Developments in Fine Line Resist Stripping

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ABSTRACT

As real estate demands on printed circuit board's lead to ever decreasing track and gap spacing, developments throughout the manufacturing processes have been widespread. Now, even the perceived "simple" processes, which have been long overlooked are beginning to reach their limits, and need to be replaced with more advanced and technical solutions. The use of photo image-able resists is widely known and their use is common throughout the industry in the formation of the discrete circuit profile that is to be built up in the subsequent electroplating steps. However as line and space requirements get smaller, the limitations of both generic and proprietary photo-resist strippers is being approached, thus increasing the risk of rework and/or etch defects after SES or DES

In this paper, the concept for the next generation of resist stripper solutions is introduced, with specific emphasis upon development of new solutions targeted at the ever demanding fine line applications. The novel formulation used minimises the initial swelling of the resist that occurs during the initial phase of the stripping mechanism, therefore actively reducing the mechanical "lock in", or entrapment, of dry films that can result in poor stripping performance.

Testing shows that as the line and space dimensions decrease, the current technologies for resist stripping are no longer capable, the proposed process is shown to have better fine line stripping capability with less attack on metals, and in a single step process that is compatible with current equipment.

BACKGROUND

Ink based screen printable etch resists were the main stay of PCB manufacturing until the late 1960s when dry film resists as we know them were first introduced by DuPont[1]. With the advent of dry film resists (dry films) the manufacturing of PCB became more streamlined and when combined with the use of photo lithography, much more accurate and technically capable. As always, Engineers are looking for methods to update and move forward, and today many R&D teams are evaluating direct mask creation, or even direct writing of the track itself through the use of "ink jet" type technologies, but with an industry that is able to produce 15um line and spaces with photo imaging, its unlikely that dry films will be replaced in the near future.

Accepting that photo imageable dry, and liquid films are here to stay, it is also safe to assume that the demands placed on them have also become greater. The PCB sector makes use of Laser Direct Imaging (LDI) techniques where the traditional Hg or Xe lamps and phototools have been replaced with lasers for improved accuracy and more flexible printing. The IC substrate manufacturers have developed the SAP and MSAP (Semi and Modified Semi Additive Process respectively) to enable finer lines and the use of Secondary Imaging Technologies (SIT) has again led to increased requirements of dry film properties.

That is not to say that manufacturers have sat idle while other areas have been developed. The latest series of films and inks are indeed high technology in their own right. The required modifications have been made to give the improved resolution, faster exposure times and lower exposure energies. Finer lines and spaces means smaller features, which in turn necessitates stronger bonding to the Copper substrate and better coverage and conformance to that substrate. All of which results with a huge array of different dry films and inks, with a huge array of different structures and properties. This is excellent as it means that the film or ink you want is almost certainly available. However, at some stage of processing you will need to strip it off again, and at that point, all of the advances made elsewhere begin to stretch the capability of the resist stripping processes.

Traditionally, photo resist strippers were based on simple hydroxides, and this was later expanded through the use of proprietary systems to include the amine chemistries. These have been working admirably for many years, but as the developments in imaging has led to finer lines, and as the developments in films and inks has led to better adhesion and stability, these "basic" strippers are no longer suitable for fine line photo resist removal and a new breed of strippers is needed.

While it is safe to say that both photo imageable dry films and liquid inks are widely used, it can also be said that due to their thickness and the effect of acid hardening etc, the dry film applications are often the more demanding, so for the purpose of this investigation, we will only discuss dry film from this point forward. However many of the points raised would be equally valid for liquid films.

DRY FILMS

Dry films are not strictly "dry" as they are really stabilised and bound "fluid systems" however, compared to inks or liquid films, they are for all intents and purposes dry and we should treat them as such. There is now a large list of manufacturers, each with a wide range of dry films covering each and every application. With this in mind, the selection of a suitable new film can be daunting to say the least, and until a single universal film exists, or other technologies are developed to the point where dry films are no longer needed, this will remain the case. With literally hundreds of different dry films on the market.

While dry film manufacturers each tailor their products to give unique and desirable properties, dry films in general share many basic component types. However, dry films are a very complex blend of chemicals and plastics, and typically contain most or all of the following

- Monomers – typically based on poly functional acrylates or methacrylates that form the core of what is the dry film itself.

