Desmear and Plating Through Hole Considerations and Experiences for Green PCB Production

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Abstract
With the latest legislations from RoHS and WEEE dominating the horizon of the PCB landscape there is a need for manufacturers and their suppliers to understand their impacts. The requirement to remove lead from the industry and therefore the need for lead-free soldering operations means a large amount of stress is placed on the PCB substrates. The laminate material suppliers are responding to the new legislation by introducing newer varieties of materials that have better heat stress handling capacities as well as some added benefits like reduced z-expansion. Another concern for the laminate manufacturers is the need to remove halogen based, flame retardants like bromine from their resin systems. This paper will discuss the relevant legislations and the impact of these on the desmear and plating through hole processes. We will introduce and discuss the changes that are taking place in the laminate materials sector needed to meet the newer requirements. We will discuss the most significant advances in the halogen free as well as Pb-free capable materials. The significance of the changes and their influence on the desmear and PTH processes will be highlighted. Test results from investigations and experiences with the newer materials will be presented and compared to results normally found for the more standard materials. We will propose options for handling the various issues arising from these new materials and so help to prepare PCB manufacturers for the coming turbulence in the industry being generated by the new legislative demands.

Introduction

The most significant legislation for this topic is the Restriction of the use of Hazardous Substances (RoHS)[(1)] in electrical and electronic equipment directive. This new directive affects the metals; Lead, Mercury, Chrome (VI), and the resins PBB and PBDE (bromine containing), which have to be under 0.1%w/w in the finished product as well as Cadmium that has to be under 0.01% w/w. This legislation will come into force in the member states of the European Union where from July the 1st 2006 it is banned to sell electrical and electronic goods to households that do not comply with this directive. This means that component parts of the goods, including PCBs, have to comply months before this date, realistically from around the New Year. It is forecast that this will also apply throughout the world as the requirements from Europe are quickly adopted. The main concerns for this topic are the ban of lead and bromine. Both of these ultimately influence the laminate material choice for the PCB industry and so affect the performance and requirements of the desmearing and metallisation processes.

Lead Free Considerations

The ban of Lead means that conventional solder will no longer be tolerable. This means that alternatives have to be used. The market is full of various choices, with even regional preferences. A typical group of lead-free solders are so called SAC alloys, being based on Tin (Sn), Silver (Ag) and Copper (Cu). These solders have typical melting points from 213-240°C as compared to that of standard 63/37 solder of 183°C. This means that there is a minimum temperature increase of 30°C. For reflow oven technology for these Lead-free solders the typical profiles show peak temperatures of 260°C, again over 30°C more than for conventional solder. This extra heat during assembly will place more stress on the PCB and so suitable laminate materials have to be employed.

There are existing materials, especially exotic blends of plastics and resins, that are Lead-free capable already. There has been a large increase in epoxy based Lead-free capable laminate materials developed over the last year and a half. These typically employ hardeners that are used in combination with multifunctional epoxy resins to provide better temperature stability and lower Coefficients of Thermal Expansion (CTEs). Another typical trend for these materials is the inclusion of filler materials mainly to reduce CTEs as well as other physical characteristics. The main features of these materials are the ability to withstand high temperatures for longer periods of time before delaminating and significantly reduced CTEs so that stress on the barrel of copper plated in holes is reduced so reducing the occurrences of barrel cracks and inner layer connection failures.

Table 1 – Normal versus Pb-Free Capable Dielectric Materials1[2]

Base Material	Curing System	T_g (°C)	T-260°C (min)	T-288°C (min)	T_d (°C)
FR4 Epoxy High T_g	Dicyandiamide	175	8	0	300
FR4 Epoxy Mid Range T_g	Dicyandiamide	150	10	0	305
FR4 Epoxy Standard T_g	Dicyandiamide	135	15	0	315
FR4 Epoxy High T_g	Phenolic	175	> 60	40	360
FR4 Epoxy Mid Range T_g	Phenolic	150	> 60	9	340
FR4 Epoxy Standard T_g	Phenolic	135	> 60	13	357

Table 1 shows typical values for the different material T_g ranges of standard materials and the newer Lead-free capable materials. It shows that the T_g is not so important in determining the temperature capability of the material but the curing agent and resin mix is. Even a lower T_g standard epoxy material with phenolic curing can have a better temperature stability that that of a similar material but with higher T_g.

As well as the new types of resin systems the use of fillers is common for Lead-free capable materials, these give benefits in for physical properties like reducing CTE and can give benefits for electrical properties like D_f and D_k. By including these fillers the properties of the materials naturally change. This means that drilling performances will change as well as the response to subsequent processes like desmear and metallisation. The changes may be minimal but also need to be characterised and understood.

