Effect of Molecular Structure of Phenolic Resin on Solder Dip Resistance and Peel Strength of Printed Circuit Adhesives

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Synopsis

Phenolic resins were synthesized by using various kinds and amounts of catalyst and changing the mole ratio of formaldehyde and phenol. The solder dip resistance and the peel strength were measured for two-component printed circuit adhesives mixed with poly(vinyl acetal) resin, and the relation between these properties and the molecular structure of the phenolic resins were studied. Catalysts such as ammonia, amines having low boiling points, and alkaline earth metal oxide and hydroxides give resins with good properties. When the mole ratios of ammonia to phenol and formaldehyde to phenol are respectively 0.05–0.10 and 1.5, the resins obtained have good characteristics. The solder dip resistance is improved by aging the resin solution at moderate temperature.

INTRODUCTION

In case of manufacture of a printed circuit by a copper-clad laminate process, the adhesive which is applied for bonding copper foil to an electric insulating board made of the thermosetting resin plays a very important part and, therefore, must have various good characteristics. Along with the recent progress of printed circuit techniques, more severe characteristics are required of the adhesive. Among these, a resistance to solder dipping in the final step of printed circuit manufacture and bonding strength of copper foil to the electrical insulating board are most important. The former is called solder dip resistance and the latter, peel strength. It is known that a superior adhesive can be obtained by using a mixed composition of phenolic resin and poly(vinyl acetal) as adhesive component,[1–4] but no report is available yet which systematically deals with the relations between solder dip resistance and the molecular structures of phenolic resin and of poly(vinyl acetal), and between peel strength and their molecular structures. In this report, the relations are discussed between solder dip resistance and the molecular structure of phenolic resin which is one of the main component of printed circuit adhesive, and between peel strength and that of the phenolic resin.

EXPERIMENTAL

Materials

Poly(vinyl formal) (abbreviated PVF): Vinylec-F of Chisso Corp.; poly(vinyl butyral) (abbreviated PVB): Denka-butyral #4000-2 of Denki Kagaku

Kogyo Co.; novolak-type phenolic resin: synthesized with hydrochloric acid catalyst by Kowa Kogyo Corp.; electrolytic copper foil: product of The Furukawa Electric Co.; phenolic resin-impregnated paper: product of Mitsubishi Gas Chemical Co. Phenol, formalin, ammonia aqueous solution, amines, and alkaline catalysts of extrapure grade were used for synthesis of phenolic resin. Solvents of extrapure grade were used.

Preparation of Specimens

Phenolic resins were synthesized as follows: Phenol, formalin, and a catalyst were put into separable flask equipped with a stirrer and a reflux condenser. The flask was set in an oil bath having heating and cooling units. With the oil bath temperature raised to, and then maintained at, 120°C, the contents of the flask were refluxed and reacted (initial reaction). Then, by cooling the oil bath, the contents were quickly cooled below 50°C. The initial reaction was stopped at the point of emulsifying of the refluxed contents. When using a large amount of ammonia catalyst (30 and 40 mole-%), as the time from start of reflux until emulsifying was very short, the initial reaction was done at 70°C. Then, the reflux condenser was taken out, and the flask was connected to a vacuum pump through a condenser and chilled trap. By raising the oil bath temperature gradually, the dehydrating condensation reaction was done under reduced pressure. Ethyl alcohol was then added to the flask to dissolve the product.

PVF was dissolved in a mixed solvent of toluene–ethoxyethanol (mixing ratio 1:1) of solid content 12.5%. PVB was dissolved in a mixed solvent of toluene–ethyl alcohol (1:1) of solid content 15%. Novolak-type phenolic resin was dissolved in methyl isobutyl ketone of solid content 50%. Adhesives were prepared by weighing each resin solution into a glass beaker to get a determined solid composition and stirring it. Sample sheets of copper foil were coated with the adhesives by roller-coater, dried 20 min at room temperature, successively 25 min by irradiation of infrared ray lamps, and then heated 5 min in an air oven precisely controlled at 150°C. Phenolic resin-impregnated paper was used after drying in a vacuum drier at 90–100°C and below 10 mm Hg pressure. Copper-clad laminate was prepared by laminating the adhesive-coated copper foil and 12 sheets of the phenolic resin-impregnated paper and pressed 60 min at 160°C and 75 kg/cm² pressure.

