Development of FR-1 Materials for Lead-free Soldering

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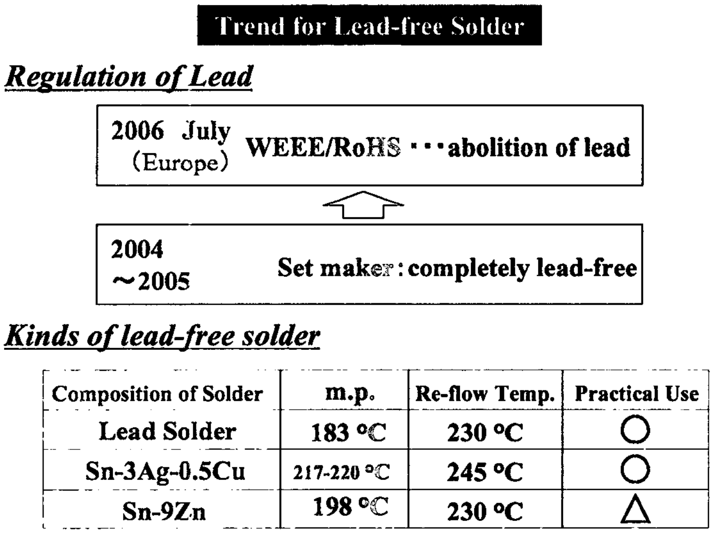
1. Introduction

Due to the concern for environmental protection that has increased globally in the electricity and electrical devices sector, the use of six detrimental substances, such as lead, will be forbidden by WEEE(Waste Electrical and Electronic Equipment)/RoHS (Restriction on Hazardous Substances) in Europe starting July, 2006. In preparation for this each major electrical equipment manufacturering company is beginning to move towards lead abolition in 2004.

Using the Sn-Ag-Cu solder and Sn-Zn solder, lead-free solder has been carefully examined. The Sn-Ag-Cu solder is used due to its solder reliability, workability, and the infrastructure of the equipment. (Fig. 1)



Trend for Lead-free Solder

Regulation of Lead

2006 July (Europe) WEEE/RoHS ･･･abolition of lead

2004 ~2005 Set maker : completely lead-free

Kinds of lead-free solder

Composition of Solder	m.p.	Re-flow Temp.	Practical Use
Lead Solder	183 °C	230 °C	○
Sn-3Ag-0.5Cu	217-220 °C	245 °C	○
Sn-9Zn	198 °C	230 °C	△

Fig. 1

Since the melting point of this solder is higher compared with lead solder, the mounting temperature in the re-flow process is raised from the maximum temperature of 225 degree C to the maximum temperature of 245 degrees C. Because this solder's spreading rate is inferior to lead solder, it is necessary to have a longer re-flow time while the solder melts. Thus, in the case of using the Sn-Ag-Cu solder; it is important to be cautious with the heat load of a substrate or parts, so it is necessary to check the adaptability.

When our company product lineup (Fig. 2) is taken as an example, we used a substrate packaging board for FR-1 materials. The heat load mentioned does not become a problem in glass epoxy materials, FR-4, and CEM-3 materials, which have a margin in heat resistance. However, in FR-1 materials that do not have a margin in heat resistance, faults, such as a de-lamination, may be generated during mounting conditions, or the PWB design, etc. (Fig. 3)

The Categorization of Circuitry Materials

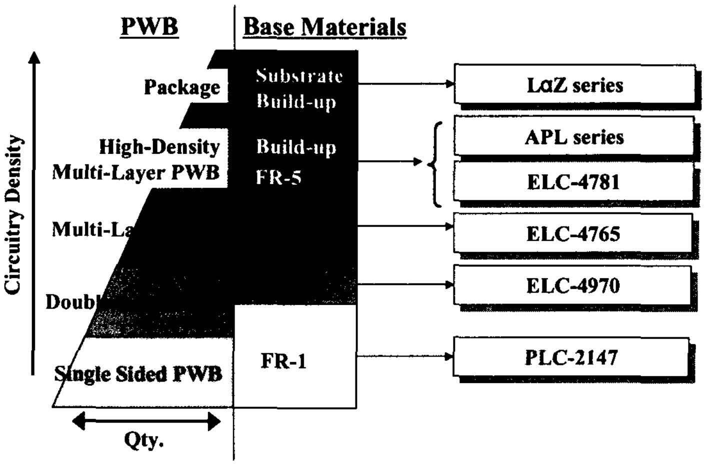
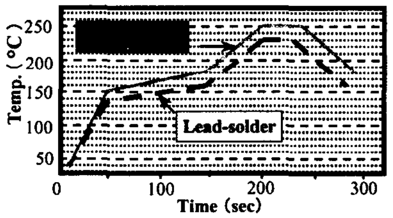