In previous published studies[3] it was shown that for higher Tg and higher technology epoxy materials the desmearing capability is generally reduced, the roughness achievable is reduced and the instances of hole wall adhesion issues are increased. The conclusion from the study was that higher cross-linking leads to higher chemical resistance of the material and this in turn leads to reduced desmear attack and roughening. The extremely high temperature resistance of these epoxy materials with the use of phenolic curing systems causes some concern regarding the response to desmear as well the metalizing of these materials, especially the activator for electroless copper systems and the effect on conductive polymer direct metallisation systems. These new types of material need to be assessed with all current processes so that optimised processing parameters can be set-up.

Bromine Free Considerations

The removal of bromine from the basic formulation of laminate materials means that alternative flame retardant systems have to be implemented. These materials are referred to as 'Halogen Free' materials. Typical alternative flame-retardants are based on Phosphor compounds included in the resin system or added separately, other additives and fillers like metal hydroxides amongst others. For older generations of halogen free materials fillers and additives were commonly employed. For the more modern generation of materials it appears as if the use of Phosphor based resins or fillers is in vogue. Also a significant number of modern halogen free materials tend to include fillers. It appears that there is again a significant change in the formulation of materials entering the laminate market so that they are able to fulfil the halogen free legislation. This change means that once again the PCB manufacturer has to be aware of the influence on its processes and their lifetimes. This means that assessments need to be made with these newer materials so that process optimisations can be made.

Desmear Studies

One of the key process steps that will be affected by these newer materials entering the market is desmear. The main purpose of this process is to wet the board and holes and remove smear from innerlayers. The permanganate desmear system is the most commonly one used in the PCB industry. This operates by using a swelling step to wet and then soften the resin making it more susceptible to attack from the permanganate etch step that oxidises and etches resin smear from innerlayers as well as the hole wall surface with a final step that cleans away remaining manganese residues left by the permanganate step. The highly chemical resistant epoxy materials being introduced to cope with Lead-free soldering show lower desmearing responses. Atotech has been making a characterisation study of laminate materials to help to understand the response of different material types. Graph 1 shows some typical desmear responses for some of the newer Lead-free capable materials on the market compared to a standard Di-cy cured high T_g material and standard T_g material. Different Sweller systems of different aggressiveness were chosen to see if one or the other was more suitable for each material.

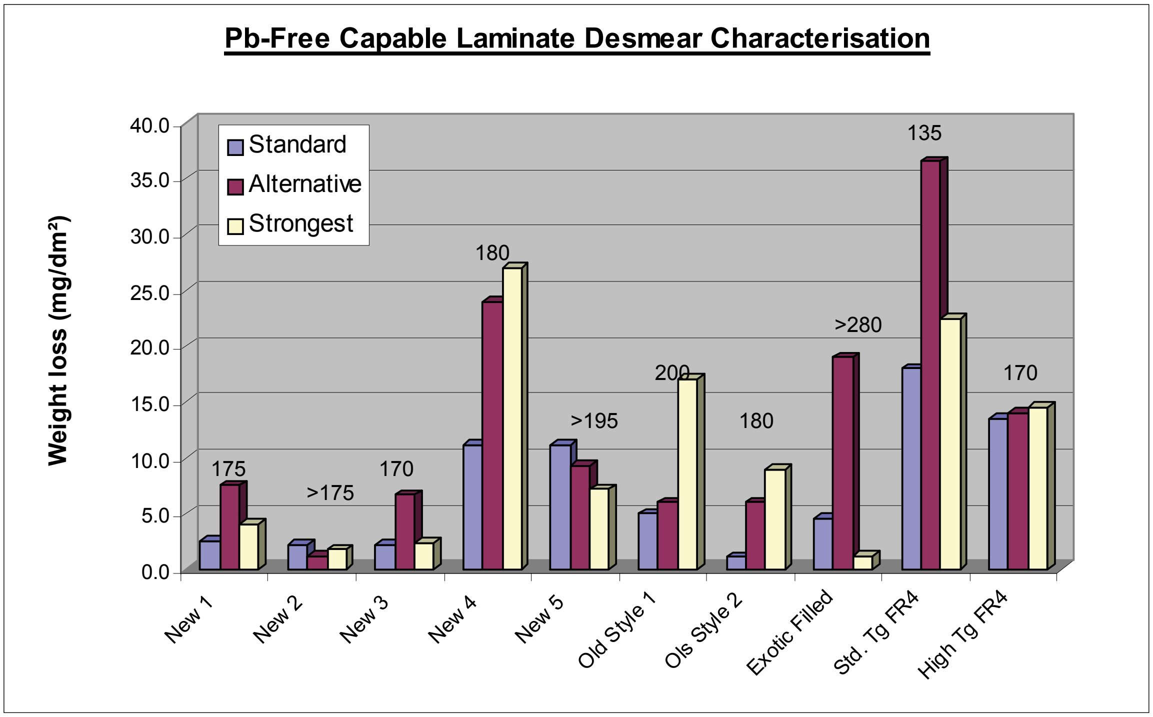

Chart 1 – Typical Desmear Responses for New Pb-Free Materials and Standard Materials

