

USE OF NON ETCHING ADHESION PROMOTERS IN ADVANCED PCB APPLICATIONS

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ABSTRACT

Throughout the manufacturing cycle of both simple and complex Printed Circuit Boards, there are many occasions where there is a need for enhanced and reliable adhesion between two materials. The most common of these being the adhesion between an inner layer core and the epoxy resin used during bonding, and also that between the outer layer circuitry and its encapsulating soldermask. Traditionally, the enhancement mechanism used is based on etching or chemical roughening processes, where the additional surface area created leads to improved adhesion and hence strength. However as line and space sizes decrease these etching processes begin to reach their limitations and a new method of adhesion promoter is required.

While the improved adhesion to a wide range of materials is of great interest, it is not the only advantage offered through the use of non etching adhesion technologies. At high operating frequencies, the surface roughness that is characteristic of etch based adhesion promoters leads to increased signal loss. Through the use of Non Etching Adhesion Promoters (NEAP) a smooth track profile can be created which offers an enhanced signal transmission characteristic which is of critical importance when developing the next generation of electrical circuitry.

Based on tests carried out with commercially available chemistry, this paper discusses the advantages available through the use of NEAP processes for inner layer bonding and soldermask pretreatment. The process is characterized with a view to high volume manufacturing and its performance is reported through short and long term reliability testing. The work described shows that NEAP processes currently available on the market are viable alternatives over existing etch based adhesion technologies and offer increased adhesion to a wider range of materials, plus the added benefit of enhanced signal transmission in high frequency applications.

Key words: non-etching adhesion promoter, NEAP, adhesion, soldermask, signal loss, high frequency

CHANGES IN BONDING ENHANCEMENT

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.



Figure 1. Typical Black Oxide Structure

However, as the technology requirements and production demands increased, the limitations of the black oxide process became apparent, and it was subsequently superseded with high volume horizontal processes which are now more commonly known as the "Oxide Alternatives". 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.



Figure 2. Typical Oxide Alternative Structure

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. The oxide alternative processes 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^[1] 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 decrease the Isoelectric Point (IEP) of a surface and so increase the adhesion factor compared to the oxide alternative processes.

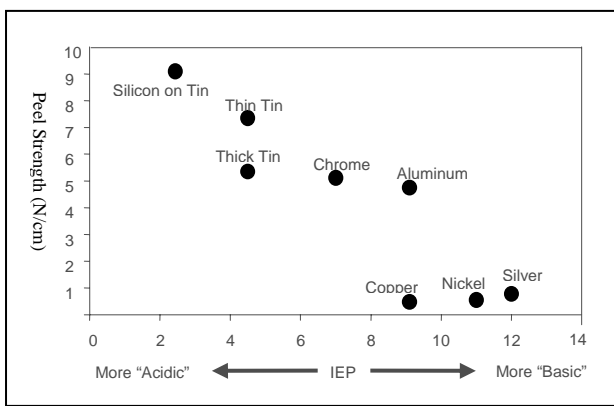


Figure 3. – Isoelectric Points For Various Metal Surfaces^[2]

While it has been stated that these white oxide processes have 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 10um. 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 herald 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 roughening and/or 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, it has been proposed that a conversion coating needs to be applied to the Copper circuitry. Based on the understanding gained of the IEP, these conversion layers are typically based on Tin and are then followed with a coating of an organo-silane layer which is used in order to create the chemical adhesion with the resin system.

The process proposed is made up of simple steps as outlined below and is best utilized in a fully horizontal procedure.

Process	Time	Temp
Alkaline Cleaner	30s	40°C
Rinse		T _R
Acid Cleaner	30s	40°C
Rinse		T _R
Immersion Tin	35s	35°C
Rinse		T _R
Activation	20s	40°C
Rinse		T _R
Silane Filming	30s	30°C
Drying		60°C

Alkaline Cleaner

Used when aggressive cleaning is needed, such as the removal of heavy organic residues (i.e. dry film resist and oily fingerprints.)

Acid Cleaner

For removal of any heavy oxides, anti-tarnish layers or detergents from the Copper surface.

Immersion Tin

Designed to deposit 50 –150 nm of pure Tin onto the Copper surface.