- Binding agents – present to hold the dry film together prior to polymeristion during exposure

- Photo initiators – activated by the UV light during the exposure step to create free radicals within the dry film, these then initiate the polymerization of the acrylate monomers into the cross linked dry film.

- Stabilisers – present to stop thermally activated polymerization, thus ensuring activation only during exposure.

- Plasticisers – help to define and control the mechanical properties of the exposed dry film.

- Anti halation agents – stop the diffusion and back scatter of UV light during exposure and ensure a clear final image.

- Dyes – to improve contrast between the exposed and unexposed area of the images for inspection and alignment purposes

While the above list is not exhaustive, its clear that the combination of components within a dry film is potentially endless, and that each dry film will be different, however, the core basis of any dry film, is so far, the same. Namely a blend of acrylate monomers that are cross linked through the action of UV initiated photo initiators, with dyes and other additives that give each film its unique properties.

It is this "core" of basic elements that allows for the use of universal pretreatment, developing and stripping chemicals. If each dry film was truly unique then it would need at a minimum, a dedicated developer and stripper chemical. However, we are fortunate that along with the monomers, most if not all dry films contain a binding agent that is also typically based on an acrylate or styrene but more importantly also contain carboxylic acid[2]. As the binders are still present in the final cured dry film, all resist strippers rely on the presence of these carboxylic acid to allow film removal.

Resist Stripper Mechanisms

It is widely known that developer and stripper solutions are respectively, based on weak and strong alkali solutions, and this is associated with the presence of the acid groups within the binder system. For developing, as the acrylate monomers have not yet been cross linked, the unexposed dry film structure is entirely dependant upon the action of binding agents, so though a simple neutralisation reaction with the carbonate developer solutions, any unexposed dry film develops clear. A very similar group of reactions occur during film stripping, although due to the additional cross linking that occurs at UV exposure, that the process has to be carried out in a much stronger alkaline media.

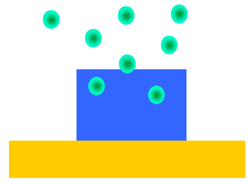
As has been said, dry films contain typically carboxylic acid groups within their binding agents, and it is these acids which are neutralised during stripping processes. Unlike developers, resist strippers can be based on either hydroxide or amine bases as both solutions have sufficient potential to break the bonds within a heavily cross linked and bound photo polymer.

The general reactions are shown below for both hydroxide (1) and amine based solutions (2)

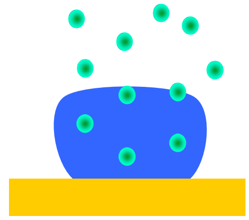
$$Na^+OH^- + R^1COOH \rightarrow R^1COO^-Na^+ + H_2O \quad (1)$$

$$RNH_2 - R^1COOH \rightarrow R^1COO^- + RNH_3^+ \quad (2)$$

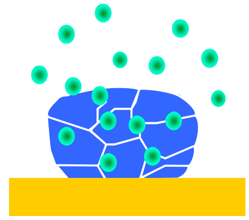
Both reactions follow the same general steps and lead to what are commonly seen as the 4 stages of photo resist stripping



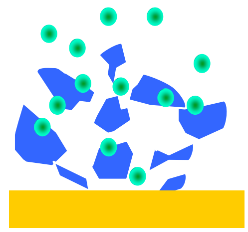
1. The alkaline solution, begins to diffuse into the dry film layer and the film begins to swell as it is "absorbing" liquid. Diffusion is dependant upon the hydrophobic nature of the film.



