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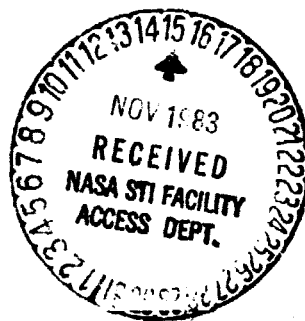
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NASA TECHNICAL MEMORANDUM

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FLEXIBLE COMPOSITE FILM FOR PRINTED CIRCUIT BOARD

Kenji Yabe, Masayoshi Asakura, Hirofumi Tanaka, Atsuhiko Soda



Translation of "Furekishiburu insatsu haisenbanyo fukugo fuirumu",
Japanese Patent No. 50-96900 (1975) Applicant: Toray K.K.;
Date of Application, December 27, 1973; Date of Disclosure,
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9. Abstract

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FLEXIBLE COMPOSITE FILM FOR PRINTED CIRCUIT BOARD

Kenji Yabe, Masayoshi Asakura, Hirofumi Tanaka, Atsuhiko Soda

1. Title of Invention

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Flexible composite film for printed circuit board.

2. Scope of Patent Claim

A flexible printed circuit for a printed circuit board in which layers of reaction product composed of a combination of phenoxy resin - polyisocyanate - brominated epoxy resin and in which the equivalent ratio of those functional groups is hydroxyl group : isocyanate group : epoxy group = 1 : 0.2 to 2 : 0.5 to 3 are laminated on at least one side of saturated polyester film.

3. Detailed Description of the Invention

This invention provides composite film for a flexible printed circuit board with outstanding adhesion with metal foil, combustion resistance, dimensional stability and solder resistance. Saturated polyester films typified by polyethylene terephthalate have long been used as the substrate of flexible printed circuit boards, but they have unsatisfactory solder resistance and dimensional stability. For example, when soldering electronic components onto printed circuit boards, the film layers partially melt or contract due to the solder. In addition, contraction of the film, while slight, occurs in the course of adhesion to metal foil and etching of metal foil, thereby complicating production of printed circuit boards and enhancing the development of curling. Furthermore, the combustion resistance required for safety due to flames resulting from spattering or overheating due to abnormal current has been inadequate. Thus, the inventors have conducted thorough research

"Numbers in the margin indicate pagination of the foreign text."

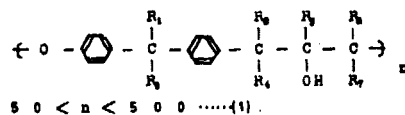
to eliminate these defects, and have discovered that they could be eliminated by using a composite film of saturated polyester on at least one side of which is laminated a reaction product composed of a combination of phenoxy resin - polyisocyanate - brominated epoxy resin in which the equivalent ratio of those functional groups is hydroxyl group : isocyanate group : epoxy group = 1 : 0.2 to 2 : 0.5 to 3, thereby completing this invention. Combinations of phenoxy resin and polyisocyanate improve the solder resistance of polyester film, and the dimensional stability (printed circuit boards with good precision and great thermal contraction cannot be produced since adhesion with metal foil, masking and etching operations are generally conducted in this temperature range) at low temperatures of 80 to 120°C is greatly improved for printed circuit boards requiring precision. Conversely, coating film has the defect of combustion more readily than the stock film. Thus, various examinations of combinations with fire retardants have been made, but while the incombustibility has been improved somewhat using conventional additive type fire retardants (for example, halide aromatic compounds, alkyl halide compounds, phosphorous compounds etc.) and flame-proofing agents (for example antimony oxide), the thermal contraction rate at low temperatures and the solder resistance are less than the magnitude of improvement due to the addition of these fire retardants, and there is no major practical difference from the state prior to coating. Conversely, not only are the anticipated incombustibility and solder resistance achieved through the use of brominated epoxy resin, which is a reactive type fire retardant, and through selection of the three in equivalent ratios of hydroxyl group : isocyanate group : epoxy group = 1 : 0.2 to 2 : 0.5 to 3, but the dimensional stability at low temperatures is surprisingly improved over that in the case of combinations of phenoxy resin - polyisocyanate due to the synergism, and precise printed circuit boards can be produced.