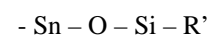
Activation

Ensures an even coating of the organo-silane layer, activation fully converts all available Tin surface into oxides and/or hydroxides. Tin oxide/hydroxide surface is desirable as stronger polar bonds can be formed between these and the polar groups within the Silane.

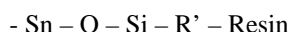
Silane Filming

Aqueous solution of organo-silanes applied and dried. The organo-silane adhesion promoter has the ability to form covalent bonds to the Tin oxide/hydroxide as well as to the organic resin, this subsequently results in a strong interface linking the Copper and resin.

The organo-silane group found to be the most suitable and form strong bonds with the metal oxides follow the basic structure of



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



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 rooted in the potential for the formation, and growth of Tin dendrites or whiskers, and their potential effect on isolation defects. Whilst the NEAP processes currently employ the use of a Sn layer within the circuitry, during the pressing or lamination step, all of this metallic Sn is converted wholly into the stable Cu_3Sn intermetallic so that no free Sn is available to undergo any dendritic growth

ADHESION MECHANISMS

In the etch based adhesion promoters, the majority 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^[3]. 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.

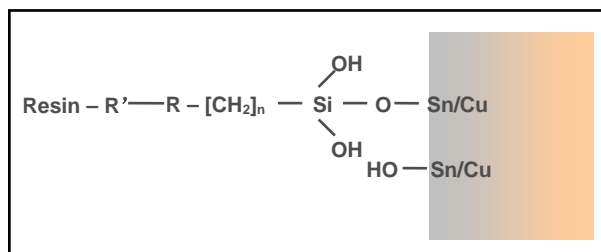


Figure 4. Schematic Of NEAP Adhesion To Resin Systems

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, the NEAP processes available are able to bond with a wide range of materials. In general, the adhesion mechanism occurs through addition reactions, although certain condensation reactions also occur (Figure 5). However, the important fact is that the final adhesion is the result of formation of strong covalent bonds.

From Figure 5 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.

SURFACE CHARACTERISTICS

Figure 6 shows a comparison of tracks before and after treatment with a NEAP process as well as with an etch

based adhesion promoter. As can be seen, it is clear that the NEAP treated track is comparable in size and surface morphology to the track before treatment, while the change associated with an etch based system is quite dramatic.