2. Carboxylic acid groups within the binding agents are neutralised to form soluble polar salts ($NaRCOO^-$ or $RCOO^-$). Which further accelerate the diffusion of the solution into the film. Swelling is greatly enhanced due to the increased diffusion



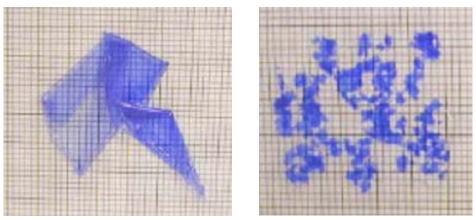
3. The presence of the polar salts and the water within the dry film lead to an increase of internal stress and the film begins to physically rip itself apart (known as rupture) and at this point the film begins to particulate and strip



4. The solution continues to penetrate through the film as it ruptures and also begins to attack the interface between the dry film and the Copper surface. At this point the film lifts and becomes "stripped"

The major difference between an amine based system and the more simple hydroxide is the rate of diffusion and hence, the speed of rupture.

It is widely recognised that the generic hydroxide strippers remove the film in sheets, or features while the proprietary stripers which are predominantly based on amines make the film particulate into small features. (see Figure 1) The reason for the differences lies in their relative rates of diffusion and rupture. Hydroxide based process have much higher rate of diffusion than the amines, so while there is a degree of swelling, the diffusion occurs at sufficient speed that the Copper-resist interface is attacked before the film has undergone sufficient swelling to allow for rupture, as such the film lifts before it breaks up. With the amine bases, the opposite occurs, the diffusion rate within the film is slower so that there is a higher degree of salt formation and the resist begins to swell much faster and to a higher degree. This leads to much more internal stress within the film and hence the particulation or break up of the dry film.



Stripped with 3% NaOH | Stripped with 5% Amine

Figure 1
Different Particle Sizes Achieved with Hydroxide and Amine Based Strippers

DEVELOPMENT OF STRIPPERS

While it is typical to see generic hydroxide strippers being used for inner layer type "print and etch" applications, the use of amine based chemistry has become wide spread for "plate and etch" or outer layer "pattern plate" applications.

After such plating processes, the dry film is "sandwiched" in-between, or bounded on two sides by the plated tracks as shown in Figure 2. While a hydroxide based stripper can be suitable for such applications, they rely heavily on the diffusion mechanism and as the diffusion can now only occur from the top of the dry film, they became too slow to be suitable for high volume processing.

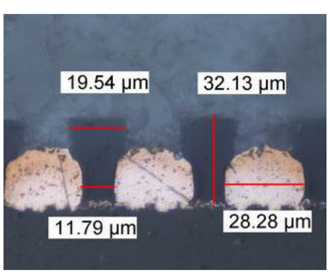


Figure 2
Dry Film Features In-Between Plated Tracks

In view of the limitations of the hydroxides strippers, and their benefit of much lower attack on Tinplating masks, the amine based strippers were adopted for "plate and etch" applications. The theory behind such a shift was simple, by breaking up the film into tiny particles; the film should strip much better than the hydroxides .

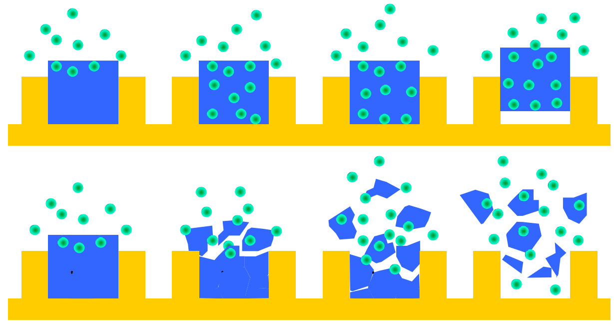


Figure 3
Faster and Improved Stripping With Amine Chemistries

In addition to the benefits associated with the finer lines, the breaking up of the dry film was also seen as an aid in overplated features. During pattern plating, the differences across a circuit design can lead to localised areas of higher Current Density, this results with heavier plating, which in some cases can become so thick that it is greater than the thickness of the dry film, when such an instance occurs, the plating takes on the cross section shape similar to a mushroom. In such cases, removing the resist from under the head of the mushroom is impossible with a hydroxide stripper, yet the amine solutions were found to help dramatically due to the breaking up of the film into smaller particles.

Figure 4
Overplating of 100um Dry Film Features

With these two major benefits, the amine based strippers fast became the work horse of the photo rest removal processes, and it was not until lines began to approach the 50um area, that they also began to suffer from issues. Further as the SAP processes led to features as low as 20um, the amines also began to see major issues with fine line stripping.

