The Properties of Soldering Mask Hardened by Means of UV Using Acrylate and Methacrylate Oligomers

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SYNOPSIS

The properties of soldering masks based on epoxyacrylic, epoxymethacrylic esters, and monomers: 2-ethylhexyl acrylate, triethylene glycol dimethacrylate, and triethylene glycol phthalate dimethacrylate have been described. The thixotropic properties, printability, adhesion to the surface, and resistance to soldering have been determined. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Soldering masks, hardenable in ultraviolet radiation, constitute a protection of printed plates used in common utensils. In the liquid state, they should possess suitable properties such as viscosity, securing good printability, and proper thickness of the layer. After hardening, they should have good adhesion to the surface which is, e.g., Cu, and resistance to soldering by Sn and Pb.

The structure of the monomer or oligomer used in mask production, on the one hand, affects the hardening rate and, on the other hand, hardness, flexibility, stability, and good adhesion to the surface of the coating obtained after hardening in ultraviolet radiation. According to Neerbas,[1] oligomers used for this purpose should possess suitable acid value, hydroxyl value, and acrylic functional groups. Their concentration has influence on the rate of the hardening reaction and the extent of the crosslinking coat. Other parameters characterizing the mask such as viscosity, adhesion to the surface, and thermal resistance depend upon the concentration of the UV polymerization initiator and filler. Some authors suggest that the thermal properties and adhesion to the surface are influenced by the structure of the filler grains; thus, they recommend fillers of elongated shape.[2]

In this article, we applied acrylic and methacrylic oligomers to prepare soldering masks. The influence of the oligomer's acid value, kind, and quality of photoinitiator and amount of the filler on the properties of the masks were studied.

EXPERIMENTAL

Materials

To prepare the mask, used were diane–epoxide resin of LE = 0.50, where LE = equivalent of epoxy groups/100 g of epoxy resin (Epidian 5, Chemical Plant Sarzyna, Poland); DMP-30, an accelerator (Rohm and Haas); hydroquinone, acrylic, and methacrylic acids (Merck); 2-ethylhexyl acrylate of viscosity 12–15 cP at 20°C and acid value LK = 4.16 mg KOH/1 g; triethylene glycol dimethacrylate (TGM-3, Russia) of viscosity 145–150 cP at 20°C and LK = 14.5 mg KOH/1 g; triethylene glycol phthalate dimethacrylate (MGF-9, Russia) of viscosity 3 cP at 20°C and LK = 0.22 mg KOH/1 g; a photoinitiator which is a mixture of Irgacure 907 and Irgacure 500 at the ratio 1:3 (Ciba-Geigy), and the fillers Carbosil ECh-5 (Germany) and talc M 0.5 (Figs. 1 and 2).

Synthesis of Acrylate Oligomer

Diane epoxy resin, 365 g, of LE = 0.50 val/g, 0.0373 g of hydroquinone, 125.7 g of acrylic acid (n_D^{20}

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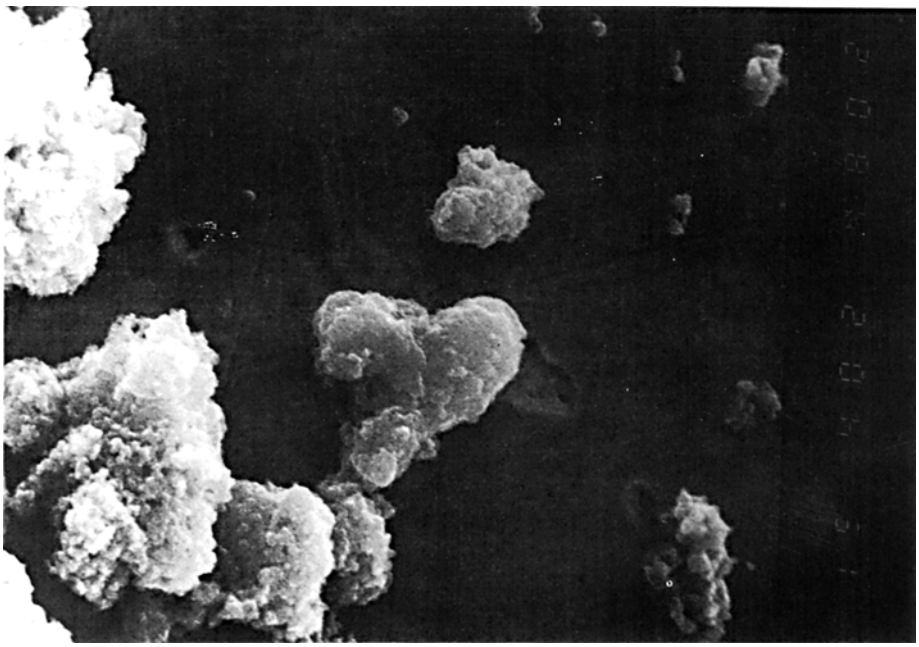