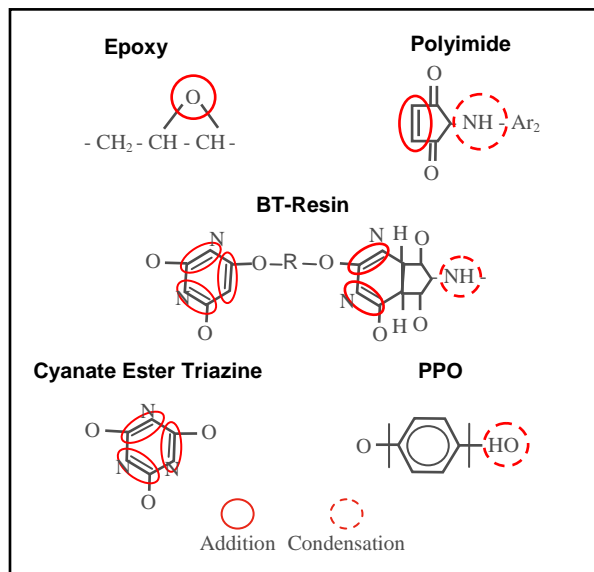


Figure 5. Functional Groups Available On Resin Systems

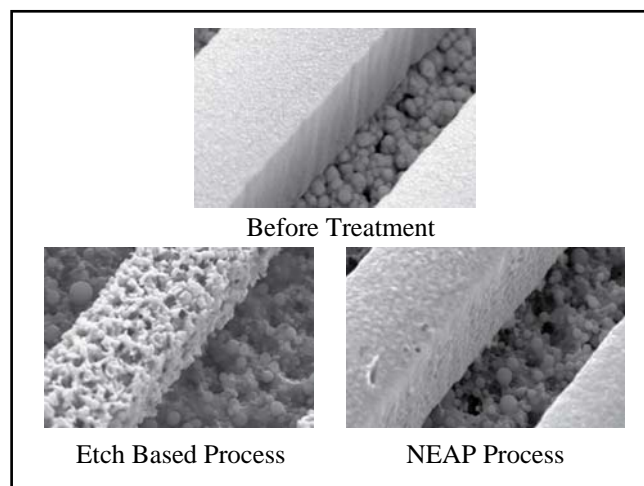


Figure 6. Comparison Of 12um Track Treated With NEAP And An Etch Based Process

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

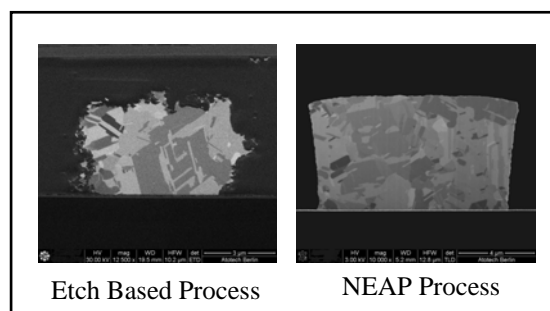


Figure 7. Cross Section Of 12um Track Treated With NEAP And An Etch Based Process

Using Atomic Force Microscopy (AFM) it is possible to record surface roughness parameters for the tracks and from Table 1 it is clear that the etch based process leads to significant roughening of the Copper track.

Process	R _a (um)	R _{rms} (um)	R _{max} (um)
Untreated	0.03	0.04	0.28
Etch Based 1	0.41	0.39	2.94
Etch Based 2	0.22	0.27	1.61
NEAP	0.05	0.06	0.3

Table 1. – Surface Roughness Characteristics

This is of importance for two main reasons. Copper removal associated with etching leads to uncontrolled track geometry, and it also requires that board manufacturers apply additional etch compensation factors for the final pre-treatment step. Without such compensation it is possible to create uneven line and space features after etching, even though the pattern may have been of uniform design (see Figure 8).

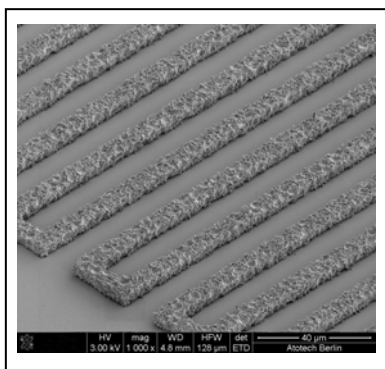


Figure 8. – Uneven Feature Size Arising From Lack Of Or Poor Etch Compensation

In order to compensate for this, it is possible to design the track wider than the required size and then “etch back” to the desired dimension. This requires that the track spacing is reduced, and can lead to issues as the finer spaces may be beyond a manufacturers current capability. With a NEAP based adhesion process, as no additional etch compensation is required, the track design can remain within current imaging technology and results with even and uniform line and space features as shown in Figure 9.

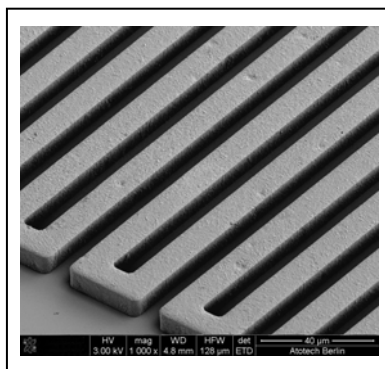


Figure 9. – Even Features After Treatment With NEAP

Further, it is clear that if there an etching step is required, as line features become smaller there will become a point at which there is no Copper track remaining after etching. From Table 2 it can be seen that if one is targeting a 6um L/S pattern, an etch based adhesion process is not suitable as the line is completely removed during processing, further, it is also apparent that the etching based adhesion promoters are limiting fine line capability as they lead to unnecessary track width reductions.

With NEAP processing however, a track will remain at its plated dimensions without any loss in overall performance of adhesion, enabling both finer lines and also more consistent track uniformity.

