The Advent of Non-Etching Adhesion Promoters For Use Within the Printed Circuit Board Industry

R Massey
Atotech GmbH
Erasmusstraße 20.,
Berlin
Germany.

SHORT HISTORY OF ADHESION PROMOTION

As circuit board design became more complex there arose the need for multiple layers or cores within the final product. This in turn generated the need for pretreatment methods which enhanced the adhesion of such cores with the resin system in use.

Initially, such pretreatment was based on the growth of columnar Copper oxide crystals on the copper circuitry. This "Black Oxide" process was named after the characteristic black colour of the oxide layer and continues to be used in appreciable volumes today. However, as the technology requirements and production demands increased, the limitations of the black oxide process became apparent, and it was subsequently superseded with the high volume horizontal process which are now more commonly know as the oxide alternatives.

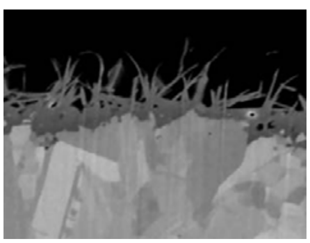

Figure 1. Typical Black Oxide Structure

Unlike their predecessor, the Oxide Alternative processes do not grow the adhesion layer on the surface of the circuitry; they etch down into the Copper. In addition to the roughening associated with this etching, the oxide alternatives also form an organo-metallic coating which gives some level of chemical adhesion between the treated surface and the prepreg material being used.

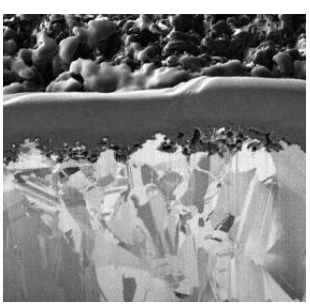

Figure 2. Typical Oxide Alternative Structure

The oxide alternatives such as the BondFilm® process are now widely seen as the standard adhesion process on which the PCB industry relies; they however have limitations which are now in need of addressing. While their short treatment times, simple chemical control and high capacity horizontal processing led to their rapid and wide scale adoption within the industry, their etching nature and limited chemical bonding has led to issues with fine line capability and variable adhesion strength respectively. The concept of a "White Oxide" has been offered by a number of sources in order to address the variable adhesion strengths, and while these have been shown to lead to improvements, they have not been widely adopted as they do not also address the issue with fine line features. These white oxide processes gain their name from the use of metals such as Tin being deposited after the oxide alternative process. The use of such metals occurred as they were thought to lead to an increase in the isoelectric point of a surface and so increase the adhesion factor compared to the oxide alternative processes.

While it has been stated that these white oxide process has not been widely adopted, they have become the basis of the next generation of adhesion promoters.

The PCB industry, by which it is mean both HDI and IC substrate applications, is now facing more challenges then ever before., High Tg and Halogen Free laminate materials have become the "norm" in "PCB" while the advanced line and space requirements of the IC substrate are rapidly approaching sub 10µm. In addition, both areas have applications for high frequency requirements where faster signal transmission speeds or less signal loss is paramount. While each of these is an individual challenge, they must be achieved while maintaining the high capacity, easy and reliable process routes that the industry demands.

The next generation of adhesion promoters turn their back on the etch based adhesion processes as these limit both track geometry control and high frequency signal transmission and have heralded the approach of the Non-Etching Adhesion Promoter (NEAP) technologies

NON-ETCHING ADHESION PROMOTERS (NEAP)

It has been shown that "traditional" adhesion promoter systems make use of the combined effect of etch based roughening with a degree of chemical bonding. As their name suggests, the NEAP based technologies move away from this mechanism and in turn rely entirely on chemical bonding between the Copper circuitry and the encapsulating prepreg resin system.

In order to facilitate adhesion to such a difficult transition element, there is a need for a conversion coating to be applied to the Copper circuitry. In the case of the Atotech Secure™ HFz process, this is based on the application of a pure Tin layer and then the subsequent coating of an organo-silane layer Sn which creates the chemical adhesion to the resin system.

The process is made up of simple steps as outlined below.

Process	Time	Temp
Alkaline Cleaner	30s	40^oC
Rinse		T_R
Acid Cleaner	30s	40^oC
Rinse		T_R
Immersion Tin	35s	35^oC
Rinse		T_R
Activation	20s	40^oC
Rinse		T_R
Silane Filming	30s	30^oC
Drying		60^oC

Alkaline Cleaner

This optional cleaning step is used primarily where aggressive cleaning is needed, such as the removal of organic residues like dry film resist and oily fingerprints.

Acid Cleaner

The acid cleaner is used in order to remove any heavy oxides, anti-tarnishes or detergents from the surface prior to immersion Tin deposition.