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The reasons for using saturated polyester film in the base film are that it has the pliability, mechanical strength and electrical properties required in such applications as flat cables and substrates for electronic machine wiring even though it has the aforementioned defects. It also has the economy of film, and is indispensable. Furthermore, saturated polyester film is desirable in applications where the greatest solder resistance is required, as the internal wiring of telephones, since very thin film can be used.

The saturated polyester used in this invention would be a homopolymer or copolymer of glycol ingredients (ethyleneglycol, butane diol, diethyleneglycol, propylene glycol etc.) and dicarboxylate ingredients (terephthalic acid, isophthalic acid, phthalic acid, sebacic acid, adipic acid, naphthalene dicarboxylic acid etc.). It would be polyester capable of film formation, and typical examples would be polyester terephthalate as well as its copolymers. In addition, polymers other than saturated polyester may be incorporated in slight amounts so long as they do not harm the properties of film.

The phenoxy resin of this invention would have the following formula.



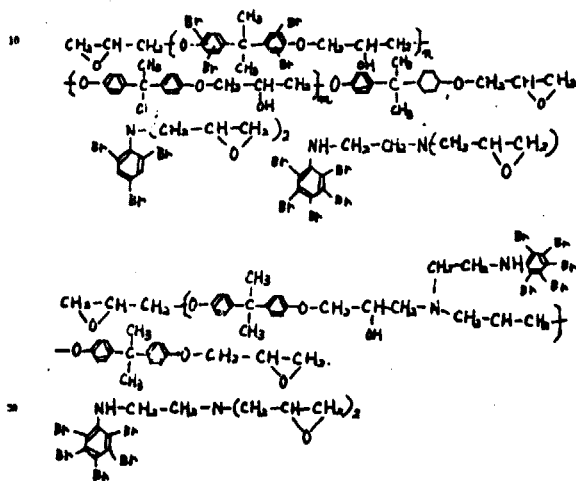
(Wherein, R₁₋₇ represents hydrogen atom or alkyl group). Typical examples would be resins represented by R₁₋₂ = CH₃, R₃₋₇ = H.

In addition, the polyisocyanate in this invention would be compounds containing two or more isocyanate groups per molecule. Typical examples include tolylenediisocyanate, diphenylmethane diisocyanate, hexamethylene diisocyanate, 3,3'3'-triisocyanate

triphenylmethane, polymethylene polyphenyl isocyanate, isocyanates produced through reaction of isocyanate and amine (for example, the trimer of 2,4-tolylenediisocyanate), as well as di-, tri-isocyanate and polyethyleneglycol, monoglyceride, polyisocyanates in prepolymer form produced through additive reactions with polyesters which have hydroxyl groups at both ends, isocyanates produced through reaction of polyisocyanate and polyol (for example, the polyisocyanate produced through reaction of three molecules of 2,4-tolylenediisocyanate and trimethylolpropane), polyisocyanate produced through the reaction of polyisocyanate and water (for example, the isocyanate produced through reacting three molecules of hexamethylene diisocyanate and one molecule of water), and block form polyisocyanate.

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The brominated epoxy resin used in this invention would have the formula illustrated below, beginning with diglycidyl ethers of tetrabromobisphenol A (the hydroxyl group contained in the epoxy resin need not be considered when calculating the equivalent ratio).



Examples of the hardener of the brominated epoxy resin include acid anhydrides, benzyldimethylamine and tris (dimethylaminomethyl) phenol as required. In this case, hardeners with active hydrogen such as polyamine, polyamide and polyethylene imine must be avoided since they readily react with polyisocyanate.

Table 1 illustrates the advantages and disadvantages of combinations of the aforementioned phenol resin - polyisocyanate - brominated epoxy resin when the equivalent ratio of the three is other than hydroxyl group : isocyanate group : epoxy group = 1 : 0.2 to 2 : 0.5 to 3. The equivalent ratio of hydroxyl group : isocyanate group : epoxy group must equal 1 : 0.2 to 2 : 0.5 to 3 in order to produce composite film for superior printed circuit boards in which the various properties are balanced.

