (DE).

(74) Agents: **ALBRECHT, Thomas** et al.; Kraus & Weisert,

Thomas-Wimmer-Ring 15, 80539 München (DE).

(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY,
MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO,
NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK,
SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

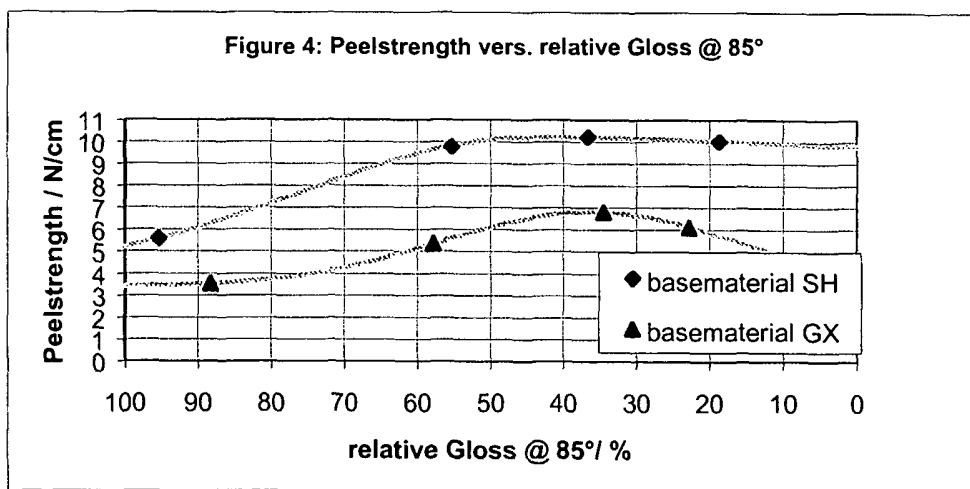
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT,
RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: METHOD FOR METALLIZING INSULATING SUBSTRATES WHEREIN THE ROUGHENING AND ETCHING
PROCESSES ARE CONTROLLED BY MEANS OF GLOSS MEASUREMENT



(57) Abstract: The invention relates to a control of etching processes of insulating substrates by means of gloss measurement. By this method a surface roughness can be achieved which leads to good adhesion of metals layers deposited in subsequent metallization steps. This method is particularly suited for the production of printed circuit boards.

**METHOD FOR METALLIZING INSULATING SUBSTRATES WHEREIN THE
ROUGHENING AND ETCHING PROCESSES ARE CONTROLLED BY MEANS
OF GLOSS MEASUREMENT**

5 Description of the invention

The invention relates to a method for metallizing insulating substrates by etching the insulating substrates with etching solutions at a concentration, at a temperature and for a time sufficient to achieve roughening of the surface of said substrates and subsequent metallization, wherein the roughening and etching
10 processes are controlled by means of gloss measurement. By this method a surface roughness can be achieved which leads to good adhesion of metals layers deposited in subsequent metallization steps. This method is particularly suited for the production of printed circuit boards.

Prior to the metallization of non-conductive substrates, pretreatment of the surface
15 is necessary in order to achieve good adhesion properties of the metal coat. The adhesion properties may be measured as peel strength. Generally a peel strength of preferably 2 – 20 N / cm, most preferably 6 – 10 N / cm is required.

The kind of plastics to be used is not specifically limited, and includes various plastics heretofore known. Examples are general-purpose plastics heretofore
20 extensively used for chemical plating such as ABS resins, general-purpose engineering plastics having a heat resistance at 150°C or less, such as polyamides (nylon PA), polyacetals (POM), polycarbonates (PC), modified polyphenylene ethers (PPE), polybutylene terephthalates (PBT) and the like, super engineering plastics having a heat resistance at 200°C. or more, such as
25 polyphenylene sulfides (PPS), polyether sulfones (PES), polyether imides (PEI), polyether ether ketones (PEEK), polyimides (PI), liquid crystal polymers (LCP) and the like, polymer alloys such as polycarbonate/ABS resins and the like.

