Radiation Curing Technology
in Liquid Photo-Imageable Solder Mask (LPISM)

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Abstract

Development of electronics industry grows along with the progress in Radiation Curing Technology (RCT). Especially, photolithographic method contributes to the development of higher precision microcircuit technology. Liquid Photo-Imageable Solder Mask (LPISM) is electronic material of alkali developing type with dual-curing system that used both UV-curing and thermal curing. LPISM used for the application of printed circuit boards (PCB) in almost all electronics products.

World market of LPISM has been growing. Recently, a market of LPISM has been developing rapidly in Asia and increasing remarkably in China. The progress of the RCT of LPISM has been growing, and the ultra-high photosensitivity that can support Laser Direct Imaging (LDI) has been enabled.

1. Introduction

LPISM is protective coat of PCB based on RCT. LPISM is formed selectively on the surface of PCB by photolithography method. The primary purpose of LPISM is to protect circuits through electric insulation by physically avoiding formation of a bridge at soldering. With Solder Mask (SM) used initially, thermal-curing ink was coated selectively at pattern printing to form a masking, and this was replaced by UV-curing ink due to the request in enhancement of productivity. Photo-imageable ink of solvent developing type was substituted later for the UV type to meet with requirements for high-resolution. At present, photo-imageable ink of alkali developing type is the mainstream to cope with environmental loads and request for reducing costs. This paper reports the market of alkali developing type LPISM and RCT applied to LPISM.

2. World Market

Figure 1 shows ratio of LPISM in SM. Percentage of LPISM has been increasing along with introduction of lighter and more compact PCBs. The market of LPISM has been growing as shown in Figure 2. It can be anticipated that the production of LPISM reaches 25,000 tons/year in 2006. The majority of this increase is attributable to the marked growth in the Chinese market. As for PCB, at the beginning, conductive circuits were mounted on the single side. Later, double-sided or even multilayer PCBs emerged while their applications were expanded. At present, module circuit boards for substrate use of CPU and even flexible circuit boards to be incorporated in the liquid crystal driver are available. It is expected that flexible circuit boards will be used extensively in the future.

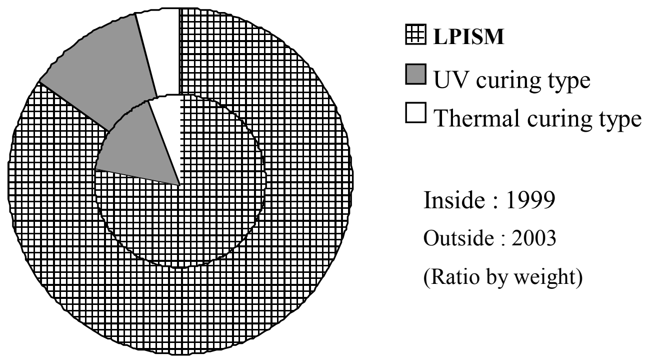


Figure 1. Ratio of LPISM in SM.

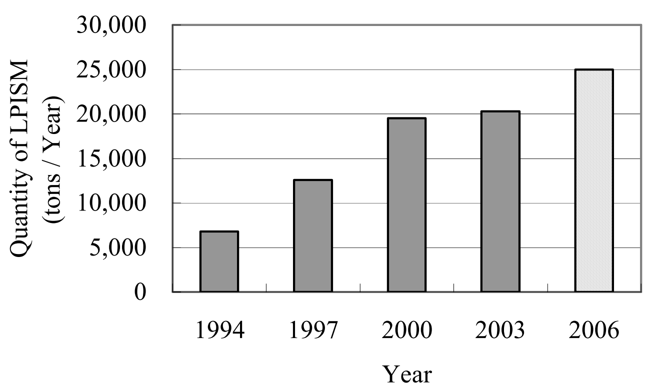


Figure 2. World market of LPISM.

3. Technology

3.1 Composition of LPISM

Composition of LPISM is shown in Figure 3. In addition to main resin, monomer, photoinitiator, epoxy resin, and catalyst are thermal-curing components for dual-curing system that used both UV-curing and thermal curing. Solvents are added for the sake of ease of coating and are evaporated out before UV curing. Filler for improvement of heat resistance, color pigments for appearance, and additives for reological adjustment are also included. Commonly, two-component type of LPISM is used for extension of the shelf life and is mixed just before an application.

