Development of Polyimide Over-coat Ink "UPICOAT" and Its Application

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ABSTRACT

An aromatic polyimide film shows a high heat resistance as well as electric characteristics, and is widely employed as material for electronic devices such as an electronic camera, a personal computer, and a liquid crystal display. For instance, the aromatic polyimide film is bonded to a copper foil via an adhesive such as an epoxy resin to produce a flexible printed circuit (FPC) or a substrate for tape automated bonding (TAB). UPICOAT is an overcoat ink which have been developed for the purpose of an application for TAB technology. UPICOAT coated film has quite low initial modulus of 40 kg/mm^2 which gives low repulsive force at bending and very low warpage of substrate. It also has excellent electric reliability as keeping 10^9 Ω of insulation resistance after 1000 hours test (85% RH at 85 ℃) as well as high heat resistance with 5% weight loss temperature of 410 ℃.

INTRODUCTION

UPICOAT is an over-coat ink comprised of soluble polyimidesiloxane, crosslinking agent (epoxy resin), catalyst for crosslinking, antifoaming agent, fillers, and solvent.[1)] The processing temperature of TAB technology is usually below 200 ℃. By the reason that the curing temperature is relatively low for the precursor such as polyamic acid, UPICOAT uses soluble polyimides. UPICOAT has been developed as a screen printing ink which requires high solid content for forming of a certain coating thickness. Therfore, the developement of this material has been started from the study on the solubility of polyimides for various solvents. In general, the solubility of polimides increases in the cases of introducing the asymmetric flexible chain, introducing the large bulky side-unit, and reducing the regularity or symmetry of main chain by way of co-polymerization.[2)] The polyimides derived from 2,3,3',4'-biphenyltetracarboxylic dianhidiride (a-BPDA, UBE) usually shows good solubility.[3)] The a-BPDA-based polyimides do not have essentially regularity by the reason of the random sequences of head-to-head, head-to-tail, and tail-to-tail bondings. In this report, the studies on the soluble polyimide based on a-BPDA, the method of cross-linking, the some properties of UPICOAT, and the application for TAB technology are shown.

EXPERIMENTAL

Polyimides were obtained by thermal imidization at 180 ℃ for 5 hours from the equimolar mixture of a-BPDA and dimamines in several kind of solvents. The a-BPDA was only employed as aromatic tetracarboxlic dianhydride. Diamines used in this study are shown in Table-1. The screen printing ink was obtained by kneading with a triple roller from the polyimide dope added some components such as cross-linking agents, catalysts, fillers, etc.

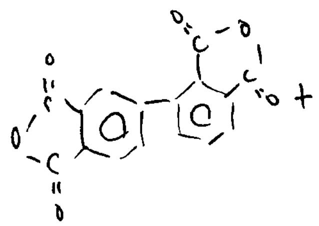
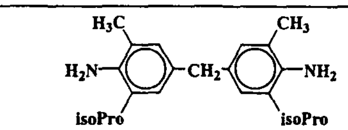
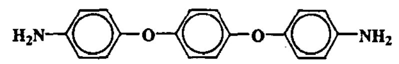
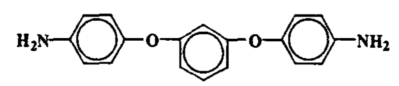
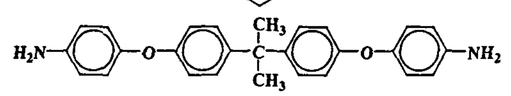
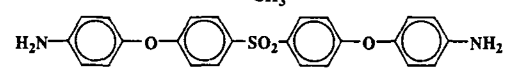
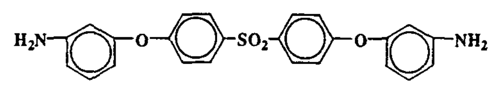
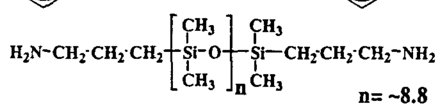