Base materials used for the production of printed circuit boards (PCB's) comprise, for example, a rigid non-conducting or dielectric base made up of a fibrous material such as glass fibers, paper and the like in combination with a polymer such as an epoxy resin. Multilayer boards (MLB's) comprise several PCB's
5 laminated to one another by means of an adhesive. In addition to rigid boards (as described above), flexible boards can be produced employing thermoplastic dielectric layers such as fluorocarbon polymers, Nylon polymers, polyimides, Kevlar-reinforced polymers, polyparabanic acids and polyesters. Flexible boards are manufactured without fiber reinforcing. Production of both of these types of
10 printed circuit boards are described in Printed Circuits Handbook, Second Edition, edited by C. F. Coombs, Jr., McGraw-Hill, 1979, which is incorporated herein by reference. Laminated combinations of flexible and rigid boards are also finding utility in some applications for MLB's.

Additionally substrates can be applied which comprise rigid base layers and non-
15 reinforced layers made for example from epoxy resin.

In a first step a substrate is treated with a swelling solution. Conventional swellers which usually comprise an organic swelling agent and a base like sodium hydroxide can be used.

Subsequently the surface of the substrate to be treated is etched. The etching
20 treatment selectively dissolves the surface of resin substrate to achieve an anchor effect. This treatment can improve the adhesion of the electroplated coating and the appearance of the coating surface. The etching procedure is carried out by various methods. For example, the substrate to be treated is immersed in a properly heated mixed solution of chromic acid and sulfuric acid. When a substrate
25 of ABS resin is treated, the etching treatment dissolves out butadiene rubber as a constituent due to oxidative effect of chromic acid, giving anchor pores of about 1 to about 2 μm in pore size on the resin substrate, while the butadiene is caused to undergo oxidative decomposition, producing a polar group such as a carbonyl group.

After pretreatment and prior to applying the metal coat, and in order to promote its deposition on the non-conductive surface, the non-conductive surface is treated - for example with a two step activator comprising a stannous chloride sensitizer solution followed by a sensitizer solution of divalent palladium chloride according to the process of Bergstrom et al., U.S. Pat. No. 2,702,253.

Thereafter a first and often second and final metal layer is being deposited. The applied electroless metal coating often is copper. In this case, a solution being applied contains cupric ions and a reducing agent such as formaldehyde, which reduces the cupric ions in the solution to copper metal when in the presence of palladium, which acts as a catalyst for the reduction. The electroless copper may have subsequent metal coatings applied to it by electrolytic means.

When manufacturing multilayer circuits, it is necessary to carry out a preliminary process to remove resin smears resulting from forming a bore. The removal of these smears should insure a reliable contact of conducting multilayers-copper inner layers with a chemically formed copper coating. The purification of the bore effected by removal of epoxide, with simultaneous roughening of the outer surface of the substrate, insures in addition a better adhesion of the subsequently deposited metal coating.

Since roughening of the substrate surface and desmear are achieved at the same time, only one of both parameters has to be controlled during the treatment. In the following, the term "etching" is used to denote both roughening of the surface and desmear where applicable.

Good adhesion of the metal layer is important above all because of the thermal load which the circuit board is exposed to during subsequent soldering. It is known to carry out the above-mentioned preliminary process with alkaline potassium or sodium permanganate solutions, when, as a rule, before oxidation, swelling with an organic solvent and/or a surface-active agent is carried out, which however requires significant treatment time. Because, in most cases, only small backetching rates are achieved, it has already been proposed to increase the etching rates, for example, by using ultrasound, increase of the temperature,

increase of the concentration of permanganate by using sodium permanganate or increase of OH-ion concentration.

Numerous methods are known for removing resin smear and roughening the surface of an insulating surface. One approach is a mechanical one and involves channeling a dry or wet stream of abrasive particles through such holes. A similar method is the use of hydraulic pressure to force a thick slurry of abrasive material through the holes. However, these mechanical methods are generally slow and difficult to control. Furthermore, complete removal or smear in all holes in a given circuit board is difficult to achieve.