Figure 1 Micrograph of Carbosil ECh-5 (magnification ×4000).

= 1.4202), and 1.3 g of DMF-30 were placed into a glass reactor of 1 dm^3 volume equipped with a mechanical stirrer and thermometer and heated to 80°C. The addition process was carried out with a gradual temperature increase up to 120°C. Heating was finished when the acid value equal to 2–9 mg KOH/1 g was reached. Then, the mixture was cooled to 100°C and dissolved in triethylene glycol dimethacrylate or in triethylene glycol phthalate dimethacrylate.

Synthesis of Methacrylate Oligomer

Methacrylate oligomer was synthesized according to the above-described procedure, but instead of acrylic acid, 131.4 g of methacrylic acid (n_D^{20}

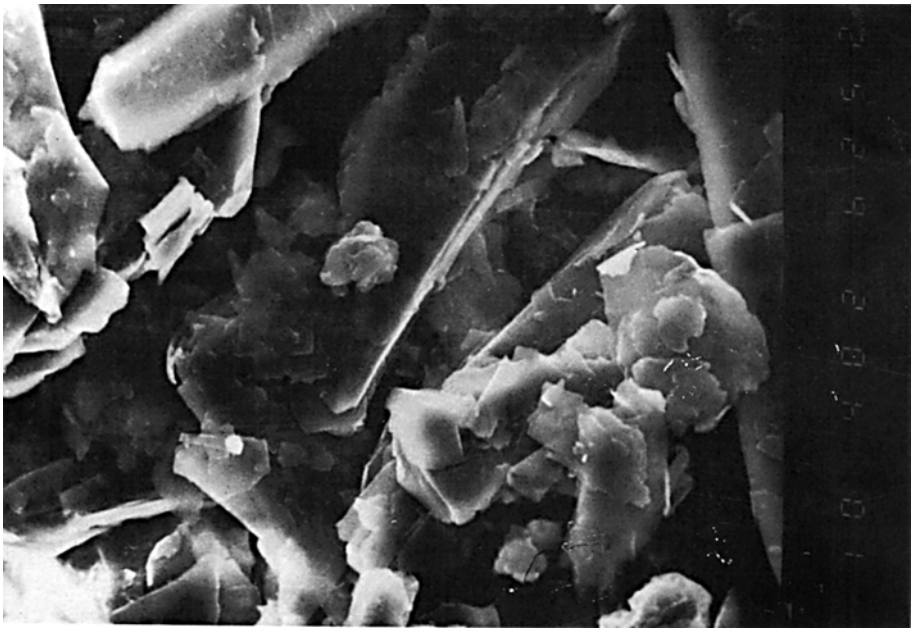


Figure 2 Micrograph of talc (magnification ×4000).