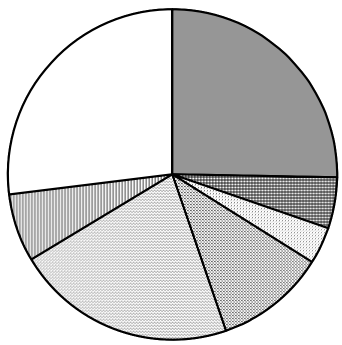
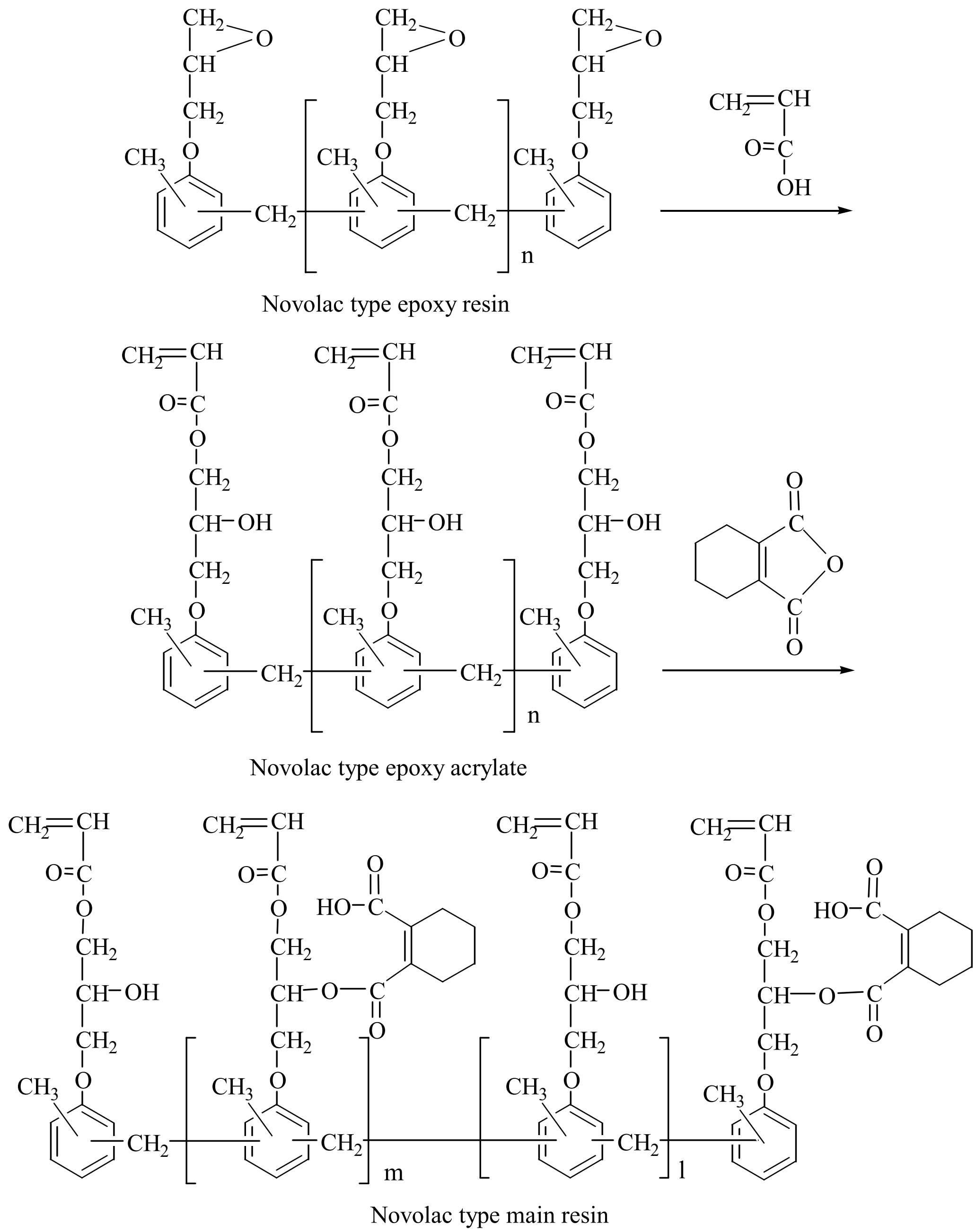


Figure 3. Chemical composition of LPISM.

3.2 Raw materials of radiation curing system

3.2.1 Main resin

The main resin containing pendant two functional groups such as carboxyl groups and acryloyl groups can dissolve in 1wt.% sodium carbonate solution. As shown in Scheme 1, a synthesis method of novolac type main resin is reaction of acid anhydride with obtained epoxy acrylate by reaction of novolac type epoxy resin with acrylic acid. Novolac type main resin was developed by TAIYOINK MFG. CO., LTD. at the first time and commonly used even today. Meanwhile, LPISM for module and flexible circuit boards required softness in curing coating used different type of main resin, which backbone structure changed from novolac type epoxy resin to bis-A or bis-F type epoxy resin. Moreover, copolymer of methacrylic acid and methyl methacrylate in which photosensitive monomer is added, are also used. It is widely recognized that a resin which only posses carboxyl group, lack photosensitivity. The main resin containing only carboxyl group without photosensitive group is also used for LPISM. However, expression of the LPISM's characteristics is difficult, because main resin without acryloyl group deteriorates photosensitivity of LPISM.