- 5 Chemical methods have also been used to desmear holes. Generally, the chemicals used attack the smeared resinous coating. The chemicals include, for example, concentrated sulfuric acid (down to about 90 percent concentration). Smeared epoxy resin, which is usually less than about 0.001 inch thick, can be removed with about one minute's treatment with concentrated sulfuric acid.
- 15 Unfortunately, the high sulfuric acid concentration required is very hazardous and requires extraordinary precautions by operators. Also, undesirably rough holes are produced. In addition, the concentrated sulfuric acid rapidly absorbs water, which limits its useful life span and can cause variations in the immersion times required to desmear the holes.
- 20 Another chemical smear removal agent which has been employed is chromic acid. While it is easier to control etch rates with chromic acid because it is a slower etchant than concentrated sulfuric acid, it still requires operator caution and special equipment. Permanganate has also been used for smear removal and for etching of various materials. For example,
- 25 US 3,506,397 relates to the treatment of ABS resin with a composition containing phosphoric acid and potassium permanganate.

US 3,598,630 and US 3,647,699 are also related to phosphoric acid/potassium permanganate solutions for treating ABS polymers.

Increased etching efficiency has also become desirable because in many situations it is necessary that the etchant composition not only be capable of desmearing small areas of resin, but also be capable of "etching back" the resin. The term "etchback" is used in the art to refer to the removal of resin from, for example, the barrel of a hole in a printed circuit board to expose a portion of the layers of copper or the like. In essence then, the copper layer protrudes slightly into the hole in the board. While for practical purposes etchback is any resin removal which is greater than simple desmearing, in some cases rather specific etchback requirements are necessary.

- 10 US 5,019,229 describes a method of and an apparatus for etching an epoxy resin having a high backetching rate, in particular bores with printed circuit boards, with stable, strong, basic alkaline permanganate etching solution wherein the solution is stabilized by electrochemical anodal oxidation, and permanganate and OH-ion concentration is controlled by measuring the same by using electrochemical and/or photometric measuring method with subsequent metering of the solution in accordance with deviation of a measurement value from a nominal value.

The methods for improving the control of roughening and desmear developed so far have been almost exclusively focused on optimizing the composition of the etching solution. They all have the drawback that during the process the chemical composition and concentration of the compounds changes which results in unreliable desmear and roughening results.

The control of etching of a copper metal surface with optical devices is already known from the literature. In JP 01-298790 the etching completion time in fabrication of printed circuit boards is determined by observing the intensity change of a monitoring light reflected from the board. For etching solutions for copper containing ammonium salts, the proper wavelength described is 390-496 nm. The reflected light intensity changes used for the endpoint determination may also be used for controlling such conditions as a rate of transporting the laminates, concentration of the etching solution, etching temperature, etching solution feed rate and etchant removal conditions.

Muenzel et al. in "New dielectric materials for microvia technology", Technical paper S01-1, IPC, 1998, p.14 found that gloss and copper peel strength depend on the curing temperature of the metallized base material. A one hour bake at a temperature of 150°C was used after 0.7 µm chemical copper plating. The measured peel strength data correlate with the enhanced surface roughness achieved at higher curing temperatures. However, Muenzel et al. do not teach the correlation between the peel strength and surface gloss / roughness and the utilization of its optimum ratio in controlling desmear / etching processes. Furthermore, Muenzel et al. suggest that only a higher curing temperature leads to increased peel strength.

Therefore, it is the aim of the present invention to provide a method for easy and reliable control of the roughening and desmear processes for non-conductive surfaces.

This aim is achieved by a method for metallizing insulating substrates comprising the steps of etching said insulating substrates with etching solutions at a concentration, at a temperature and for a time sufficient to achieve roughening and/or desmear of the surface of said substrates, and subsequent metallizing, which method comprises the following steps:

- (i) etching the substrates using varying etching parameters selected from etching temperature, etching time and etchant concentration,
- (ii) determining the gloss value of the surface of the etched substrates obtained in step (i) above by an optical gloss device,
- (iii) metallizing the etched substrates obtained in step (i) above,
- (iv) determining the peel strength of the metallized substrates obtained in (iii) above,
- (v) correlating the peel strength and the gloss value obtained in (ii) and (iv) above,

(vi) using said correlation to determine the gloss value correlating with the maximum peel strength and

(vii) controlling the etching parameters such that any deviation of the actual gloss value from the gloss value obtained in step (vi) is minimized.