Measurements

Test pieces (25 × 25 mm) for measuring solder dip resistance were made by cutting the copper-clad laminate. Putting each test piece on a solder bath maintained at 235 ± 2°C, seconds were measured from the start until blisters occurred with a stop-watch. Solder dip resistance was expressed in seconds.

Test pieces (15 × 120 mm) for measuring peel strength were made by cutting copper-clad laminate. Only the copper foil of each test piece was cut 10 mm wide at the central portion with a razor and the copper foils of both edges were stripped off. Then, the strength was measured for peeling the 10-mm-wide copper foil from the laminate in a 90° direction. Measurements was carried out with a Schopper tension tester at a tensile speed of 90 cm/min.

1~5 : Guide rolls
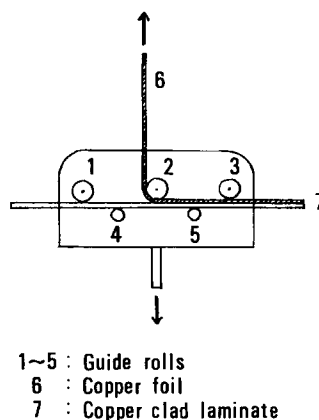6 : Copper foil
7 : Copper clad laminate

Fig. 1. Peel strength-measuring device.

To keep the peeling angle at 90°, the device shown in Figure 1 was used. In all cases of this report, peeling occurred at the interface between copper foil and the adhesive.

RESULTS AND DISCUSSION

Comparison Between Novolak and Resol

To determine the effect of difference of molecular structure between novolak and resol, the adhesive characteristics were measured by changing the mixing ratio of PVB and novolak or resol. In the solder dip test of the novolak series adhesives, all copper foils of test pieces separated from the laminate when they were taken out of the solder bath after 5 min dipping.

In Table I, a big difference is recognized in solder dip resistance and peel strength between novolak and resol. It is found that resol is more suitable regarding these characteristics. It is considered that, since novolak has no hydroxymethyl group, the adhesive cannot yet be crosslinked by heating until

TABLE I
Comparison Between Novolak and Resol

Phenolic resin, %		PVB, %	Peel strength, kg/cm	Solder dip resistance at 235°C, sec
Novolak	25	75	1.23	5
	35	65	1.26	5
	45	55	1.02	5
	55	45	0.66	5
	65	35	0.29	5
	75	25	0.05	5
Resol	25	75	1.40	21 ± 3
	35	65	1.42	34 ± 5
	45	55	1.34	56 ± 8
	55	45	1.22	80 ± 8
	65	35	0.98	76 ± 6
	75	25	0.76	119 ± 20

the making of the laminate and therefore is made into a molten state by heating at the time of solder dipping. On the other hand, resol, when heated, becomes three-dimensional in structure by itself, and also PVB is crosslinked by the reaction between the hydroxyl group of PVB and the hydroxymethyl group of resol.[5] It is inferred that owing to the very tight three-dimensional structure of the adhesive, it shows a good solder dip resistance.

Peel strength tends to decrease with increase of phenolic resin in both cases of novolak and resol. The decreasing tendency of novolak is more remarkable. It is presumed to be due to the difference in functionality between novolak and resol as in the case of the solder dip resistance.