Scheme 1. Novolac type main resin

3.2.2 Monomer

The requirements of acrylate monomer that used LPISM are combine high reactivity and higher softening point to ease of tackiness at exposure. For that reason monoacrylate monomers are inapplicable to use LPISM. Figure 4 showed the structure of dipentaerythritol hexa acrylate (DPHA). DPHA is best suitable monomer and thus exhibits (1) high Tg of the cured coating, (2) superior photosensitivity, (3) tack-free dry coating, (4) heat resistance, and (5) development.

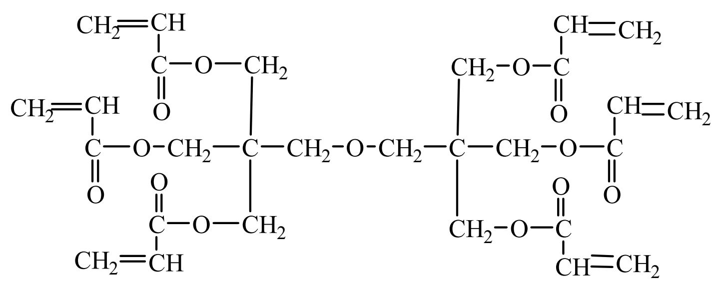
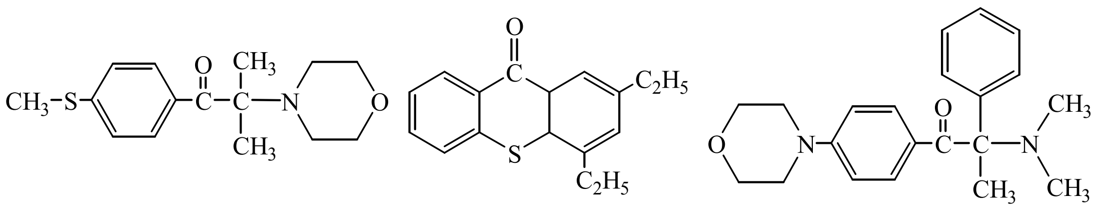


Figure 4. Structure of dipentaerythritol hexa acrylate.

3.2.3 Photoinitiator

One of requirements for the photoinitiator is that no mist should be generated in the drying and the exposure processes. Photoinitiators and sensitizers shown in Figure 5 are selected appropriately in view of the light source. Novel photoinitiators entirely different from the conventional ones used LPISM for LDI.



IRGACURE 907 KAYACURE DETX-S IRGACURE 369

Figure 5. Structure of photoinitiators.

3.3 Processes

3.3.1 LPISM formation process

A formation process of LPISM is shown in following (1)-(6). (1) LPISM in liquid state is coated on the entire surface of PCB. (2) Organic solvent is volatilized in the hot-air convectional oven to obtain tack-free dry coating. (3) UV light is irradiated via a mask. (4) Unexposed area is removed through development in the alkali solution to create a desired pattern. (5) Thermal curing is carried out at 150 ℃ for 1 hour to give a cured LPISM. (6) According to circumstances, LPISM requires post-UV process along with thermal curing.

3.3.2 UV exposure equipment

So far, diffusion light with the metal halide lamp is used commonly. This is currently shifting to semi-parallel light by the high-voltage mercury lamp or to parallel light via optical system due to requests for higher resolution. As for module circuit boards used for severer, the requirements are imposed, split projection, (step and repeat) method is normally used. The mask is changed from silver salt film to dry photographic plate while diazo films are not used at all today. As for a clearance between mask and coating, vacuum contact is normally used to control oxygen inhibition. In the case of the split projection method and LDI, UV exposure is made under atmosphere where improvement of the surface curing is required. Recently, by remarkable development of a laser diode, LDI is capable of depicting directly a pattern by laser light from the digital data without using a mask. This technique has been attracting attentions because correction of dimensions of the pattern depicted is possible and mask production process is unnecessary.