5 Thus, according to the present invention, an easy to apply optical control device is used to monitor the etching process in order to achieve the desired surface appearance and a good adhesion during the metallization steps.

Surprisingly, the applicant found a clear correlation between the gloss of the treated substrate surface and the peel strength of metal coats deposited
10 subsequently. This correlation can be used to determine optimized treatment parameters for various substrate materials irrespective of the etching composition used. Therefore, it offers a method which is universally applicable for all kinds of surface treatment processes.

Typical parameters used to control the etching process are treatment time,
15 temperature and concentrations of compounds applied in the etch solutions.

For this purpose a standard gloss meter like REFO 3-D by Hach Lange is applied. Gloss meters are devices that illuminate a test surface at a defined angle of incidence and measure the amount of light at a defined angle of reflection. Specular gloss is quantified by measuring the amount of light reflected from the
20 sample and comparing it with the amount of light reflected when a polished black glass calibration standard is measured under the same conditions. The glass standard is assigned a value of 100 gloss units and in practice the highest attainable gloss values for non-metallic paints tend towards 95 gloss units.

Additionally to the absolute gloss value, a relative gloss value may be assigned in
25 the current invention. It is set to 100% per definition for the amount of light reflected from the corresponding substrate without applying swelling and desmear processes:

$$\text{relative gloss value} = \frac{\text{current gloss value}}{\text{gloss value of unetched surface}} \cdot 100\%$$

In the present invention the decrease of gloss (ratio between starting value and actual value) after treatment in the etching baths correlates well with the degree of surface roughening (the area of the original smooth outer layer diminishes). This -
5 at first - leads to an increase in peel strength.

As shown in Fig. 1, further etching may lead to lower peel strength values (over etching), this can still be seen and judged by a further decrease of gloss, but often not in any increase of roughness data (e.g. obtained by interferometer).

The knowledge of the relation between gloss and peel strength enables a constant
10 control of the etching process within an optimal range.

Possible changes in the power of etching attack (e.g. during ageing of production bathes) can be easily discovered and corrected.

One suitable instrument for gloss measurement is the REFO 3-D reflectometer by Hach Lange with inspection angles of 20°, 60° and 85°. A preferred angle for the
15 present purpose is 85°.

Advantages of the present invention are:

- Ability of controlling the roughening process within an optimal range regarding:
minimum possible roughness and maximum possible peel strength of the
20 applied metal layers
- Easy, fast and cheap analysis (online analysis is possible)
- Non-destructive analysis (non touching, automatic measurement is possible)

- Cost saving compared to usually necessary analysis method consisting of plating (electrolessly & galvanically) followed by tempering and peel strength measurement
- Possibility of statistical evaluation of evenness of resin cure process (lamination) and desmear process, e.g. within each panel (different areas) or per basket or per lot

The determination of the treatment parameters of the substrate in the etching composition is in the following explained for adjusting the treatment time. It may similarly also applied for optimizing other suitable parameters.

- 10 After applying a sweller, the insulating substrate is treated with an etching composition at different etch times. Practically useful have proven intervals of t/min = 0, 2, 6, 8, 10, 12, 15, 20, 25, 30. In most cases, a maximum treatment time of 15 min is useful.

Any suitable etching solution can be used for etching a non-conductive substrate.

- 15 Solutions based on permanganate and chromic acid respectively are most widely used. The term "etchant concentration" is in the following described choosing these two solutions, but may as well be applied to any other etching solution.

- Etching solutions based on permanganate contain either potassium or sodium permanganate, optionally sodium and potassium manganate and one or more bases to adjust the pH to a value of about 13 – 14.
- 20

- Preferred concentrations of potassium permanganate are 10 – 150 g/l, more preferably 40 – 100 g/l, of sodium permanganate 20 – 200 g/l, more preferably 60 – 100 g/l. Sodium and potassium manganate can be applied in preferred concentrations of 5 – 50 g/l. Bases used can be sodium or potassium hydroxide in a concentration of 20 – 200 g/l and sodium or potassium carbonate (20 – 200 g/l) etc.
- 25

In this case etchant concentration relates to the concentration of sodium or potassium permanagante, sodium or potassium managante and the bases, for example sodium or potassium hydroxide or sodium or potassium carbonate.