NEXT GENERATION RESIST STRIPPERS

The main reason that the amine based processes suffered from poor performance was a direct result of the reason that they became so popular in the first place. In order for the film to break up into smaller parts, it was necessary for it to be able to build up internal stresses, and these were achieved through the action of swelling. As line became closer together the space available for such swelling was obviously reduced and at some critical pint, the swelling was leading to the film becoming mechanically entrapped between the plated tracks. As shown in figure 5

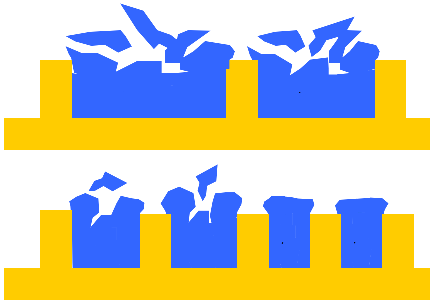


Figure 5
Available Swelling Decrease as Lines Become Closer

With modification, the amines were adjusted so that film break up occurred at lower swelling levels, but now these modified amine strippers are struggling and can leave residues at the base of fine tracks, where the swelling and rupture is minimised.

In order to resolve such issues, the latest generation of fine line resist strippers has been developed based on different stripping concepts. As the formulation of dry films has had undergone no dramatic changes, the overall stripping reactions are the same as previously, with stripping still occurring through neutralisation of the carboxylic acids in the binder systems. However, the next generation of stripper has taken a step back towards their older hydroxide based parents.

The issues stopping the success of fine line stripping with amines was the heavy requirement for swelling, yet given time, a hydroxide could be surprisingly effective. In view of this, the new fine line strippers make use of a "low" or "no swell" mechanism in order to lift and undercut the film, and once free of the plated surface, swelling occurs to allow for rupture of the film and a cleaner stripper solution.

Processes based on this concept began to appear around 2006[3] and were seen to be based on 2-step processes, were the bulk of the dry film was lifted in the first step, and then any micro residues were subsequently removed in the second step. While these process were seen to be effective, their equipment requirements, made them difficult to install. Subsequently, they became superseded by a more traditional single step chemical, using the same mechanisms.

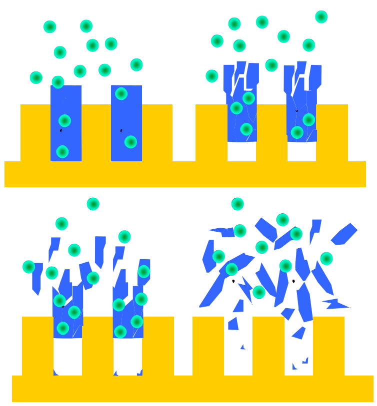
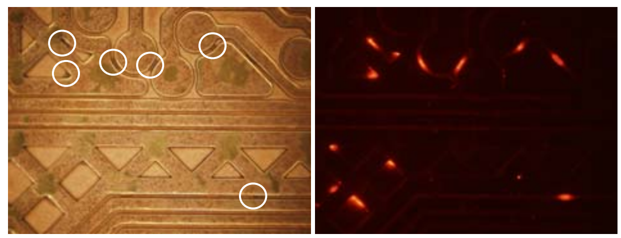


Figure 6
Low Swell Stripper Mechanism

PROCESS PERFORMANCE

Inspection of dry film residues is quite straight forward when looking for large areas of resist, however as lines become smaller, the associated residues also reduce, and optical inspection becomes more difficult. While techniques such as Scanning Electron Microscopes (SEM) can resolve this, they are slow to perform and also require physically small samples. Ultra Violet (UV) or fluorescence microscopy offers a simple optical technique that allows rapid scanning of a circuit and is sufficiently sensitive to detect residues that are not visible under white light. Under UV, organic materials such as dry film will fluoresce, and this allows for easy identification of incomplete stripping. In figure 7a, with the exception of the few obvious residues identified, the circuit would appear to have been fully stripped of all dry film. However, under UV examination, it is clear that there are many other residual dry film particles of sufficient size to lead to defects during etching.



a b

Figure 7
UV Inspection Allows Easy Identification of Dry Film Residues

Through use of this technique, a large number of sample boards have been treated with hydroxide, amine and low swell stripper processes and then inspected in order to determine which offers best stripping performance at finer line resolutions.