Table I Composition of the Studied Masks

	Mask No.																
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Acrylate oligomer				100	100	100	100	100	100	100	100	100	100	100	100	100	100
Methacrylic oligomer	100	100	100														
2-Ethylhexyl acrylate	15.7	12.5	14.0	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	16.7
Triethylene glycol dimethacrylate (TGM-3)				37.5		37.5	37.5	37.5	37.5	37.5	37.5	37.5	37.5			37.5	41.7
Triethylene glycol phthalete dimethacrylate (MGF-9)	33.3	37.5	32.0		37.5									37.5	37.5		41.7
Irgacure 907	2.9	2.5	3.0	1.5	2.5	4.5			1.0	1.25	1.5	2.08	1.5	2.5	2.5	2.5	3.3
Irgacure 500	5.9	5.0	6.0	3.0	5.0		3.0	4.5	2.0	2.5	3.0	4.15	3.0	5.0	5.0	5.0	6.7
Carbosil ECh-5	9.8	12.5	10.0	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	16.7
Talc M 0.5	22.4	45.0	36.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	45.0	100.0

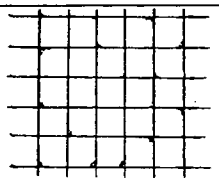
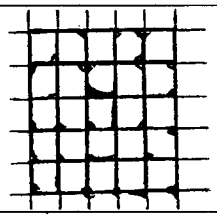
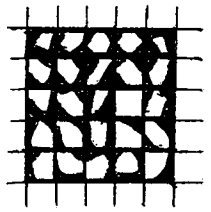
Class	Description	Appearance of surface of cross-cut area from which flaking has occurred (Example for six parallel cuts)
0	The edges of the cuts are smooth; none of the squares of the lattice is detached.	-
1	Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area not distinctly greater than 5 % is affected.	
2	The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area distinctly greater than 5 %, but not distinctly greater than 15 % is affected.	
3	The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area distinctly greater than 15%, but not distinctly greater than 35% is affected.	

Figure 3 Classification of test results.

= 1.4310) was added into 365 g of diane epoxy resin of LE = 0.50 val/g. The obtained oligomer of LK = 2–9 mg KOH/1 g was dissolved in the above-mentioned oligoesters. Composition and properties of the obtained substances are given in Table I.

Preparation of Masks

After mixing the components, masks were homogenized using a rolling mill and conditioned for 7 days (Table I); then, their viscosities were examined and print was made by the use of the hand-operated screen printer through the monofilament/polyester, mesh count 100T/cm and 130T/cm. The coat put on the glass–epoxylaminate foiled with copper was visually estimated and then subjected to crosslinking in the dryer type 53-60B (ITR, Poland) using ultraviolet light of the maximum wavelength of 366 nm. Adhesion to the surface and resistance to soldering of the obtained coats were examined.

Table II The Influence of the Acid Value of Epoxy Methacrylate Oligomer and Oligoester Used and the Mask Properties

Mask No.	LK of Methacrylate Epoxy Oligomer (mg KOH/g)	Printability Through Monofilament Mesh 130T and 100T	Class of Adhesion to Copper		Resistance to Soldering (Mesh 130T and 100T)
			Before Soldering	After Soldering	
1	0	Bad	—	3	Bad
2	2.6	Good through 100T	3	Beyond scale	Bad
3	9.0	Bad	2	2	Bad

Table III The Influence of the Acid Value of Epoxy Acrylate Oligomer and Oligoester Used and the Mask Properties

Mask No.	LK of Epoxy Acrylate Oligomer (mg KOH/g)	Printability Through Monofilament Mesh 130T and 100T	Class of Adhesion to Copper		Resistance to Soldering (Mesh 130T and 100T)
			Before Soldering	After Soldering	
4	1.4	Good	1	1	Bad
5	2.8	Good through 100T	0	0	Good (100T)
6–12	3.4	Good	1	1	Good (100T)
13	7.2	Good	2	3	Bad

Testing Procedures

Viscosity and thixotropic properties of the studied compositions were measured by the use of a viscometer Brookfield Model DV II (USA). Printability was checked by the hand-operated screen printer RDR-50 (Unitra, Poland) on the monofilament/polyester mesh count 100T/cm and 130T/cm. Mask hardening was made using a device consisting of a 53-60B dryer and two medium-pressure mercury vapor lamps of 220 W at an input current of approximately 80 W/cm from Philips. Adhesion to the surface was examined by a cross-cut area method according to ISO 2409 Standard (Fig. 3). Resistance to soldering was studied according to the Polish standard (BN-86/3311-04, Printed Boards, Soldering Test).