Etching solutions based on sulfuric acid and chromic anhydride generally contain
5 sulfuric acid in a concentration of about 50 – 1500 g/l, more preferably 200 – 800 g/l and chromic anhydride in a concentration of about 30 – 800 g/l, more preferably 50 – 300 g/l. Etchant concentration relates to the concentration of sulfuric acid and chromic acid.

Figure 2 shows the decrease in relative gloss in % versus the dwell time (etching
10 time) for a permanganate etch system.

After the etching steps the such treated substrate is metallized, preferably with copper. After metallization the peel strength of the coating is measured. The peel strength is an indicator for the adhesion properties of the metal coating.

Generally a peel strength of preferably 2 – 20 N / cm, most preferably 6 – 10 N /
15 cm is required.

The peel strength was measured by pulling stripes of 10mm width of the metal layer deposited at a speed of 40mm / min using a drawing automat LCTM-6 by Chatillon and a Strength Measuring Instrument 708 manufactured by Erichsen.

As can be seen from Figure 3, the peel strength depends from the dwelling time of
20 the etching composition. It first increases with dwelling time, reaches a maximum and then decreases again. With the method according to the present invention an optimum dwelling time can easily be determined by choosing the maximum peel strength at a minimum dwelling time from a graph according to Figure 3. For example, according to Figure 3 one would choose a dwelling time for the
25 described permanganate etching composition of about 8 – 12 min. for both substrates.

Figure 4 illustrates the dependence of the peel strength of the metal coating from the relative gloss value. A maximum peel strength is achieved at a gloss value of about 55%.

Once the most suitable gloss value has been determined for a certain substrate
5 base material, both the relative and absolute gloss value can be applied to monitor etching processes continuously. In other words, once the correlation between the gloss value and the peel strength has been determined by proceeding as outlined above, it is only necessary to control the etching parameters such that any
10 deviation of the actual gloss value measured in the etching process from the pre-determined gloss value correlating with the maximum peel strength is minimized.

The invention is more specifically described by the following examples.

The base material used is either ABF-SH or GX (halogen-free), products of Ajinomoto Fine-Techno Co., Inc. Japan. All tests have been performed under the same conditions.

15 An overview over the process steps and conditions applied is given in Table 1.

After the usual pretreatment of the substrates according to the step 1., the substrate is then exposed to an etching composition with a composition according to step 2.

The gloss is measured before and after the swelling and etching steps. An
20 overview of the results is given in Table 2. The substrate is then metallized with copper applying a standard process *Neoganth* by Atotech Deutschland GmbH and as described in the process steps 4. – 12. in Table 1. The resulting peel strength of the copper coating is shown in Table 2.

Example Conditions**Table 1:** Process steps for treatment of insulating substrates applying an acidic manganate / permanganate etching solution

		Temperature T/°C	Time t/min
gloss measurement at an angle of 85° (before a)desmear)			
1.Sweller:		80	var.
Securiganth MV Sweller conc.	500ml/l		
NaOH	3g/l		
2.Permanganate:		80	var.
KMnO ₄	81g/l		
K ₂ MnO ₄	13g/l		
NaOH	39g/l		
Na ₂ CO ₃	88g/l		
3.Reduction:		44	2
Securiganth P 500 Reduction Solution	100ml/l		
H ₂ SO ₄	40ml/l		
b)gloss measurement @ 85° (after desmear)			
4.Conditioner:		44	2
Neoganth MV Conditioner	40ml/l		
5.Micro Etch:		23	1
Sodiumperoxodisulfate	150g/l		
H ₂ SO ₄	15ml/l		
6.Pre Dip:		23	1
Neoganth MV Pre Dip	10ml/l		
7.Activator:		44	4
Neoganth MV Activator	200ml/l		

	13		
pH	11,3		
8.Reducer:		23	2
Neoganth 406	2ml/l		
H ₃ BO ₃	5g/l		
9.Electroless Copper:		35	30
Printoganth MV Plus			
Cu	2g/l		
NaOH	6g/l		
HCHO, 28%	16ml/l		
9. a)Tempering		150	30
10.Acid Cleaner:		23	4
Cleaner FR	100ml/l		
H ₂ SO ₄	200ml/l		
11.Acid Dip:		23	1
H ₂ SO ₄	50ml/l		
12.Acid Copper:		23	85
Cupracid HL			
Cu	18g/l		
Current density	2A/dm ²		
12. a)Tempering		170	30

Rinsing with water for 1min after each process step (except after steps 6. & 11.)