Immersion Tin

The immersion Tin process is designed to deposit 0.05 – 0.15µm of pure Tin onto the copper surface.

Activation

In order to ensure an even coating of the organo-silane layer, the Activator step fully converts all available Tin surface into oxides and/or hydroxides A Tin oxide/hydroxide surface desirable as stronger polar bonds can be formed between the these and the polar groups within the Silane.

Silane Filming

Once an even Tin-oxide layer has been formed an aqueous solution of organo-silanes is then applied and dried. The organo-silane adhesion promoter has the ability to form covalent bonds to the Tin hydroxide (Sn-OH) as well as to the organic resin, this subsequently results in a strong interface linking the Copper and resin.

The organo-silanes of the following general structure were found to be suitable coupling agents and form strong bonds with the metal oxides.

- Sn – O – Si – R' –

During the subsequent lamination process, strong covalent bonds are formed between the organo-silanes and the prepreg in the resin system

- Sn – O – Si – R' – Resin

As previously discussed **all** adhesion is derived from the organo-silane mixture, and as such, no etching or roughening of the copper is required in order to achieve adhesion.

The presence of Tin has been raised as a concern as there has been the long standing distrust of its occurrence within multilayer boards. This has been routed in the potential over the formation and growth of Tin dendrites or whiskers and their potential effect on isolation defects. Whilst the NEAP process does indeed deposit a layer of Sn onto the circuitry, during the pressing or laminations step, all of the metallic Sn is converted wholly into the stable Cu_3Sn intermetallic which has not been shown to give rise to dendritic growth.

ADHESION MECHANISMS

In the etch based adhesion promoters, more than half of the adhesion strength arises from the increased surface area and roughness generated during etching. The NEAP processes do not use such a method and use only chemical bonding in order to achieve the desired adhesion. In view of this, it is essential that the adhesion layer applied during the NEAP treatment is compatible with the commonly used resin systems and further is able to form a strong and permanent chemical bond

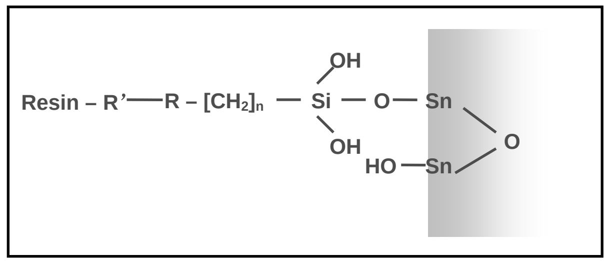

Figure 3. Schematic of NEAP Adhesion to Resin Systems

As there are a wide range of different resin systems in use, the need for a universal NEAP treatment is paramount, fortunately, through careful selection and manipulation, NEAP processes are available that are able to bond with a wide range of materials. In general, the adhesion mechanism occurs through either condensation or addition reactions, but the important fact is that the final adhesion is the result of formation of strong covalent bonds.

From Figure 4 it can be seen that for the resin systems shown there are functional groups available with which the NEAP chemistries can form and it is this which leads to the enhanced adhesion compared to the etch based adhesion promoters.

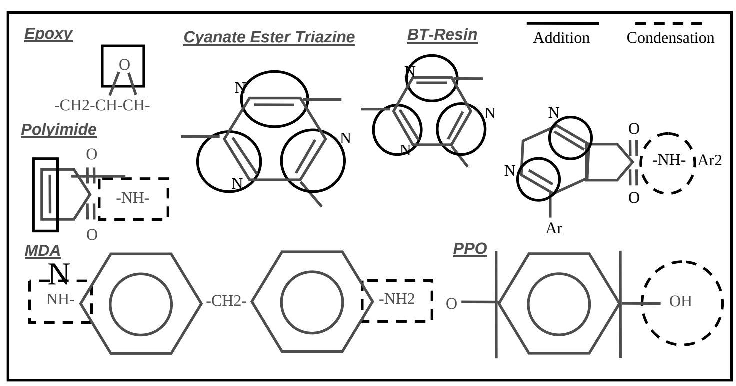

Figure 4. Functional Groups Available on Resin Systems

SURFACE CHARACTERISTICS

Figure 5 shows a comparison of 12um tracks that before and after treatment with a NEAP process and a widely used etch based adhesion promoter. As can be seen, it is clear that the NEAP treated track is comparable to the track before treatment.