Table-1 Diamines used in this study

	Abbreviation
	M-MIPA
	TPE-Q
	TPE-R
	BAPP
	BAPS
	BAPS-M
	DAPSi

RESULTS AND DISCUSSION

SOLUBILITY The solubilities of various polyimides (PI's) in several solvents are listed inTable-2. The all aromatic polyimides (run 1-6) based-on a-BPDA are soluble in basic solvent such as NMP. The polyimide having bulky side proup such as an isopropyl radical (run 1) indicates higher solubility as compared with the other PI's. On the other hand, the solubilities of PI's having polysiloxane unit become higher as increasing amount of polysiloxane unit. The polyimide of run 10 can be solubilized in all the solvents used in this study. The solubilities of PI's of runs 9 and 10 are above 50 wt% in non basic solvents such as triglyme. The viscosities of 50 wt% triglyme solutions of runs 9 and 10 are around 100 poise at room temperature even if the molecular weights are high (Mn~30000; estimated from GPC). This may be caused by the flexible nature of polymer chain. The polyimidesiloxanes such as runs 9 and 10 are useful for the base polymer of screen printing ink.

PROPERTIES AS COATING RESIN In the case of the flexble printed circuit, the CTE mismatching of each constituents causes serious warpage. Therefore, the CTE controll of the constituent materials is one of the most important subject as well as the adhesion force of the interface between each components. Some properties of the coated films derived from the polymer listed in Table-2 are shown inTable-3. The adhesion properties of the coated films to the substrates (electrodeposit copper foil and UPILEX-75S) are estimated by the cross-cut peeling. UPILEX-75S is usually used as the base polyimide film for TAB tape with 75 μm thichness. Though the adhesion properties of the coated films to the copper foil are good for all PI's in Table-2, those to UPILEX-75S are fair for the polyimidesiloxane alone. The warpage of the UPILEX-75S film coated by the polyimides shown in Table-3 with 20 μm thickness is estimated as the radius of curvature. As the radius of curvature becomes large, the warpage becomes small. As for the all aromatic polyimides, the warpage is extremely high. This is caused by the CTE mismatching and the high modulus of the coated film. On the other hand, as the polysiloxane content of polyimides becomes large, the warpage of the UPILEX-75S coated by the corresponding polyimidesiloxane remarkably decreases. When the tensile modulus of coated film becomes lower than 40 kg/mm^2, the warpage of laminate can not be seen. Whereas the CTE of polyimidesiloxane such as run 10 is in the arround of 1x10^{-4} /℃, the internal stress is quite low for the low tensile modulus of the coated film. It is concluded that the polyimidesiloxane with high polysiloxane content is suitable for the over coat base resin for the flexible printed circuit.

Table-2 Solubility of various polyimides

Run	Diamine			Solubility						
	aromatic(Ⅰ)	DAPSi(Ⅱ)	Ⅰ:Ⅱ	BC	T	TG	DO	CH	NMP	*
1	M-MIPA		-	×	○	○	○	○	○	**
2	TPE-Q		-	×	×	×	△	×	○	
3	TPE-R		-	×	×	×	△	×	○	
4	BAPP		-	×	△	△	○	△	○	
5	BAPS		-	×	×	×	○	×	○	
6	BAPS-M		-	×	×	×	○	×	○	
7	BAPP	DAPSi	9:1	×	×	○	○	○	○	
8	BAPP	DAPSi	7:3	×	○	○	○	○	○	
9	BAPP	DAPSi	5:5	△	○	○	○	○	○	
10	BAPP	DAPSi	2.5:7.5	○	○	○	○	○	○	

*; BC:butylcellosolve, T:toluene, TG:methyltriglime, DO:dioxane
CH:cyclohexanon,NMP:N-methyl-2-pyrrolidone
**; ○:soluble, △:swell, ×:insoluble

Table-3 Properties of coated film

Polymer Run	Tensile modulus Kg/mm^2	Adhesion property* Cu	Adhesion property* UPILEX-75S	Warpage Radius of curvature(mm)
1	brittle	○	×	—
2	230	○	×	10.1
3	270	○	×	12.6
4	220	○	×	11.2
5	260	○	×	10.0
6	240	○	×	10.0
7	170	○	○	9.8
8	92	○	○	19.8
9	65	○	○	39.4
10	10	○	○	∞