Fig. 2

Lead-Free Soldering of FR-1 by Re-Flow

Re-low condition using lead-free solder



Heat resistance of FR-1

Material	Mounting method	Heat resistance
Single sided	Flow	○
	Re-Flow	△
Double sided	Re-flow + Flow	
	Re-flow + Re-flow	×

Double-sided can not be used for two times reflow
(included the other CCL maker's product)

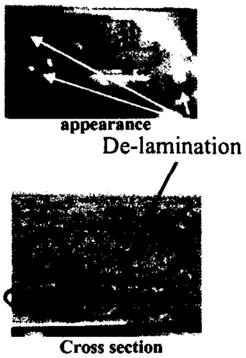


Fig. 3

It is said that there are 6,800,000 m^2/month sold in the market of FR-1 materials all over the world. (Fig. 4) The double-sided board, in which most is mounted by the re-flow system, amounts to no less than 600,000 m^2/month. However, due to the present heat resistance of most FR-1 materials, if lead free solder is introduced completely, it may be very difficult to mount FR-1 materials by the re-flow process.

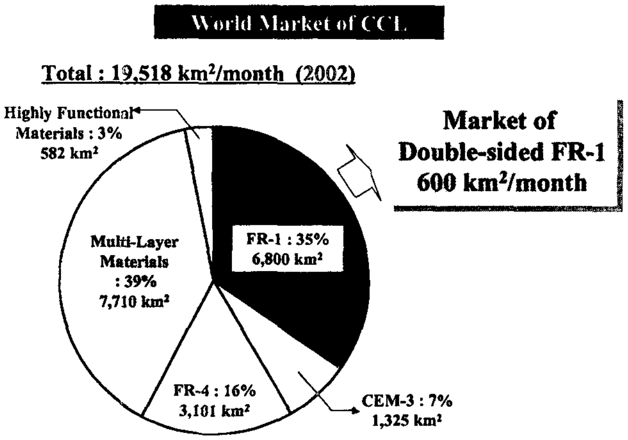


Fig. 4

The greatest advantage of FR-1 materials is cost competitiveness, and when the present home-electronics market is considered, development of FR-1 materials corresponding to the re-flow mounting process of lead-free solder is needed. On the other hand, the halogen fire retardant in which we are also cautious about as a dioxin generation source is being kept at arm's length, and the tendency for halogen-free materials has become strong.

Sumitomo Bakelite started the development of FR-1 material corresponding to lead-free solder re-flow mounting and halogen-free.

2. Development Process

2-1 Set Up of the Target

The development target is shown in Fig. 5.

Direction of Development

Target

Items	Condition	Target
Re-Flow Heat Resistance	Max. 250 °C x 2 times	No Blister
Re-Flow Heat Resistance after Moisture Treatment	C-96hr / 40 °C / 90%RH + Max. 250 °C x 2 times	No Blister
Flam Resistance	UL Method	94 V-0 Halogen-free
Punchability	70 °C	Same as Existing

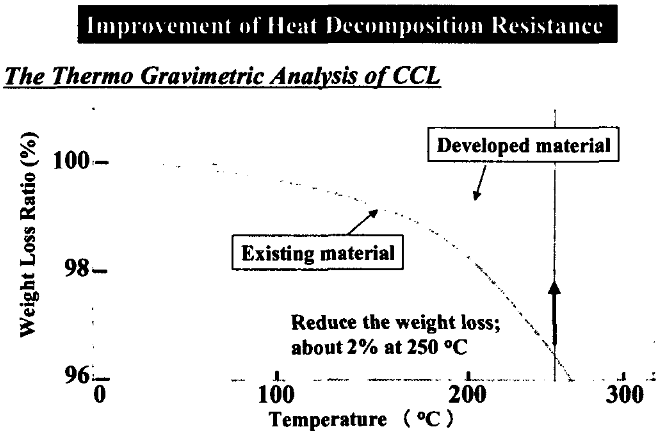
Fig. 5

2-2 Contents of Development

Since it corresponded to lead-free solder re-flow mounting, we considered the improvement of heat-resistance in the three plans shown below:

(1) The heat-resistant remedy by improvement of the heat decomposition

Paying close attention to the heating weight loss of FR-1 materials, we considered the controlling of chemical weight loss when heating. The weight loss curve of the developed material at heating is shown in Figure 6. The chemical weight loss successfully reduced into about 2% under 250 degree C range in which lead-free solder re-flow mounting is assumed.