A range of test samples were prepared with Hitachi RY3219 dry film and exposed with collimated light (Perkin Elmer OB8120 printer) to produce a pattern with line and space features at 10 – 40 um. After developing in 1% Na_2CO_3, and plating in Cupracid TP, the parts were processed through resist strippers as shown in Table 1 under 1.5-2 Bar spray pressure.

Treatment	Concentration	Time (seconds)	Temp (^oC)
NaOH	35 g/L	60 - 120	50
Amine	100 ml/L	60 - 120	50
Low Swell	140 ml/L	60 - 120	50

Table 1
Process Conditions for Test Vehicles

Following exposure to the stripper solutions, rinse and dry, the samples were inspected under white and UV light in order to determine the presence of any dry film residues

The UV microscopy results are shown in Table 2, where its is clear that the three different strippers, and hence the 3 different mechanisms perform very differently.

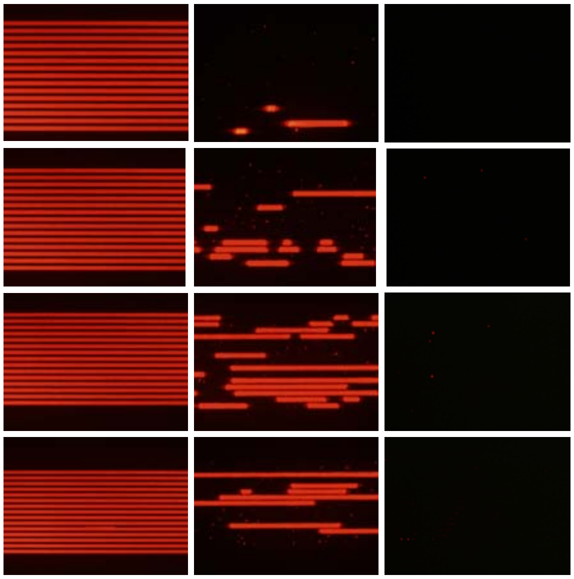


Table 2
UV Microscopy Images of Residues Seen on 10 – 40um Line and Space Features and RY3219 Dry Film

The simple hydroxide based stripper clearly shows high levels of residues even at 40um features and so is confirmed as unsuitable for fine line pattern plating, The amine based process performs much better with only moderate levels of residues, but residues that are of sufficient level to require rework or would lead to unacceptable scrap levels after etching. Secondary processing through the resist stripper, and longer contact times did give improvements in film removal, but even with 4 minutes and two passes through the stripper, the amine based process exhibited residues under UV inspection.

The new low swell process was the only process under investigation that offered clear and complete removal of the dry film without the need for a second exposure, and even at 10um line and spaces gave complete removal of the dry film.

Additional confirmation testing as detailed above, using a DuPont FX920 dry film, confirmed the same trend, with only the low swell process giving adequate removal of the dry film at all line and space conditions (Table 3)

During inspection of the test vehicles, it was interesting to note the nature of the residues experienced. Unsurprisingly, the hydroxide process left characteristically large residues although did show excellent stripping in adjacent areas. (Figure 8) It is thought that this is associated with subtle differences in fluid dynamics across the panel affecting the mechanical forces applied to the film during the chemical spraying. Uniform fluid dynamics are essential to reliable resist removal especially with generic chemicals as without any break down of the film, once the stripper has attacked the Copper-resist interface, only the spray action can help to lift the film from in-between plated features.