The T_g of each material has been indicated for reference. This graph shows the large range of responses from the newer Pb-free materials as well as some of the older materials suitable for Lead-free applications. There is a large range of weight loss even though T_g values do not differ by so much. The standard T_g FR4 and the high T_g FR4 show the usual pattern that the weight loss is reduced for the higher T_g material but the different Sweller types have little influence. The newer materials show that the strongest Sweller is not necessarily the most effective, although the weight loss response from most of the newer materials is low. The lack of roughening associated with higher chemical resistance is clearly evident from the following SEM pictures taken after desmearing with the standard Sweller system.

SEM Holes Wall Pictures of Pb-free Capable Materials after Standard Sweller and Desmear

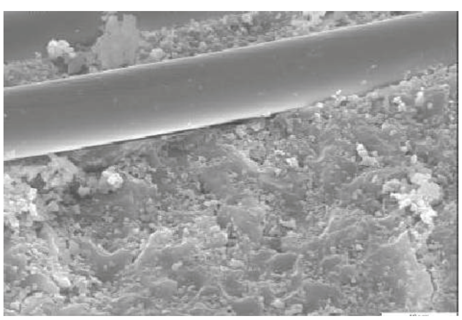

Figure 1 – New 1

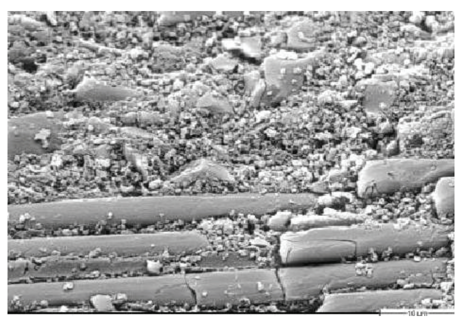

Figure 2 – Exotic Filled

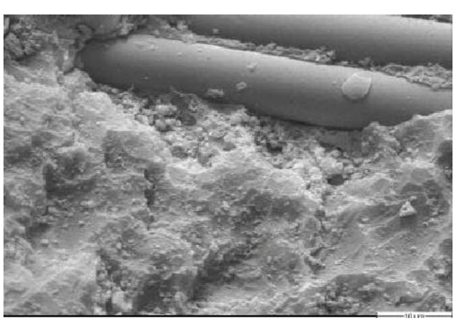

Figure 3 – New 3

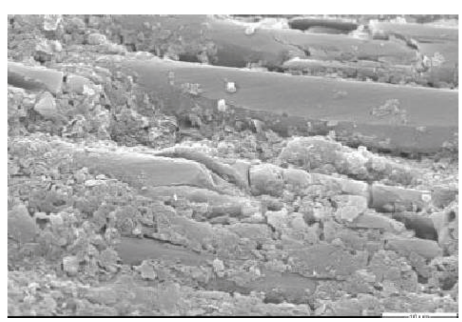

Figure 4 – Exotic Filled

The study of the weight loss for halogen free laminates that are not considered to be Lead-free capable shows also the differences between the individual materials.