Improvement of Heat Decomposition Resistance

The Thermo Gravimetric Analysis of CCL

Fig. 6

(2) *The heat resistance remedy by improvement of the impregnation.*

It is known that the heat resistance of FR-1 materials can be influenced by moisture absorption. For this reason, it is necessary to take the moisture absorption of a substrate into consideration during the actual mounting process.

Furthermore, in order to acquire cost competitiveness in recent years, mounting overseas, especially Southeast Asia, and China, is increasing and re-flow mounting which used lead-free solder with a high temperature that corresponds to moisture absorption is increasingly needed.

The voids on the inside and interface of a paper fiber were reduced by improving the impregnation of the paper fiber to resin. The result was an improvement of heat-resistance and moisture resistance.

By having optimized the molecular weight of resin and the solvent, the impregnation to a paper fiber became better. We checked that the moisture resistance of the developed materials was excellent compared to existing materials. (Fig. 7)

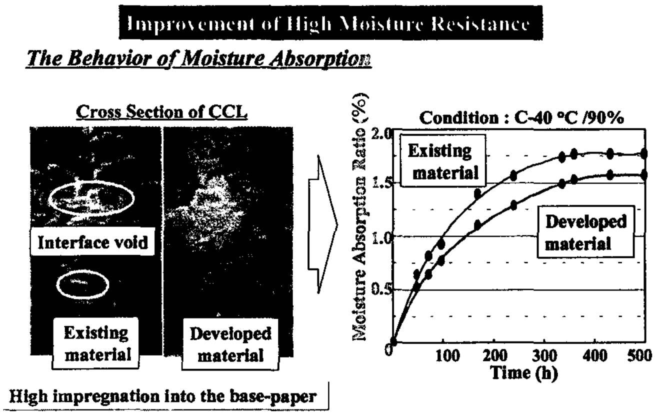


Fig. 7

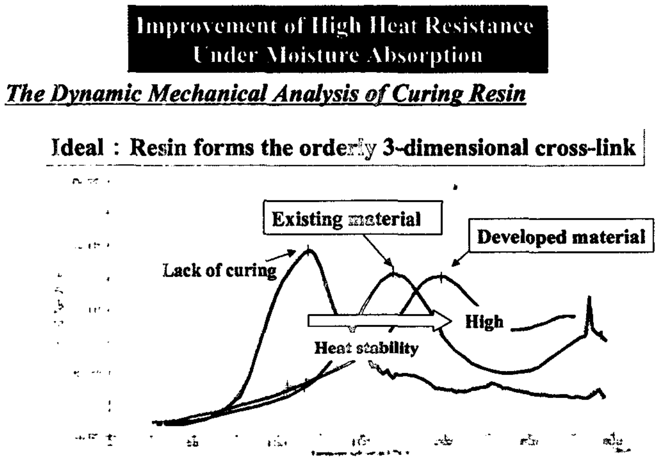


Fig. 8

(3) The heat resistance remedy by control of curing

The characteristic of thermosetting resin depends on the curing degree. The heat resistance and the fire retardancy are affected if the curing is inadequate.

The toughening of resin and the strengthening of the adhesion power were performed by raising a curing degree, and the heat resistance and the fire retardancy were raised.

Evaluation of the degree of curing was performed by DMA (Dynamic-Viscoelasticity Measurement). The curing degree was higher, so the peak temperature of the loss tangent (tan delta) of the hardening resin is high.*[1,2] Tan delta of the hardening resin of a developed material is shown in Fig. 8. The developed material has a conventionally high peak temperature of tan delta compared with the existing material, and it is judged that the hardening degree is high. Since the existing material had the low hardening degree, it is considered that the hardening agent was tougher and a high adhesion was not obtained.

3. The Characteristic of Developed Materials

3-1 The Result of the Re-Flow Heat Resistance

The re-flow heat resistance of developed materials is shown in Table 1.