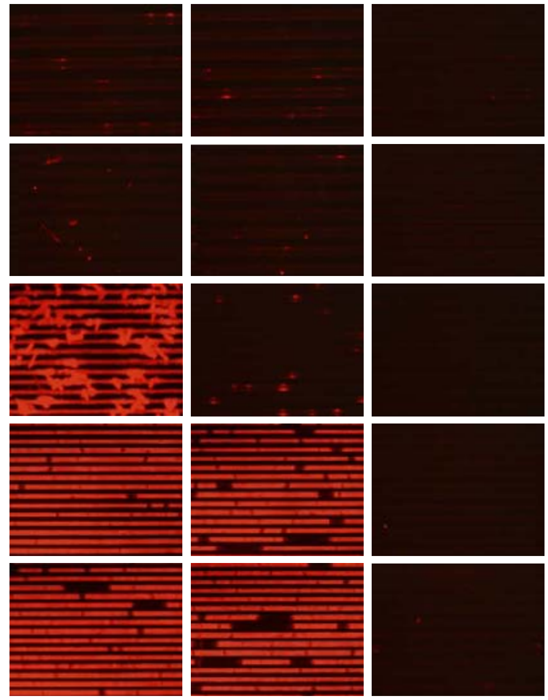


Table 3
UV Microscopy Images of Residues Seen on 20 – 60um Line and Space Features and FX920 Dry Film

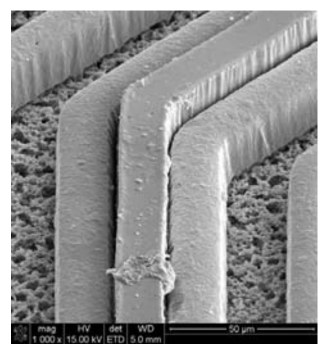


Figure 8
Large Residues Typical of Hydroxide Based Strippers

Those samples processed through the amine strippers showed a combination of large features plus much smaller residues usually located at the base of corners of tracks. In this instance, it is suggested that where there are large residues, the swelling action has resulted with mechanical lock in of the dry film, As the swelling has been restricted the rupture is greatly reduced, hence the larger residues, and as this phenomena increases as the line spacing decreases, it lends weight to the concept. In Figure 9a it is clear that the residue is no longer swollen and entrapped between the tracks, this issue due to shrinkage and dewatering of the residue during drying and sample inspection

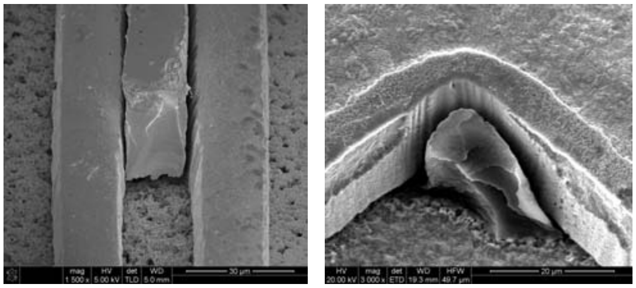


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Figure 9
Amine Based Processes Can Leave Both Large Feature as Well as Smaller Type Residues

Where the smaller residues have been found, it is thought that this arises from the small volumes of dry film involved working in combination with the effects of fluid dynamics. When the volume of dry film is low, its volumetric increase associated with swelling is reduced, and hence there is less stress generated within the particle of dry film. With reduced stress there is a reduction in the driving force for rupture and so particles will at some point reach a size at which they will no longer break into smaller particles. When this occurs, the only action available to continue and remove the residue is from attack of the Copper-resist interface. However the slow diffusion rate of the amine strippers, make the over all contact time a limiting factor. In addition, as the features become closer together, the fluid dynamics across the pattern also change and it is suggested that at smaller features, the effective spray pressure at the base of the track is lower than that for a larger feature. Thus with less direct impingement of the spray, there is less mechanical force trying to "blast" the film off the surface of the panel.

One other important aspect of a photo resist stripper, especially in fine line applications is the attack on the metal substrate. In pattern plate processing where a Tin mask is widely used, any attack on the Tin is undesirable, as once in solution, the Tin can be redeposit back onto the Copper that has been freshly exposed by the removal of the dry film. Once re-deposited, the Tin acts as an etch inhibitor during alkali etching, and the result is a short circuit. Known as "Tin transfer" this effect is more commonly seen in the hydroxide based strippers, and while the amine based strippers are not fully immune to it, they are much less prone, and it is another reason that they were adopted for pattern plating applications over the lower cost generic strippers.