Table 1

表 1

No.	1 官能基の当量比				5 特 性				
	2	3	4	6	7	8	9		
1	1	0.2 >	0.5 ~ 3	△ ~ x	△	○	○		
2	1	2 <	0.5 ~ 3	○	○	○	△ ~ x		
3	1	0.2 ~ 2	0.5 >	○	○	x	○		
4	1	0.2 ~ 2	3 <	○ ~ △	○	○	△ ~ x		
10 (不明)	1	0.2 ~ 2	0.5 ~ 3	○	○	○	○		

11 特性が非常に優れている○、優れている○、やや劣る△、劣るx

- 1 equivalent ratio of functional groups
- 2 hydroxyl group
- 3 isocyanate group
- 4 epoxy group
- 5 properties
- 6 solder resistance
- 7 dimensional stability at low temperatures
- 8 incombustibility
- 9 pliability
- 10 ○ outstanding properties
- excellent properties
- △ fairly inferior
- x inferior

In the reaction of these three ingredients, triethyl amine, stannic chloride etc. are used as hardening promoters of the phenoxy resin - polyisocyanate in addition to the aforementioned epoxy resin hardener, and the reaction temperature as well as the time can be controlled. In addition, pigments, electrostatic arrestors, inorganic additives etc. may be added as required.

Blends or primers of phenoxy resin - polyisocyanate - brominated epoxy resin are usually coated on saturated polyester film in the liquid state, and completion of the reaction in the step of evaporation of solvent is desirable in production, but the reaction may also be completed following storage of the coating film in a heated atmosphere in the wound state. Coating is usually carried out on stretched saturated polyester film, but coating may also be carried out in the course of stretching. An explanation involving the case of polyethylene terephthalate follows. Film is supplied to the coating apparatus after stretching of film in the longitudinal direction utilizing the roller peripheral speed difference, and blends of phenoxy resin - polyisocyanate - brominated epoxy resin are coated, followed by feeding into a tenter and stretching in the transverse direction. Heat treatment is carried out, and biaxial stretched film is reeled. Not only is the production cost lower in comparison to coating of biaxially stretched film when coating is implemented during such stretching, but the adhesion between the coating layer and the film is stronger, cracking is inhibited and the dimensional stability is improved. /494

The reaction temperature of phenoxy resin - polyisocyanate - brominated epoxy resin is 50 to 230°C (preferably 120 to 220°C). The thickness when coating polyester film should be 0.5 to 50 microns. When the thickness is below 0.5 microns, the effects of solder resistance and dimensional stability are inadequate, while bending and cracking readily occur when the thickness exceeds 50

microns. Corona discharge treatment and flame treatment, or combinations of the two, as well as chemical treatment should be conducted on the surface of saturated polyester film prior to coating in order to improve the coating properties of the coating solution and to raise the bonding strength.

The flexible printed circuit boards using the composite film of this invention could be produced by sticking together composite film and metal foil in advance using adhesive, followed by removal of unnecessary metal foil by etching, or only the necessary parts of the composite film could be plated with metal in another method of production.

The adhesive used on the composite film and metal foil could be the conventional polyester adhesive, or metal foil and film coated in the polymer stage of phenoxy resin - polyisocyanate - brominated epoxy resin could be stuck together, subjected to heating compression, and bonded. Consequently, the dimensional stability and solder resistance of the finished printed circuit board are improved since the coating layer combines adhesive in this case.

The measurement method used in the actual examples is discussed. The pliability was tested on a sample 5 mm wide and 90 mm long at 30 mm length while wrinkling tests were conducted repeatedly on a 60 mm length. After 10 repetitions of wrinkling tests, the test sample was removed and examined for cracks and peeling.