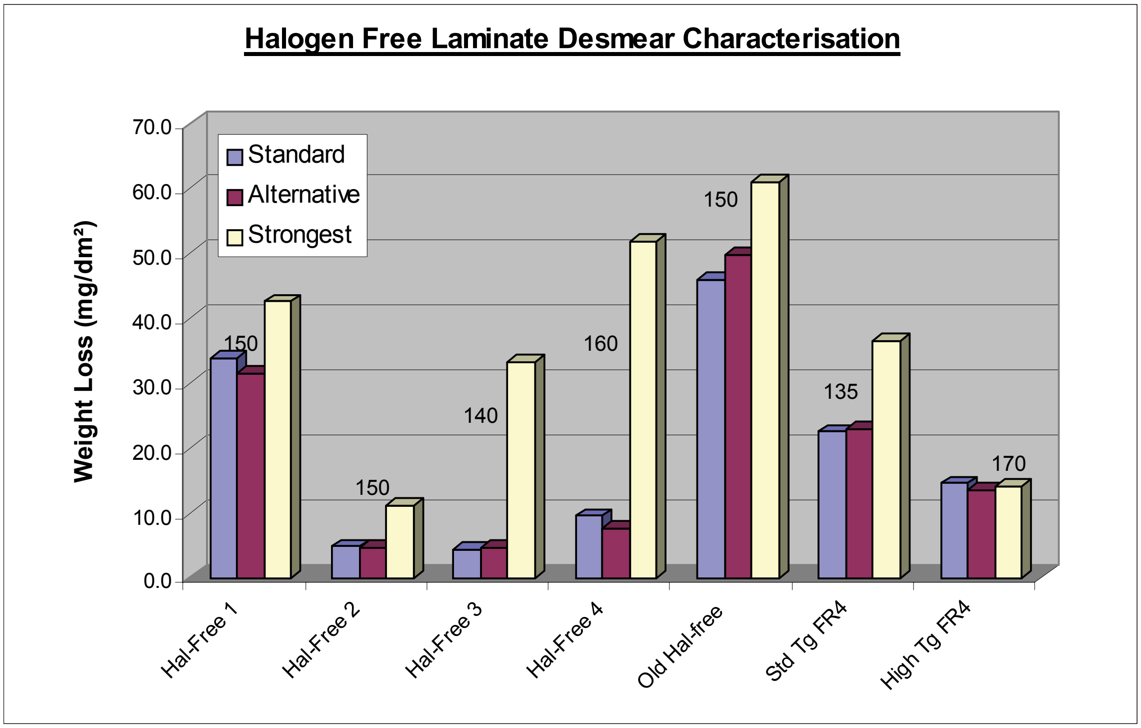

Chart 2 – Typical Desmear Responses for Halogen Free and Standard Materials

The large difference in weight loss response is clear even for relatively similar T_g values. The use of the strongest type Sweller here would provide a better weight loss for these materials similar to that experienced for standard T_g FR4 material.

SEM Holes Wall Pictures of Halogen-free Materials after Standard Sweller and Desmear

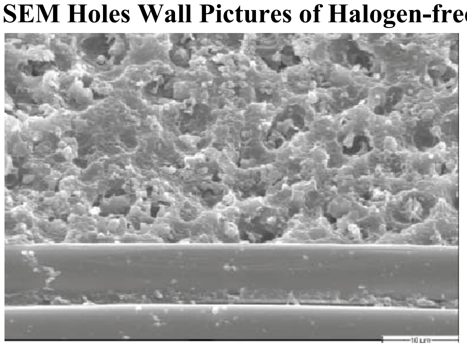

Figure 5 – Hal-free 1

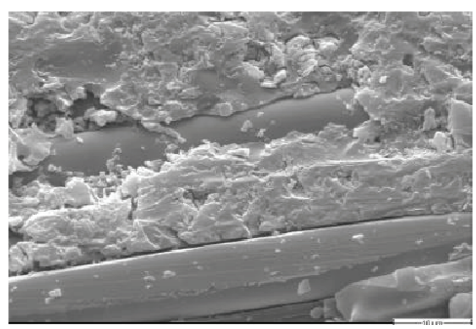

Figure 6 – Hal-free 2

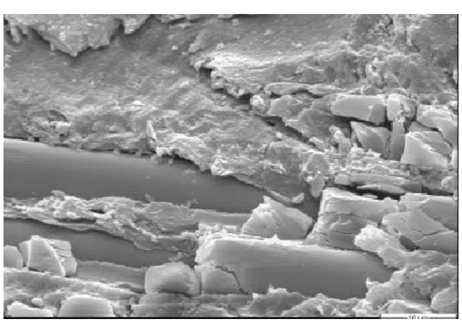

Figure 7 – Hal-free 3

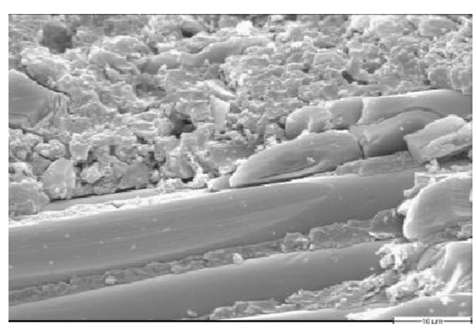

Figure 8 – Hal-free 4

Interference Microscope Hole Wall Pictures of Halogen-free Materials after Standard Sweller and Desmear