Additionally, as lines get smaller the corrosion rate on the plated feature itself should be considered, and in SAP applications the attack rate on the electroless base layer is also of paramount importance. As such any new development in resist removal should aim to minimise any corrosive attack on any of the metal systems it is likely to encounter. The etch rates for the stripper solutions under investigation are shown in Chart 1 and were measured after an exposure time of 15 minutes at 55°C and a 2 Bar spray pressure. Such long contact times were necessary in order to achieve confident and repeatable values. As can be seen the amine based, and low swell processes are comparable in terms of metal attack and both offer significant advantages over simple hydroxides in pattern plate processes were a Tin mask would be used.

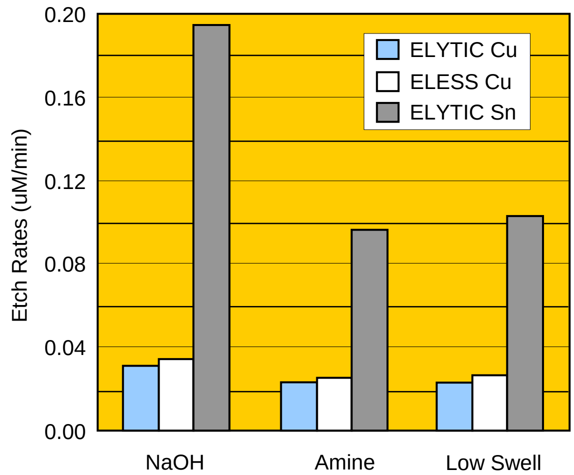

Chart 1
Dissolution Rates of Copper and Tin in Various Stripper Solutions

Production Ready

Following suitable tests, the low swell ResistStrip® IC process has been installed in a number of major manufacturers in Asia and has now been in production for over 3 years and in all cases showing improved results with respect to etch defects and reduced occurrence of photo resist residues.

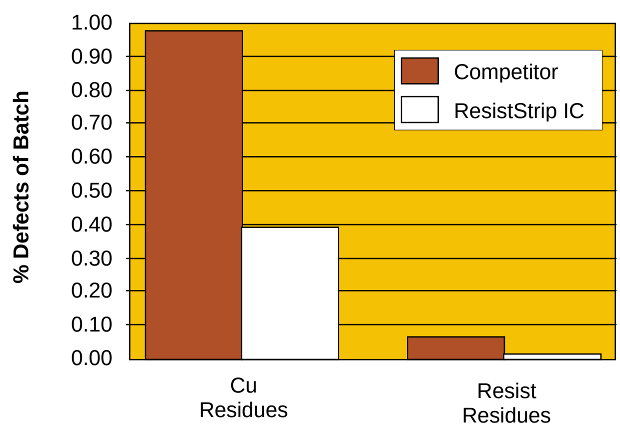

Chart 2
Production Data Experienced With ResistStrip® IC Process

Conclusions

The use of dry and liquid film photo resists is widespread within the PCB industry, and even allowing for alternative technologies, they are here to stay for the foreseeable future. Hand in hand with this goes the need for capable photo resist strippers, and as the capabilities of dry films have increased, it would appear that the advances in their removal processes has lagged behind somewhat. The commonly used stripping mechanisms today are more or less the same as those used when the processes were introduced, with film removal occurring in 4 distinct steps. Diffusion of the stripper species into the film, swelling of the film, which leads to rupture or mechanical break and finally attack of the Copper-resist interface leading to film lift.

This has been successful for over 40 years but with the drive for smaller and finer features, the traditional mechanisms and processes are beginning to fall short of the mark. A new stripping mechanism has been proposed in which the swelling of the resist is seen as the limitation for fine line capabilities and has been replaced with a fast diffusion, no swell process. Production ready chemistry based on such a mechanism is now available, and tests have shown that the new stripping process is more capable than either the simple hydroxide or the amine based processes currently available. With over 3 years of production completed, the low swell mechanism has been proven, and operating in high volume manufacturing has been shown to give tangible improvements.

With the improved capability of new resist stripping processes, the use of existing dry film imaging and removal technologies is assured for future generations of PCB as they enter the sub 25um arena and beyond.

References

[1] US Patent No 3469982 & 3622334

[2] Dietz K, *Dry Film Photoresist Processing Technology"* electrochemical Publications 2001

[3] Atotech ResistStrip IC Process released in 2006