Effects of Catalyst

Figure 2 shows a comparison of solder dip resistance between ammonia catalyst resin and sodium hydroxide catalyst resin. The ammonia catalyst resin shows a higher solder dip resistance than the sodium hydroxide catalyst resin. It is considered that difference in molecular structure of the phenolic resin between ammonia catalyst and sodium hydroxide is due to the existing forms of the catalysts in the resin. It is known that in case of ammonia catalysts, the resin containing nitrogen forms owing to participation of ammonia in the reaction.[6-10] On the other hand, it is considered that in case of sodium hydroxide catalyst, sodium phenolate forms by the reaction between sodium hydroxide and phenol and that the resulting resin contains sodium ions. The fact that phenolic resin synthesized with sodium hydroxide is more polar and hydrophilic due to the content of sodium ions, in it is distinguishable from the experimental result showing that, in case of sodium hydroxide catalyst, the contents in the flask after initial reaction were not separated into a water layer and an oil layer and that the initial reaction products were soluble in water. On the contrary, in case of ammonia catalyst, the contents in the flask after the initial reaction were separated into two layers, so that the initial reaction product is considered less hydrophilic. It is inferred that in this manner, the difference in catalyst results in the difference of molecular structure of the resultant resin and that the difference in hydrophilic property of the resin causes the difference in solder dip resistance.

Figure 3 shows a comparison of solder dip resistance and peel strength among various alkaline earth metal hydroxide or oxide catalyst phenolic resins. These resins were synthesized under the following conditions: catalyst content, 3 mole-%, and mole ratio of formaldehyde to phenol (abbreviated to F/P mole ratio), 1.5. These resins show almost the same good solder dip resistance as the ammonia catalyst resin. And it can be said that the values of peel strength of these resins are almost the same. It is considered that the reason why these resins have a higher solder dip resistance than the sodium hydroxide catalyst resin is the difference in the existing forms of the metals in the resins. Namely, it is supposed that in the phenolic resins including magnesium, calcium, or barium in this experiment, chelate compounds form as a result of coordination of hydroxymethylphenol to the metal.[11]

Figure 4 shows a comparison of solder dip resistance and peel strength among the phenolic resins synthesized with various amine catalysts and a F/P mole ratio of 1.5. All resins show a good solder dip resistance, and no differ-
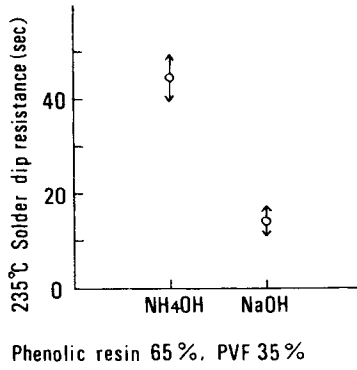
Phenolic resin 65 %, PVF 35 %

Fig. 2. Comparison between NH₄OH catalyst resin and NaOH catalyst resin.

Phenolic resin 65 %, PVF 35 %
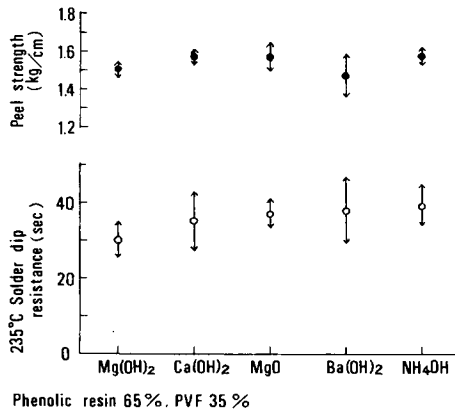
Fig. 3. Comparison of various alkaline earth metal hydroxide or oxide catalyst resins.
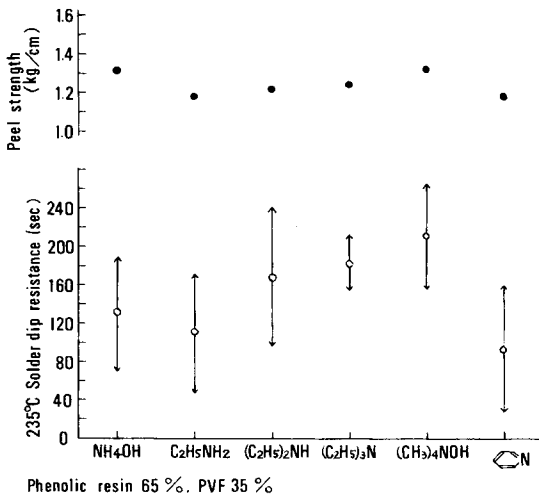