The solder resistance was measured by JIS C 6481. Copper foil 35 microns thick was bonded using polyester adhesive, and samples 25 mm square were cut out from the wiring substrate. Solder was floated for 10 seconds on the lower edge of the copper foil, and the surface was examined for warpage, contraction of

the film surface and peeling. The evaluations were O : no abnormalities, Δ : onset of peeling of test sample, x : onset of film contraction, with partial peeling from copper foil. Warpage was severe. xx : contraction of film and peeling from copper foil.

Evaluation of the incombustibility involves the oxygen index (abbreviated O.I.) of ASTM D 2863-70. Film is cut into specified sizes, followed by lamination to a specified thickness, after which four surfaces are brought into contact with a hot metal plate so as not to be disordered. These are melted, fused, and measured as specific rod-shaped samples.

Actual Example 1

Phenoxy resin of $R_{1,2} = CH_3$, $R_{3-7} = H$ in formula (1) with molecular weight of approximately 27,000 and a coating composed of triisocyanate produced from three molecules of hexamethylene diisocyanate and one molecule of water and the diglycidyl ether of tetrabromobisphenol A (including 3 wt.% of benzyldimethylamine in relation to epoxy resin as the hardening catalyst) as brominated epoxy resin (10% methylethyl solution) were blended in the equivalent ratios illustrated in table 2, and it was coated on both surfaces of biaxial stretched film (subjected to corona discharge treatment) of polyethylene terephthalate 50 microns thick (7 micron thickness on each surface). This was dried and hardened at 150°C. The properties of the resulting composite film were studied (table 2), and sample numbers 1 and 2 had outstanding pliability and solder resistance, but the O.I. was 21 to 23 and it readily burned. Conversely, No. 6 was incombustible and had good dimensional stability at low temperatures, but its pliability and solder resistance were flawed. Sample numbers 3, 4 and 5 had O.I. of 26 to 30 and were incombustible, and they were pliable. Furthermore, the dimensional stability was markedly improved over that in the case of phenoxy resin -

polyisocyanate due to the synergism of the three ingredients. It also had solder resistance, and the properties were balanced as composite film for flexible printed circuit boards.

Consequently, the ratio of hydroxyl group : epoxy group = 1 : 0.5 to 3 was clearly desirable.

Table 2

1	2	3	4	5	6	7	8
試料名	水酸基	イソシアネート	エポキシ基	0.1	柔軟性	100°C熱収縮率(%)	耐熱性 (230°C)
					MD	TD	
1	3	4	5	21	9	0.8	○
2			0.2	22		0.45	○
3			0.3	23		0.4	○
4			1.0	24		0.1	○
5			3	25		0.05	○
6			6	26	9	0.05	○
7A	11	高度化エポキシ樹脂のみ系		10	10	0.75	×
7	12	ベンゾフェノン系フィルム		10	10	0.8	×

注 13 MD: フィルムの長さ方向, TD: フィルムの幅方向。

- 1 sample no.
- 2 equivalent ratio
- 3 hydroxyl group
- 4 isocyanate group
- 5 epoxy group
- 6 pliability
- 7 thermal contraction rate at 100°C (*1)
- 8 solder resistance
- 9 cracking
- 10 no cracks
- 11 only brominated epoxy resin
- 12 stock film prior to coating
- 13 MD: longitudinal direction of film, TD: transverse direction of film

Actual Example 2

The equivalent ratio of triisocyanate in the combination of the coating composition discussed in actual example 1 was altered, and polyethylene terephthalate biaxial stretched film 50 microns thick which had been subjected to corona discharge treatment was coated on both sides to a thickness of 5 microns on a side. It was then dried and hardened at 150°C. No. 8, in which the equivalent ratio of isocyanate is less than 0.1, has inferior solder resistance, as is clarified from the results of

table 3, while No. 12, in which the equivalent ratio exceeds 3, has inferior pliability. Conversely, in Nos. 9, 10 and 11, in which the ratio of hydroxyl group : isocyanate group = 1 : 0.2 to 2, have good pliability and solder resistance, and do not burn readily. The results of aforementioned actual examples 1 and 2 indicate that the ratio of hydroxyl group : isocyanate group : epoxy group = 1 : 0.2 to 2 : 0.5 to 3 is preferable.