Target Line/Space Width (um)	Measured feature size (um)		
	No Treatment	Etch Based Process	NEAP process
6 / 6	4.3 / 6.2		4.3 / 6.8
8 / 8	6.8 / 8.7	6.2 / 9.9	7.4 / 9.3
10 / 10	9.5 / 10.6	7.4 / 11.8	9.3 / 10.6
12 / 12	10.1 / 13.0	9.3 / 13.6	10.5 / 12.7

Mean of 3 readings (+/- 0.5um)
Photomask tolerances effect measured feature size also

Table 2. – Effect of Adhesion Promoter On Fine Line Capability

While this aspect of NEAP processing has obvious advantages to the IC substrate area of the industry where the formation of ultra fine lines is not only desirable but a challenge, as will be shown later, the process is also of considerable interest in the PCB/HDI sector, where a smooth and uniform track profile is ideal in order to combat the effect of high frequency skinning effects, and so minimise signal loss.

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, and as these materials are typically based on epoxies they also contain functional groups that are fully compatible with NEAP processing. Due to the enhanced adhesion and smooth surface characteristics of the NEAP treated parts, there is a need to review the soldermask exposure and developing conditions, but this is to be expected, and would be needed even if switching between etch based process. It should however be remembered that the Cu-Sn intermetallic layer would need to be removed from the solder resist openings, however commercially available metal strippers are available for such uses.

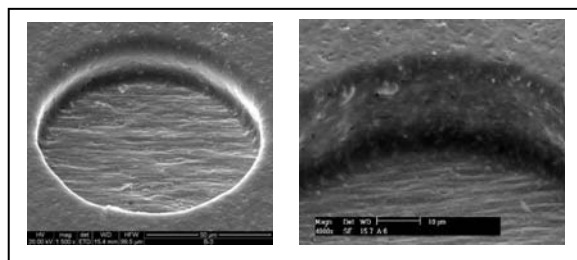


Figure 10. Solder Mask Openings on NEAP Treated Surfaces

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.

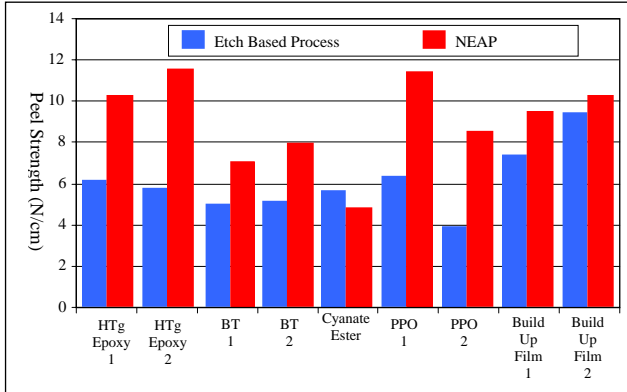


Chart 1. Adhesion With Etch Based And NEAP Treatments

As can be seen, the adhesion strength of the NEAP based process is comparable to, or improved over that achieved with the etch based process, so there is no loss of performance though the adoption of a fully chemical adhesion process.

Similarly, when we review the adhesion of NEAP processing with soldermask materials, it is clear that again there is no loss of adhesion with standard soldermasks.

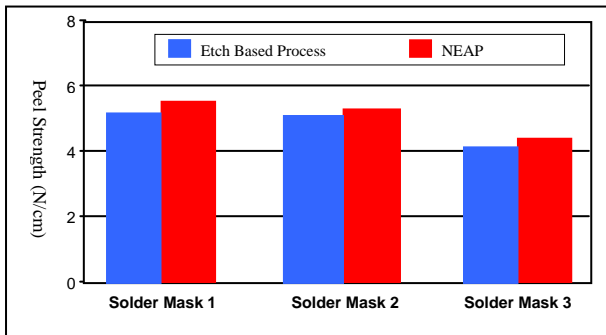


Chart 2. Adhesion Of Solder Mask With Etch Based And NEAP Treatments

Further tests (JESD22-A118 (130°C, 85%RH)) show that long term HAST reliability of NEAP treated surfaces is also not diminished and multilayer test vehicles have passed all the standard industry exposure tests.