Re-Flow Heat Resistance of Developed Materials

Pre-Heat : 150-180 °C		About 100 sec.			
Above 230		27 sec.	32 sec.	40 sec.	44 sec.
Max. Temperature		240 °C	245 °C	250 °C	255 °C
Developed Material (Halogen-free)	1st	O	O	O	O
	2nd	O	O	O	O
	3rd	O	O	X	X
Existing Material (Halogen-free)	1st	O	O	O	X
	2nd	O	O	X	
	3rd	X	X	X	

* Thickness : 1.6 mm, Double sided PWB O : No Blister
**TP : Our Own TP Cu remain ratio : 40%

Table 1

Compared with the existing materials, the developed materials had a stable heat resistance at a high temperature, and it was confirmed that the developed materials could be used for lead-free soldering in a 2-times re-flow process.

The hygroscopic re-flow heat resistance of developed materials is shown in Table 2.

It has been confirmed that developed materials have outstanding moisture resistance and has heat resistance that is stable even if it absorbed moisture. This is considered to have originated due to the moisture resistance improvement, which raised the impregnation, and the toughening of the resin and the improvement in adhesion power by having raised the curing degree.

3-2 General Properties

The general properties of the developed materials are shown in Table 3. The developed materials show characteristics better than the existing materials in all items, especially in the items that show high

Hygroscopic Re-flow Heat Resistance of Developed Materials

Max. Temperature : 245 °C

C – 40 / 90%RH		48 H	72 H	96 H	168 H	552 H (23 days)
Developed Material (Halogen-free)	M.A. ratio	0.43%	0.55%	0.67%	0.91%	1.40%
	1st	O	O	O	O	O
	2nd	O	O	O	O	O
	3rd	O	O	O	O	X
Existing Material (Halogen-free)	M.A. ratio	0.61%	0.78%	0.92%	1.19%	1.66%
	1st	O	O	O	O	X
	2nd	O	X	X	X	
	3rd	X				

* Thickness : 1.6 mm, Double sided PWB — O : No Blister

** TP : Our Own TP Cu remain ratio : 40%

***M.A. Ratio : Moisture Absorption Ratio

Table 2

General Properties

Items	Unit	Developed Material (Halogen-free) PLC-2147 GFtype	Existing Material (Halogen-free) PLC-2147 GHtype
Re-flow Heat Resistance (2 times)	°C	255	245
Hygroscopic Re-flow Heat Resistance (2 times)	°C	250	<245
Solder Heat Resistance	sec.	60	50
Peel Strength	kN/m	2.0	2.0
Flexural strength	N/mm²	144	154
Insulation resistance	Ω	3E10	1E10
PCT test(PCT-8/121)	Ω	3E10	3E9
Punchability	—	O	O
UL Approval	—	V-0	V-0

Table 3

Coefficient of Thermal Expansion of CCL Z-axis Direction

The Thermal Mechanical Analysis of CCL

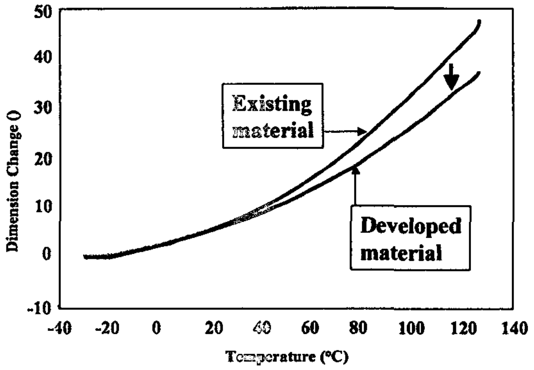


Fig. 9

insulation resistance and low water absorption due to having raised impregnation and curing degree.

The TMA (Thermal Mechanical Analysis) curve of the direction of the Z-axis of CCL (Copper Clad Laminates) is shown in Fig. 9. It should be mentioned that the developed materials also have a small coefficient of thermal expansion in the direction of the Z-axis compared to the existing materials. This is considered to create a high through-hole connection reliability in the thermal shock test. Here, the effect of having raised impregnation and the curing degree was confirmed.

4. Conclusion

Sumitomo Bakelite has developed FR-1 materials corresponding to lead-free soldering in a two times re-flow process that is halogen-free.

Because of the rapid increase in the demand for FR-1 materials corresponding to lead-free soldering using the re-flow process will be expected by 2006, lead-free solder will be introduced completely from now on. When using FR-1 materials corresponding to lead-free soldering by the re-flow process, we believe that a mutual cooperation between set makers, and PWB makers, etc. are needed for a further spread of this technology. At Sumitomo Bakelite we take a positive attitude towards taking the time to work together to create these materials in advance.

(Reference)

*1 John D. Ferry, Viscoelasticity of polymer (1964)

*2 Rheology Society of Japan, Lectures / Rheology (1992)