Table 2: Process parameters for treatment of insulating substrates

Desmear dwell time / min		absolute Gloss 85°		relative Gloss 85° / %	
Sweller	Permanganate	ABF-SH	ABF-GX	ABF-SH	ABF-GX
0	0	75,0	85,5	100,0	100,0
1	2	71,5	75,5	95,3	88,3
3	6	41,5	49,5	55,3	57,9
5	10	27,5	29,5	36,7	34,5
5	15	14,0	19,5	18,7	22,8

Peelstrength / N/cm	
ABF-SH	ABF-GX
5,6	3,6
9,8	5,4
10,2	6,8
10,0	6,1

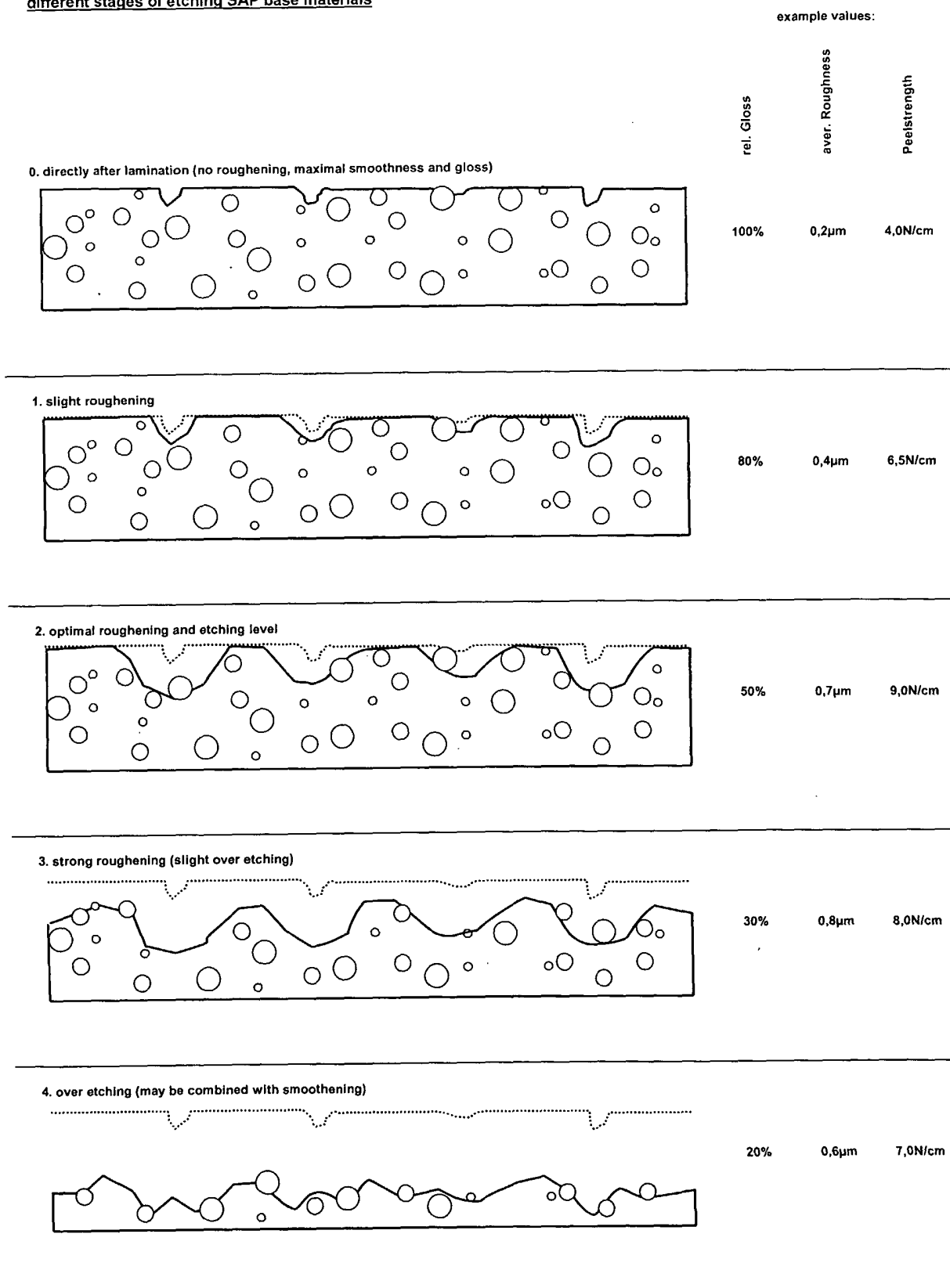
CLAIMS:

1. A method for metallizing insulating substrates by etching said insulating substrates with etching solutions at a concentration, at a temperature and for a time sufficient to achieve roughening and/or desmear of the surface of said substrates and metallizing said substrates, comprising the following steps:
- 5 (i) etching the substrates using varying etching parameters selected from etching temperature, etching time and etchant concentration,
- (ii) determining the gloss value of the surface of the etched substrates obtained in step (i) above by an optical gloss device,
- 10 (iii) metallizing the etched substrates obtained in step (i) above,
- (iv) determining the peel strength of the metallized substrates obtained in (iii) above,
- (v) correlating the peel strength and the gloss value obtained in (ii) and (iv) above,
- 15 (vi) using said correlation to determine the gloss value correlating with the maximum peel strength and
- (vii) controlling the etching parameters such that any deviation of the actual gloss value from the gloss value obtained in step (vi) is minimized.
2. The method according to claim 1 wherein the gloss value of the surface of said substrates is determined before etching to obtain the gloss value of the unetched surface and to calculate the relative gloss value of the surface of the etched substrates obtained in step (i) according to the following equation:
- 20

$$\text{relative gloss value} = \frac{\text{current gloss value}}{\text{gloss value of unetched surface}} \cdot 100\%$$

and wherein in steps (v), (vi) and (vii) said relative gloss value is used.

3. The method according to claim 1 wherein the substrate is a printed circuit board with or without drill holes.
4. The method according to claim 1 wherein the gloss value of the surface is measured at an angle between 20 – 90°.
- 5 5. The method according to claim 4 wherein the gloss value of the surface is measured at an angle ranging from 40° – 88°.
6. The method according to claim 3 wherein the gloss value of the surface is measured at an angle of about 85°.
7. The method according to claim 1 wherein the etching solution is a solution
10 containing sodium or potassium permanganate, sodium or potassium manganate and sodium or potassium hydroxide.
8. The method according to claim 1 wherein the gloss value is determined at different areas of the substrate to ensure homogeneous etching processes.
9. The method according to claim 1 wherein the etching parameters are varied
15 independently or in combination to achieve the desired gloss value.