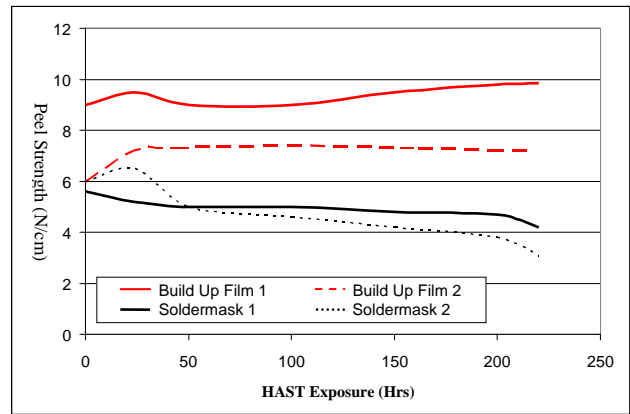


Chart 3. Peel Strength After HAST Exposure (JESD22-A118) For Build Up Films And Solder Mask Materials

HIGH FREQUENCY APPLICATIONS

As the operating frequency of electrical devices increases, the electromagnetic fields generated force 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 1-2um and this is important as this is also similar to the roughness (R_{max}) of tracks treated with etch based adhesion promoters.

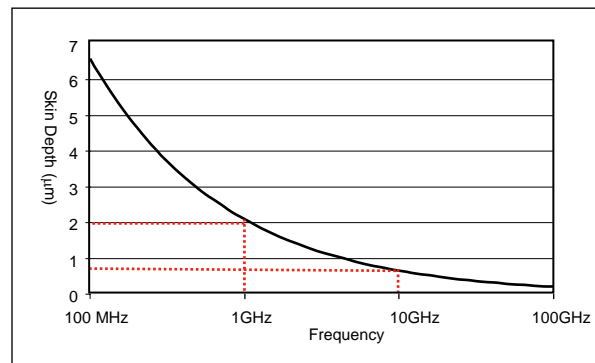


Chart 4. “Skin” Depth For Various Frequencies

While this may appear to be of no great importance, it is critical in the impact on the track resistance. As the operating 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 decreases, it leads to an increase in effective track length and hence resistance and this can lead to increased signal loss^[4,5]

Figure 11 shows this effect where in Low Frequencies (Figure 11a) a “thick” skin has no impact on effective track length, when a higher frequency is applied (b), the skin reduces in thickness and the effective track length and resistance increases, finally with a NEAP process, at the same high frequency, the signal can pass without any changes in path length or resistance.

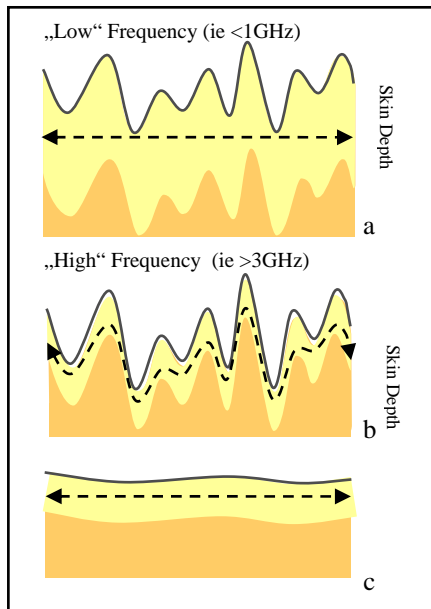


Figure 11 - Impact Of Surface Roughness And Skin Depth on Effective Track Length.

Chart 5 shows simulated signal loss associated with 10 and 60um tracks across a range of operating frequencies. And it is clear that as the frequency increases the signal loss becomes more negative, representing greater loss.