Table 3

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1	2	3	4	5	6	7
試料番号	水酸基	イソシアナト基	エポキシ基	比	6 展 示 値	耐 熱 性 (200°C)
8	1	3	1	1.5	0.5	○
9	1	0.2	1	0.2	8	○
10	1	1	1	1	2.5	○
11	1	2	1	2	2.5	○
12	1	3	1	3	9	○

- 1 sample no.
- 2 equivalent ratio
- 3 hydroxyl group
- 4 isocyanate group
- 5 epoxy group
- 6 pliability
- 7 solder resistance
- 8 no cracks
- 9 cracks

Actual Example 3

The phenoxy resin and brominated epoxy resin used in actual example 1 (containing 5 wt.% of benzyldimethylamine in relation to epoxy resin) and polyisocyanate (triisocyanate composed of 3 moles of tolylenediisocyanate and 1 mole of trimethylolpropane) were blended so that the equivalent ratio would be hydroxyl group : isocyanate group : epoxy group = 1 : 1 : 1. Coatings of 0.1 to 30 micron thickness on each side of polyethylene terephthalate biaxial stretched film of 50 micron and 75 micron thickness were formed on both sides (table 4). The dimensional stability and solder resistance of No. 13, with a thin coating layer, exhibited

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no traces of improvement. Nos. 14, 15 and 16 of this invention had improved dimensional stability, solder resistance, incombustibility, and good pliability. No. 17, in which the coating layer was thick, had good dimensional stability and solder resistance, but the pliability was inferior, and the sample could not be used.

Table 4

1	2	3	4	5	6
試料番号 (I.P.N.)	コート前の フィルム厚さ (ミクロン)	コート厚さ (ミクロン)	O.I.	100°Cでの熱収縮率 (%)	半断面積 (%)
13	50	01	24	0.002	0
14	-	03	2.5	7	0-△
15	-	1	24	0.01	0
16	75	20	01	0.05	0
17	75	30	01	0.02	0

8

- 1 sample no.
- 2 thickness of film prior to coating (microns)
- 3 coating thickness (single side microns)
- 4 pliability
- 5 thermal contraction rate
- 6 solder resistance
- 7 no cracks
- 8 cracks

Actual Example 4

Polyethylene terephthalate (I.V. 0.63) was supplied to an extruder, and was molten extruded from T dies at 285°C, producing unoriented film of approximately 500 micron thickness. This film was subjected to 3.3-fold roller stretching in the longitudinal direction, and the film was then conducted to a coating device where the coating solution used in actual example 3 was applied to both sides. The film was then introduced into a tenter type lateral stretching device, and it was stretched 3.3-fold in the transverse direction. Heat treatment under tension was then conducted at 220°C. The resulting composite film (No. 18) was a polyethylene terephthalate layer 50 microns thick, with a coating

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layer of 3 microns thickness on a side. The structure was identical with that of sample No. 15 in which biaxial stretched film had a coating. The thermal contraction rate at 100°C was MD 0.2%, TD 0.08%, and the dimensional stability was improved in comparison with that of sample No. 15. The solder resistance and incombustibility were unchanged from those of No. 15. The sample was punched using a dumbbell type test sample punch to study the adhesion between the coating layer and film, the cut surface of composite film was observed, and the existence of curvature and of cracking in the coating layer was studied. No. 15 exhibited slight cracking in six out of 30 sheets in the sample, but No. 18 exhibited cracks in only 5 out of 30 sheets. Coated samples were clearly preferable in the stretching operation in terms of adhesion of the coated layer. /497

The aforementioned coating solution was applied as adhesive to composite films of sample Nos. 15 and 18, and it was stuck to 35 micron thick copper foil under pressure at 150°C, thereby producing flexible printed circuit board. It was etched with ferric chloride, and the unused parts of copper were removed, thereby producing a flexible printed circuit board. The solder resistance was then tested at 230°C, and neither warpage nor twisting were evident, and the properties were outstanding. Conversely, flexible printed circuit board produced similarly using simple conventional polyethylene terephthalate film shrunk and could not be restored to its original shape as a result of the solder resistance test.