3.3.3 Substrate

With conventional white-yellow substrate, which is a lamination of glass fabric composite epoxy resin, a light transmits through the substrate during exposure. LPISM on the rear is also drawn as the image, which is referred to as the shoot through phenomenon. With module circuit boards, it is frequently seen that irradiation light is absorbed by black substrates resulting in insufficient curing in the deep portion. With flexible circuit boards based on the polyimide film, shrinkage of the film at drying and exposure causes curling of the printed circuit board. From workability reason, LPISM with lower shrinkage are expected.

3.4 Radiation curing

3.4.1 Spectral sensitivity

Spectral sensitivity of the ordinary LPISM and those corresponding to 405 nm LDI are shown in Figure 6. With ordinary LPISM, the surface is attacked by the developing solution in the wavelength longer than 350 nm. With LPISM for LDI, which possesses excellent-curing performance, the use of newly developed photoinitiator and resin eliminates the problem of the developing solution's attack of the surface in the longer wavelength region.

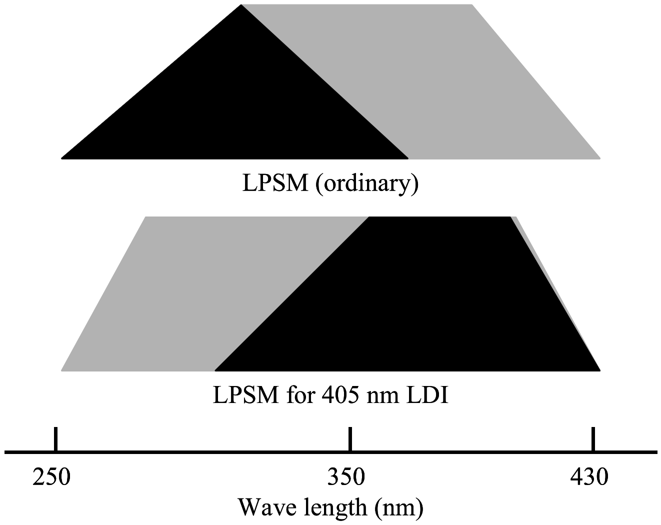


Figure 6. Spectral sensitivity of LPSM.

: Non-attacked surface, : Attacked surface.

3.4.2 Sensitivity

Table 1 shows the sensitivity of the ordinary LPISM and of LPISM for module circuit boards, which requires higher reliability and physical properties in the cured film. In the composition where softness is required, UV curing features are suppressed in part and borne by other properties.

Table 1. Sensitivity of LPISM [a)]

	Exposure energy (mJ/cm^2)					
	140	210	280	500	600	700
LPISM (ordinary)	6 (steps)	7 (steps)	8 (steps)	---	---	---
LPISM (module board)	---	---	---	5 (steps)	6 (steps)	7 (steps)

a) Kodak no.2 step tablet.

3.4.3 Reaction rate

The reaction rate of acryloyl group and epoxy group for each process steps is shown in figure 7. Although acryloyl group remains after thermal curing process, the reaction rate is improved by post-UV radiation of approximately 1 J/cm^2.

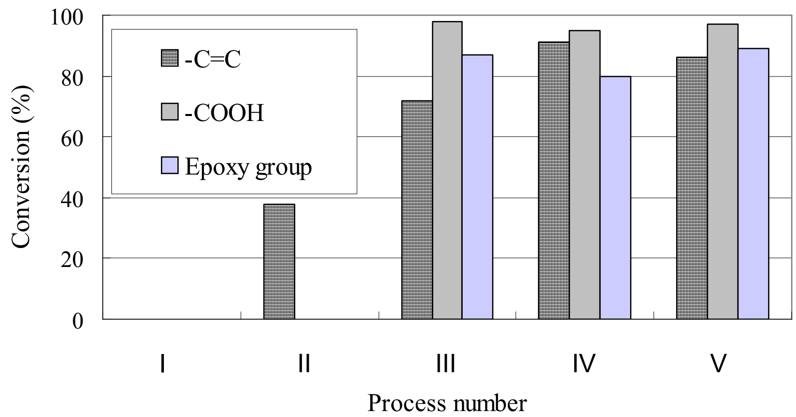


Figure 7. Process and conversion.

Process number, I: after dry, II: after (I + exposure), III: after (II + thermal curing), IV: after (II + post UV + thermal curing), V: after (III + post UV).

3.4.4 Resolution

Line sectional photographs and resolution of the ordinary LPISM and those corresponding to 405 nm LDI are shown in figure 8 and table 2. With LDI, a line of platform profile free from undercut can be formed which is considered to be attributable to permeability of the wavelength.