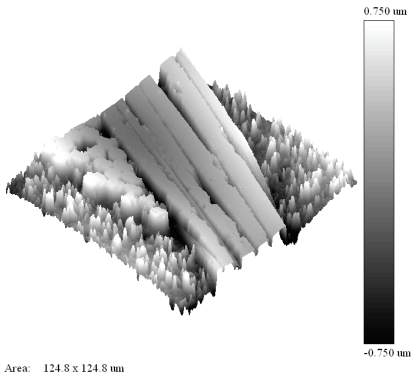

Figure 6 – Hal-free 1

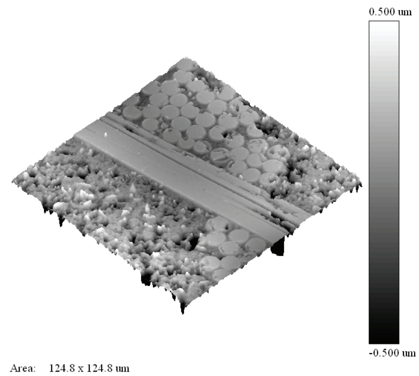

Figure 7 – Hal-free 2

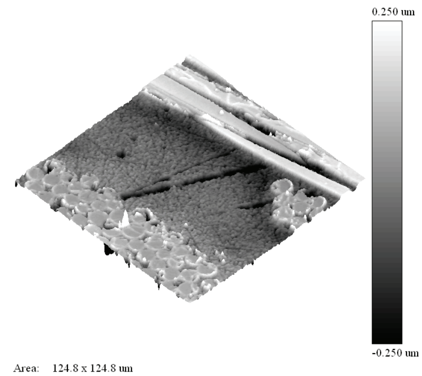

Figure 8 – Hal-free 3

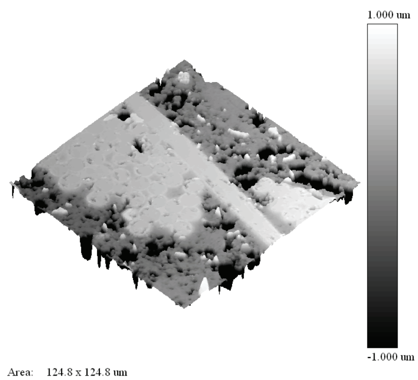

Figure 9 – Hal-free 4

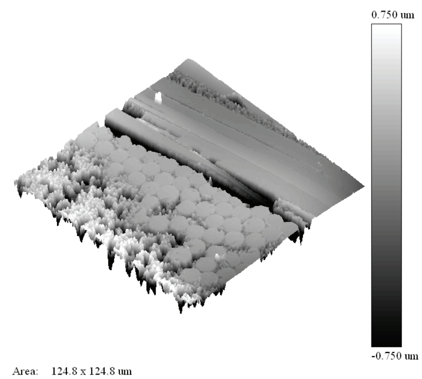

Figure 10 – Old Hal-free

The interference microscope pictures show more clearly the roughening on the surface of a hole wall after desmearing for the various materials. The different degree of filler materials is obvious with material 1 having large amounts of filler particles. It is similar to the old style halogen free material shown in figure 10. The others show less or not roughening due to filler release. This small handful of examples shows the wide variety of materials now being labelled as halogen free.

Experiences from metalizing some of these newer Pb-free capable and/or halogen free materials have shown that sometimes optimisation of a process is required to achieve the same coverage and plating results as with more normal materials.

Summary

The introduction of new legislation to reduce the impact of certain known harmful substances on the environment has had a profound effect on the types of laminate materials required for the PCB industry. The suppliers of these new materials have developed new types of materials with innovative blends of resins and fillers to meet the tough criteria of these legislations. The effect of these new materials entering the market is that existing process parameters are not necessarily suitable. The examples shown in this paper clearly indicate the wide response to desmear for the different materials. The conclusion from this paper is that there is a significant influence on processes like desmear and metallisation from the newer laminate material developments and that PCB manufacturers need to be aware of this issue and to actively work with their suppliers to re-evaluate and optimise their processes. The use of these newer materials is inevitable and programmes should be undertaken to evaluate them as soon as possible to avoid delivery issues and quality problems. This paper was not written to be negative about the newer laminate materials and their formulations, many of which bring a lot of technical as quality benefits, it is just to highlight that there are differences to common materials in use today and these differences should be taken seriously and tested.

References

1. RoHS – Directive 2002/95/EC of the European Parliament and of the Council of 27th January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic material
2. Isola – EIPC Winter Conference 2005
3. Neil Patton / Kelvin Suen – Assessment and Solutions for Hole Wall Pull-away in High Tg and High Technology Laminate Materials, CPCA 2004