*; cross-cut peeling, ○: fair ,×: poor

INK DESIGN Because the soluble polyimide does not have essentially solvent resistance, the design of cross-linking in the curing process is required. The polyimidesiloxane utilizing in UPICOAT is a-BPDA-based copolyimide derived from hard, soft, and reactive units. The hard unit is formed by aromatic diamine such as BAPP and the soft one is polysiloxane segment derived from DAPSi. The cross-linking is achieved by the reaction between reactive group of base polymer and epoxy resin accelerated by catalyst at 150~170 ℃ for an hour. The appropriate fillers such as a synthetic amorphous silica are employed for the achievement of desired flow chatacterisitcs as a screen-printing ink. UPICOAT has two grades (FS-100L and FS-510T) and the solid content of the latter is higher than that of the former. FS-100L is for the general use and FS-510T is suplyed for the fine pattern use.

PROPERTIES OF FS-100L Some properties of UPICOAT FS-100L coated film are listed in Table-4. Since the tensile modulus of UPICOAT FS-100L coated film is about 40 kgf/mm^2, the warpage of the laminates can not be actually seen for practical use. The example of insulation resistance measurements at bias test (85% RH at 85 ℃) is shown in Figure-1. As seen in Figure-1, UPICOAT FS-100L coated film has excellent electric reliability as keeping 10^9 Ω of insulation resistance after 1000 hours at bias test (85% RH at 85 ℃).

Table-4 Properties of UPICOAT FS-100L

Item	Unit	Typical Propertes	Testing Method
Tensile Modulus	Kg/mm^2	40	ASTM D-882
5% Thermal Weight Loss	℃	410	TGA
Volume Resitivilty	Ω·cm	1×10^{16}	23℃,50%RH,DC100V
Surface Resistance	Ω	1×10^{16}	23℃,50%RH,DC100V
Dielectric Constant	—	3.2	23℃,50%RH,1KHz
Adhesion Strength	Kg/cm	1.3	ICP 650-2.4.9
Moisture Absorption	%	0.3	immerse in water at 23℃,24Hrs.

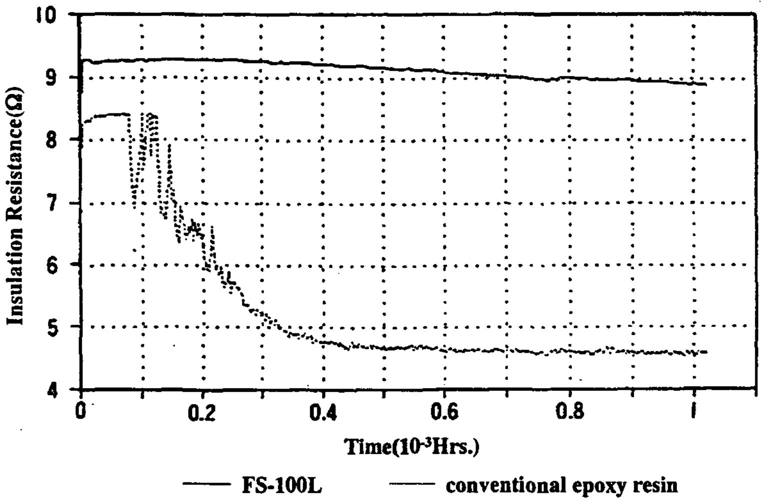


Figure-1 Migration measurement(85℃, 85%, DC30V, 30μm L/S)

APPLICATION TAB technology is now widely employed for the electronic devices such as a liquid crystal display. For the purpose of the equipement of electronic components in the small space, a TAB tape is mounted by bending. UPICOAT is used as a over coat resin at the position of TAB tape around bending, and it contributes to the field of an electronic industry such as a personal computor and a cell phone. UPICOAT releases the new categoly of a coating resin, that is, a flexble or soft coating.

References 1) Yasuno,H. *Kogyozairyo,*43,No6,1995. 2) Mita,I.*Kinozairyo*,**10**,1981.3)Yamaguchi,H. In *Recent Advances in Polyimides,1997,*Yokota,R.;Hasegawa,M.,Eds.,Raytech Co.,Tokyo,p5.