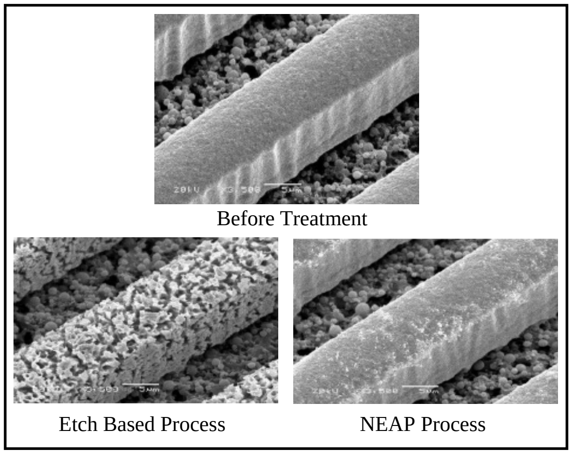

Figure 5. Comparison of 12μm Track Treated with NEAP And an Etch Based Process

This is further reinforced when tracks are viewed in the cross section and it becomes apparent how much material is removed with the etching based process.

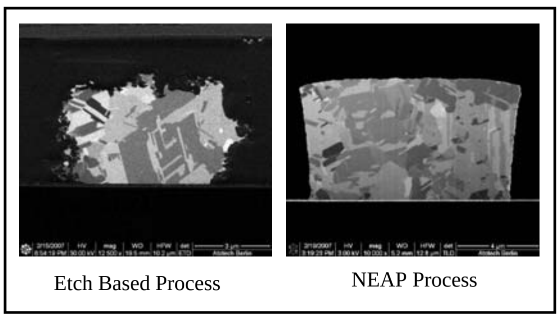

Figure 6. Cross section of 12μm Track Treated with NEAP And an Etch Based Process

This is of importance for two main reasons. As there is no copper removal during treatment, features remain at their design and plated width, thus the use of NEAP chemistries will enable finer lines to be manufactured without the need to determine complicated etch compensation factors. While this has obvious advantages to the IC substrate area of the industry, it also desirable in high frequency applications, where a smooth track profile is desirable in order to combat the effect of high frequency skinning effects and so minimise signal loss and maximise signal transmission.

ADHESION CHARACTERISTICS

While the smooth surface profile is desirable for a number of reasons, it should only be gained if the final product is “fit for purpose”

Chart 1 shows a comparison of an etch based adhesion promoter (approx 1.2um etch depth) with NEAP for a range of materials.

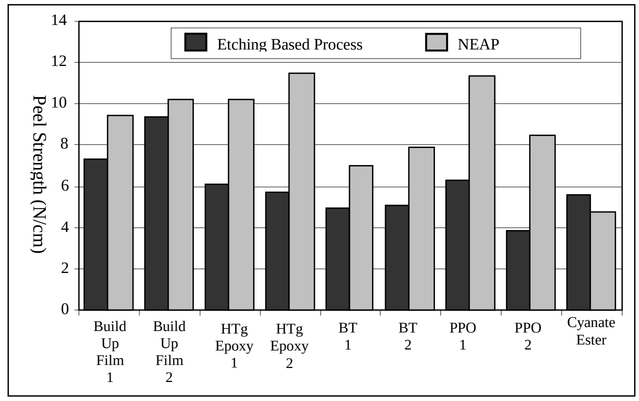

Chart 1. Adhesion with Etch Based and NEAP Treatments

As can be seen, the adhesion strength of the NEAP based process is comparable or improved over that achieved with the etch based process, so there is no loss of performance though the adoption of a full chemical adhesion process. Further tests show that long term reliability of NEAP treated surfaces is also not diminished and test vehicles manufactured have passed all the standard industry exposure tests

SOLDERMASK APPLICATIONS

It is common practice to not only improve adhesion through roughening before pressing or lamination, but also prior to the application of soldermasks. As these materials also contain functional groups that are compatible with certain organo-silanes, the NEAP process is also suitable for use with Soldermask materials. Due to the smooth surface characteristics of the NEAP treated parts, there is a need to adjust the soldermask exposure and developing conditions, but this is to be expected, and would be needed even if switching between etch based process.

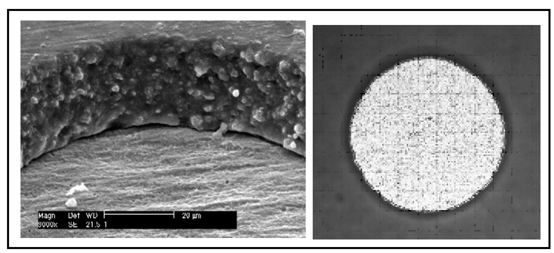

Figure 7. Solder Mask Openings on NEAP Treated Surfaces

HIGH FREQUENCY APPLICATIONS

As the operating frequency of electrical current increases, the electromagnetic fields this generates forces the current into a “skin” that is carried close to the surface of a track. The thickness of this skin is dependant upon a number of track properties but for all conditions there is a frequency at which the thickness of the skin approaches 1-2μm and this is important as this is also similar to the average roughness (R_A) of tracks treated with etch based adhesion promoters.