Phenolic resin 65 %, PVF 35 %

Fig. 4. Comparison of various amine catalyst resins.

ence is recognized among these amine catalysts. It has been reported that in a reaction of phenol and formaldehyde with amine catalysts having active hydrogen, the amine participates in the reaction and oxybenzylamine structure is formed.[12-14] But in case of amine catalysts having no active hydrogen, the resultant phenolic resins also show a high solder dip resistance. This experimental result is considered due to the fact that because of their relatively low boiling point, these amines easily vaporize at the dehydration condensation reaction and hardly become a causative substance remaining in the resins for solder dip resistance. And no difference is recognized in peel strength among these various amine catalyst resins.

Effects of Concentration of Ammonia Catalyst

Effects of concentration of ammonia catalyst which showed good results in the above paragraph were studied on solder dip resistance and peel strength in the range from 3 to 40 mole-% of ammonia to phenol. Figure 5 shows the test result of adhesives made of phenolic resins which were synthesized at a F/P mole ratio of 1.5 by changing the ammonia concentration.
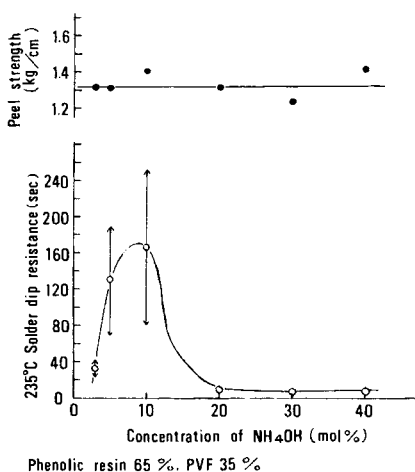

Fig. 5. Effects of concentration of NH_4OH catalyst.

The reason why solder dip resistance decreases above 20 mole-% is explained as follows: It is reported that in the reaction of phenol and formaldehyde with ammonia catalyst, with increase in ammonia concentration, the ratio of formation of hydroxymethylated products decreases and that when the mole ratio of ammonia to formaldehyde becomes above $\frac{2}{3}$, no hydroxymethylated products form.[9] Therefore, it is considered that in this experiment, with increase in ammonia concentration, the ratio of formation of hydroxymethylated products decreases and that, as a result, it becomes hard to have a sufficient three-dimensional structure for the adhesives made of these phenolic resins, and so solder dip resistance decreases.

In spite of the remarkable difference that is recognized in solder dip resistance, no effect of ammonia concentration is recognized on peel strength, and all the cases show almost the same good peel strength.