Figure 1different stages of etching SAP base materials

2/2

Figure 2: Rel. Gloss @ 85° (REFO 3-D) vers. Perm. dwell time

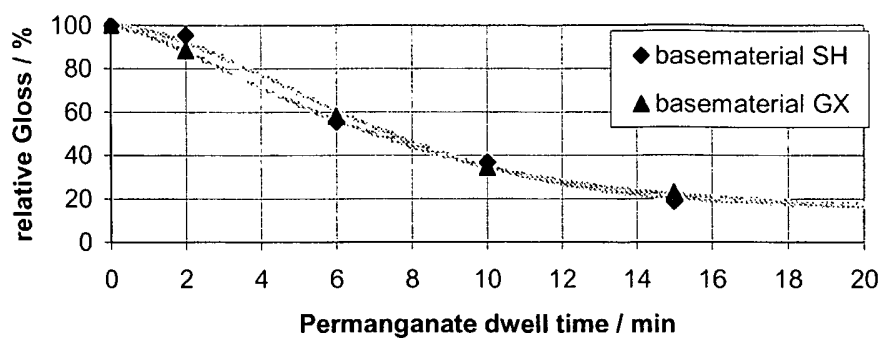


Figure 3: Peelstrength vers. Permanganate dwell time

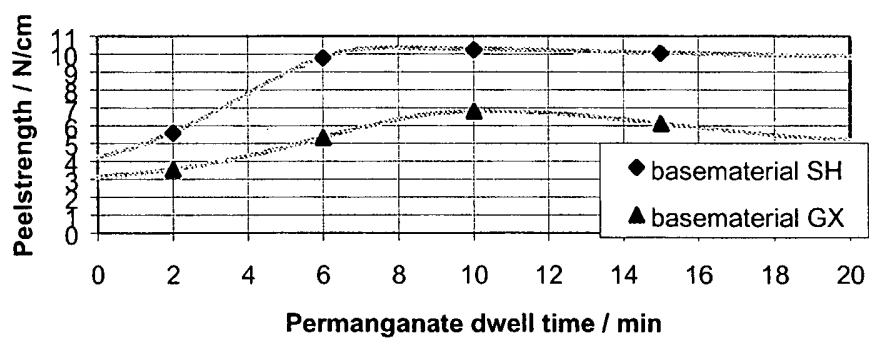
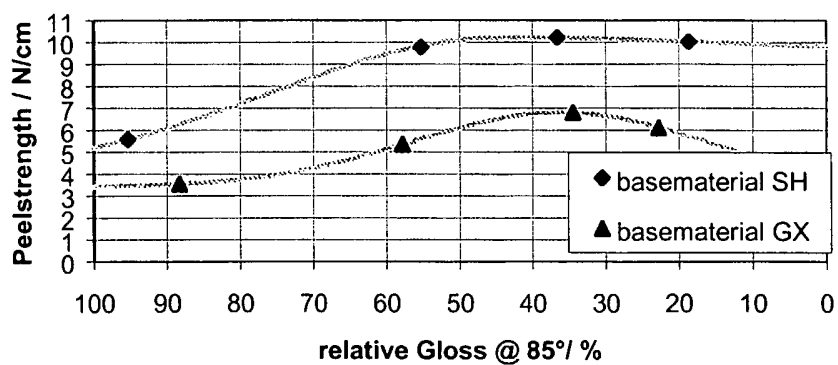


Figure 4: Peelstrength vers. relative Gloss @ 85°



INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2005/011231

A. CLASSIFICATION OF SUBJECT MATTER

C23C18/22 H05K3/38 H05K3/00

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)

C23C H05K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 612 028 B1 (SHIRAI MASAHARU) 2 September 2003 (2003-09-02) column 4, line 10 - column 50; claims; figure 4; examples	1-9
A	PATENT ABSTRACTS OF JAPAN vol. 010, no. 382 (P-529), 20 December 1986 (1986-12-20) & JP 61 173104 A (TOSHIBA CORP), 4 August 1986 (1986-08-04) abstract	1-9
A	PATENT ABSTRACTS OF JAPAN vol. 010, no. 326 (M-532), 6 November 1986 (1986-11-06) & JP 61 131869 A (HITACHI LTD), 19 June 1986 (1986-06-19) abstract	1-9
-/--		



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 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 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.
- *Z* document member of the same patent family

Date of the actual completion of the international search

18 January 2006

Date of mailing of the international search report

03/04/2006

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Mauger, J

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2005/011231

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 019 229 A (GRAPENTIN ET AL) 28 May 1991 (1991-05-28) cited in the application claims -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2005/011231

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6612028	B1	02-09-2003	JP 2001144432 A	25-05-2001
JP 61173104	A	04-08-1986	NONE	
JP 61131869	A	19-06-1986	NONE	
US 5019229	A	28-05-1991	AT 397103 B	25-02-1994
			AT 157489 A	15-06-1993
			CA 1334924 C	28-03-1995
			DE 3823137 A1	25-01-1990
			EP 0349805 A2	10-01-1990
			JP 2150432 A	08-06-1990
			JP 2752445 B2	18-05-1998