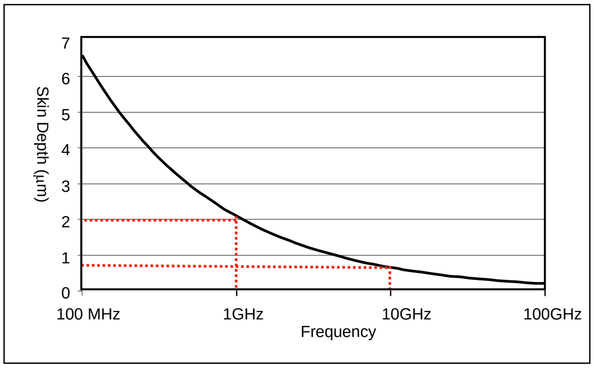

Chart 2. "Skin" Depth for a for Various Frequencies

While this may appear of no great importance, it is critical in the impact on the track resistance. As the current frequency increases, the signal is pushed into this skin, and this skin has to closely follow the profile of the track. As the skin thickness approaches the R_A of the track, it leads to an increase in effective track resistance and this can lead to increased signal loss. Chart 3 shows the simulated signal loss for 10 and 60µm track sizes across a range of operating frequencies. And it is clear that as the frequency increases the signal loss becomes more negative representing greater loss.

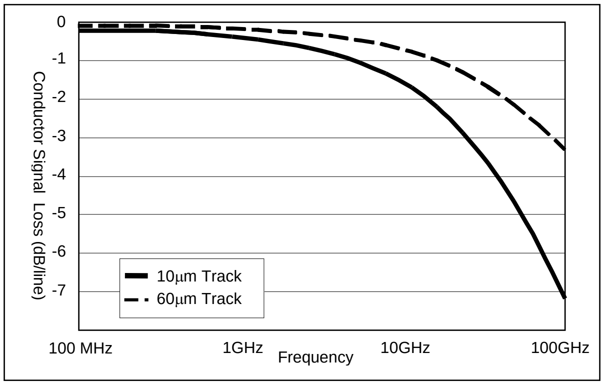

Chart 3. Simulated Signal Loss for 10 and 60µm Tracks
For a Range of Frequencies

With circuitry treated with a NEAP chemistry, there is no roughness which means that while there is an effect of increasing the operating frequency, there is no effect associated with the roughness of the track. Chart 4 shows a comparison of simulation data for a 20µm etch based track and a track treated with NEAP and it is clear that at approximately 3-5GHz the etch roughened track shows a higher level of signal loss compared to that treated with the NEAP process

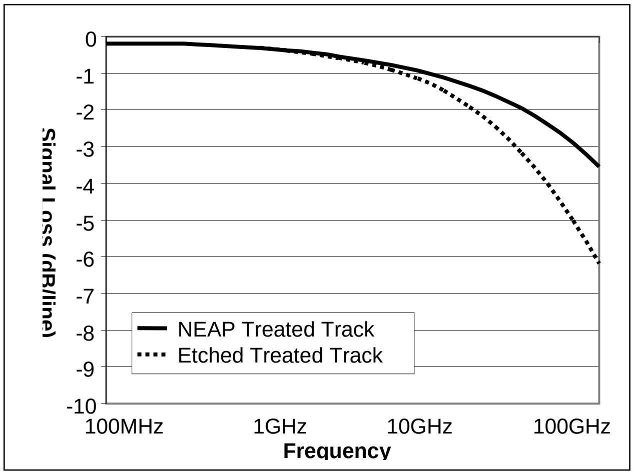

Chart 4. Simulated Signal Loss for 20um track with
Etching and NEAP Treatments

While the data represented here is achieved through computer simulation, it is clear that the adoption of the NEAP processing offers distinct advantages in the area of high frequency applications. There has been wide scale use of Low or even No Profile Copper Laminates in order to minimise signal loss, but these have then been used in combination with roughened tracks, such laminate materials if used in combination with NEAP chemistries offer unrivalled signal transmission characteristics that can not be achieved with traditional etch based adhesion promoters.

SUMMARY

For time immemorial, adhesion promotion within the electronics industry has been achieved through the use of mechanical roughening or chemical etching methods. These have, and continue to serve the industry admirably, but both are now beginning to reach their technical limitations. The ultra fine line circuitry required for next generation IC substrates can not be formed reliably through etching, and higher operating frequencies are pushing the demands on circuit geometry, and the etch based process are no longer suitable.

Non-Etching Adhesion Promoters were born out of the developments of etch based processes, turn their back on roughening based adhesion and have adopted wholly chemical bonding. Their use as both pretreatment prior to both bonding and soldermask leads not only to improvements in circuit capability and reliability, but it is anticipated that their use will in turn become as wide spread as the Oxide Alternative process are now.

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