RESULTS AND DISCUSSION

Masks obtained with the use of epoxymethacrylate oligomers were of high viscosity, unstable in time, and readily gelating, which resulted in bad printability (Table II). The coatings were irresistible to soldering, giving many blisters, and their adhesion to copper was poor, independent of the oligomer acid value. While removing the remains of flux with isopropyl alcohol after soldering, the pigment from the mask was washed away, which showed that the mask was not hardened enough. Because of chemical composition, methacrylic esters react more slowly than do the acrylate ones and the hardening time was probably too short for complete crosslinking of the mask.

In the case of masks based on epoxyacrylate oligomers in which the mixture of 2-ethylhexyl acrylate and triethylene glycol dimethacrylate was used in crosslinking, the compositions' viscosity decreased (from 290,000 to 60,000 cP) and their good printability was obtained.

The relation between the oligomer acid value and adhesion to copper as well as thermal resistance to soldering was established. The optimal results were obtained for the masks of the oligomer having an acid value of 3 mg KOH/1 g (Table III).

The addition of each kind of photoinitiator separately or in the mixture does not affect mask printability (Table IV). The data from Tables I and IV

Table IV The Influence of Kind and Quantity of Photoinitiator on Mask Properties

Mask No.	Acid Value of Oligomer (mg KOH/g)	Printability Through Monofilament Mesh 130T and 100T	Class of Adhesion to Copper		Resistance to Soldering (Mesh 130T and 100T)
			Before Soldering	After Soldering	
7		Good	2	2	Bad
8		Good	—	2	Bad
9		Good	2	2	Bad
6	3.4	Good	1	1	Bad
10		Good	—	3	Bad
11		Good	1	1	Good (100T)
12		Good	1	1	Bad

Table V The Influence of Filler Amount and Oligoester Used on the Mask Properties

Mask No.	LK of Epoxy Acrylate Oligomer (mg KOH/g)	Amount of Filler (%)	Printability Through Monofilament Mesh 130T and 100T	Class of Adhesion to Copper		Resistance to Soldering (Mesh 130T and 100T)
				Before Soldering	After Soldering	
14		23	Good through 100T	1	1	Bad
15		35	Bad	0	0	Good (100T)
16	2.8	23	Good	0	1	Bad
4		35	Good through 100T	0	0	Good(100T)
17		35	Good	1 (100T)	1 (100T)	Good (100T)
				0 (130T)	2 (130T)	Good (130T)

show that both the quality of the photoinitiator and its amount in a small range of 2–4% affect the mask adhesion to the surface and resistance to soldering. The mask containing 3% of the photoinitiator mixture shows sufficient adhesion to copper (class) and studies of resistance to soldering did not show changes on the surface in the form of blisters.

The addition of fillers (Table V) is closely connected with mask printability and its thermal resistance. A small amount of filler (lower than 23%) and a small amount of oligomer result in lower viscosity (20,000 mPs), but this causes formation of thin polymer layers (10–15 μm, a screen 130T) resistant to a thermal shock caused by a soldering bath. A larger amount of filler (greater than 35%) makes correct mask printing impossible, especially in the case of crosslinking by triethylene glycol phthalate dimethacrylate (the mask viscosity was 90,000 mPs, while with the content of 23%, 70,000 mPs). Using an oligoester of reduced viscosity—triethylene glycol dimethacrylate—the viscosity of the composition was reduced to 60,000 mPs with the same amount of oligomer, which gave a mask of good printability, good adhesion to copper, and resistance to soldering. The coating thickness determined using a screen 130T was 20–25 μm.

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