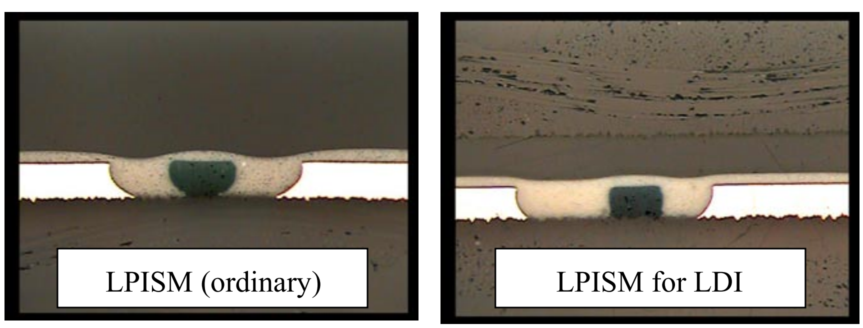


Figure 8. Resolution of LPISM (cross-section of line)

Table 2. Resolution of LPISM

	Photograph	lamp	Exposure energy (mJ/cm^2)	Line thickness (micron)	Exposure width (micron)	Line width (micron)		
						Top	Middle	Bottom
LPISM (ordinary)	Left	Metal halide	200	61	90	103	122	60
LPISM (for LDI)	Right	405 nm LD	40	58	90	94	95	80

3.5 Requirements for LPISM

It was summarized the requirements for ordinary LPISM in table 3. In addition to pattern forming features, many requirements should be met for the permanent mask. Price is also one of the important factors, however these are not shown in the table 3. Recently, requests for low-priced materials have been cited frequently.

Table 3 Requirements of LPISM

Requirement		Result	Remark
LPISM	Main agent	PSR*-4000 G23K	Main agent / Hardner = 700g / 300g
	Hardner	CA-40 G23K	
Color		Green	Cured coating
Viscosity		150 dPa・s	E-type viscometer 25deg.C
Solid content		79 wt.%	after mixed
Specific gravity		1.4	after mixed
Pot life		24 hrs.	after mixed, 20deg.C
Tack dry window		80deg.C / 60min.	Max. developable dry condition
Exposure energy		140-280 mJ/cm2	Measured on LPISM
Sensitivity	140 mJ/cm2	6	Steps,
	210 mJ/cm2	7	Kodak No,2 step tablet
	280 mJ/cm2	8	Developing time 60sec.
Resolution	140 mJ/cm2	50 micron	Min. line width,
	210 mJ/cm2	50 micron	Thickness 40+/-2micron,
	280 mJ/cm2	50 micron	Developping time 60sec.
Adhesion		100 / 100	Tape peeling
Pencil hardness		7H	IPC-SM-840C 3.5.1
Solder heat resistance		no peel	260deg.C / 30sec.
Acid resistance		no peel	10wt.%H2SO4aq / 20deg.C / 20min.
Alkaline resistance		no peel	10wt.%NaOHaq / 20deg.C / 20min.
Solvent resistance		no peel	PGM-Ac / 20deg.C / 20min.
Insulation resistance	Initial	2.1e13 ohms	IPC-SM-840C 3.8.2
	Conditioned	4.3e11 ohms	25-65deg.C / 90%RH / DC100V / 7days
Dk	Initial	4.2	Measured at 1MHz
	Conditioned	4.3	25-65deg.C / 90%RH / DC100V / 7days
Df	Initial	0.023	Measured at 1MHz
	Conditioned	0.042	25-65deg.C / 90%RH / DC100V / 7days
Electroless Au plating resistance		no peel	Ni/3micron + Au/0.03micron
Electrolytic Au plating resistance		no peel	Ni/5micron + Au/1micron
Flammability		UL94V-0	IPC-SM-840C 3.6.3

* **PSR** is a TAIYOINK MFG. CO., LTD's products name of LPISM.

3.6 Environmental requirements

In order to cope with environmental requirements, there is a trend to dehalogenate phthalocyanine pigments and dry films instead of inks in liquid state. As an alternative to epoxy resin, possibility of oxetane resin is currently investigated. Other issue concerning the environmental requirements is the increased soldering temperature associated with usage lead-free solder. However, this does not pose a significant problem with regard to the heat resistance of LPISM.

4. Conclusions

Requests in high precision for PCBs emerge endlessly. High-sensitivity, high-resolution, and a cured film with good physical properties of LPISM should be satisfied simultaneously. Hence further development of the RCT is expected.

Acknowledgement

Alkali developable type LPISM technology has its origin in the epoxy acrylate technology. Thanks to remarkable progress of the RCT, PCB market has made a great expansion. In this regard, we sincerely thank Professor T. Nishikubo, Kanagawa University, who developed precedent technologies.

References

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