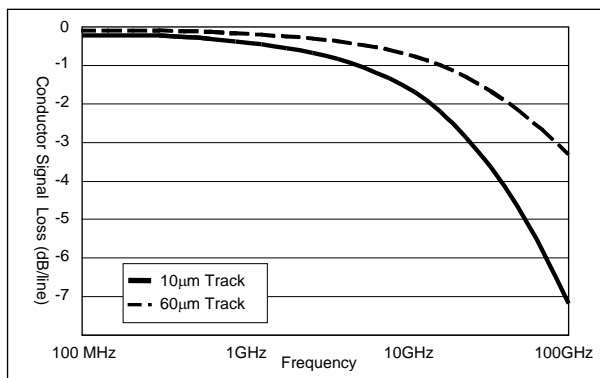


Chart 5. Simulated Signal Loss For 10 And 60um Tracks For A Range of Frequencies

With circuitry treated with a NEAP chemistry, there is no roughness which means that while the above effect still occurs, there is no additional impact from the roughness of the track itself. Chart 6 shows a comparison of simulation data for a 20um 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

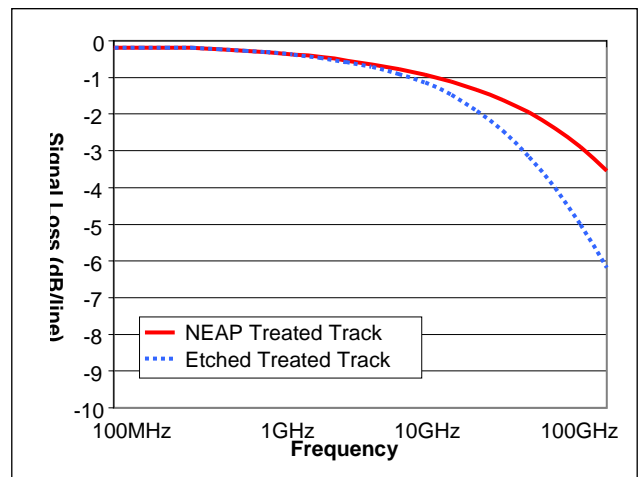


Chart 6. Simulated Signal Loss For 20um Track With Etching And NEAP Treatments

While the data represented so far is achieved through computer simulation, empirical measurements have also been carried out as shown in Chart 7. Here a 90um track has been characterised with a low loss dielectric material and while there is an offset associated with losses within the dielectric itself, it is clear that the NEAP treated track has a lower loss compared to the track treated with the etch based process. In this case approx 15% lower signal loss was recorded at 10GHz with NEAP, which is an appreciable reduction when designing a circuit.

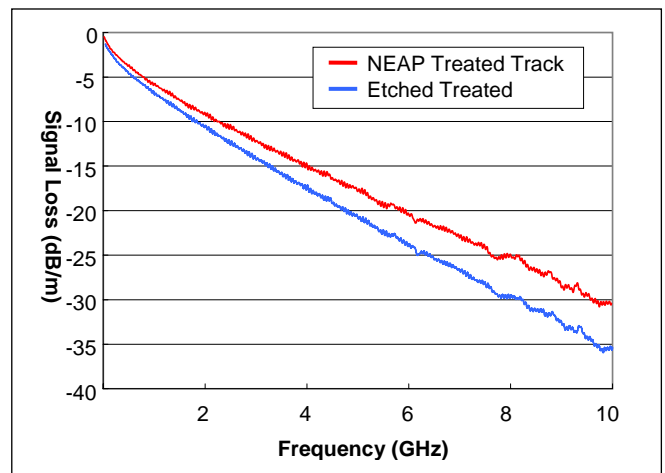


Chart 7. Signal Loss Measurements For 90um Track With Etching And NEAP Treatments (PPO Base Material)

It is clear that the adoption of NEAP processing offers distinct advantages in the area of high frequency applications. There has been significant use of Low or even No Profile Copper foils 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

Since the electronics industry began to manufacture multilayer printed circuit boards, adhesion promotion has been achieved through the use of mechanical roughening or chemical etching methods. These have, and continue to serve the industry admirably; however 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, higher operating frequencies are pushing the demands on circuit geometry, and the etch based process are no longer suitable.

Non-Etching Adhesion Promoters have been developed based on the long experiences gained from etch based processing. Their ease of horizontal processing lends them well to volume production, their enhanced adhesion to a wide range of laminates and soldermasks allows for wide scale use within the industry, while their ability to allow for ultra fine line manufacturing and low signal loss applications makes them attractive to the niche markets also. As the Oxide Alternative processes quickly replaced the older Black Oxide, it is anticipated that NEAP will in turn inherit the majority of the adhesion processes and fast become the standard by which all future adhesion is measured.

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