Effects of F/P Mole Ratio

Figure 6 shows the solder dip resistance and peel strength of adhesives made of the phenolic resins synthesized at 5 mole-% of ammonia catalyst by changing the F/P mole ratio. When the F/P mole ratio is 1.0, even if all the formaldehyde forms hydroxymethyl groups and only methylene bridge formation reactions occur when heated, one of the three active hydrogens of the phenol nucleus remains unreacted and, therefore, the resin cannot have a three-dimensional structure. It is supposed that this tendency becomes more remarkable below a F/P mole ratio of 1.0. It is supposed that the reason why solder dip resistance suddenly increases above a F/P mole ratio of 1.0 is that density of crosslinks by heat curing increases much more on account of the increase in functionality of the phenolic resin according to the increase in the amount of formaldehyde. In case of phenol having three active hydrogens, the density of crosslinks is considered not to change above a F/P mole ratio of 1.5. This inference coincides with the experimental result that solder dip resistance becomes constant above a F/P mole ratio of 1.5.
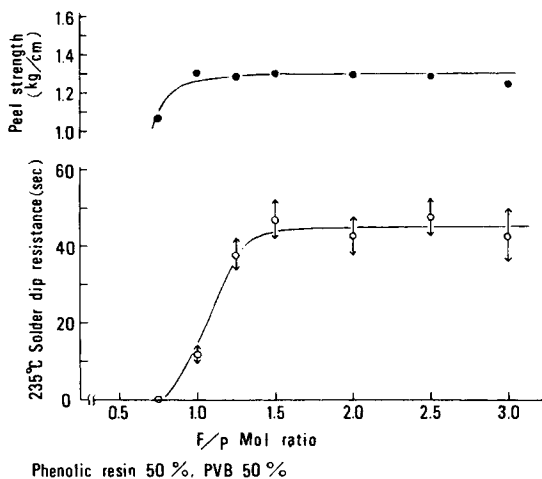

Phenolic resin 50 %, PVB 50 %

Fig. 6. Effects of F/P mole ratio.

Peel strength does not change so much as solder dip resistance owing to the change in F/P mole ratio, but it shows a tendency to decrease with decrease in F/P mole ratio below 1.0. This result is considered to be due to the fact that, though peel strength increases by addition of suitable amount of phenolic resin to PVB, it becomes more difficult for this effect to work due to the low functionality of phenolic resin below a F/P mole ratio of 1.0.

Aging Effects

The relation was studied between the change in solder dip resistance and the aging effect of the phenolic resin solution by moderate heating. A phenolic resin solution just after being synthesized under conditions of a F/P mole ratio of 1.5 and ammonia concentration of 5 mole-% was warmed at 50–70°C and small samples were collected in every determined hour. Measured vis-
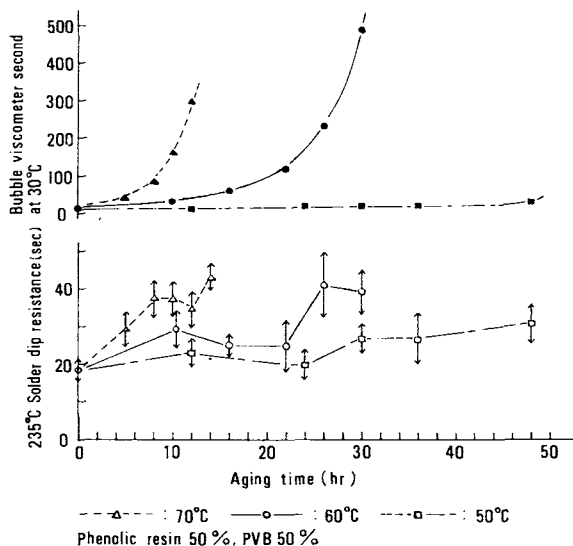
Fig. 7. Effect of aging on solder dip resistance.

cosity and solder dip resistance are shown in Figure 7. It is clear that in all cases, solder dip resistance increases according to the increase in viscosity, though necessary aging hours change due to the warming temperature. A phenolic resin solution having the same high viscosity can be also obtained by continuing much longer the dehydration reaction, increasing the degree of condensation of the resin without solvent, and then dissolving the resin in ethyl alcohol. But in this case, no increase in solder dip resistance is observed. Therefore, it is considered that gradual increasing the degree of condensation of phenolic resin in a solution state especially results in aging. This effect seems to have come from the fact that a phenolic resin having uniform molecular weight is obtained by the moderate condensation of the resin in the solution state; therefore, a molecular structure having more uniform molecular weight per unit crosslink can be obtained in the three-dimensional structure after heat curing of the resin. Aging effect of phenolic resin on peel strength was not recognized.

SUMMARY

Phenolic resins whose molecular structure is suitable for obtaining a tight, three-dimensional structure from heat curing show a high solder dip resistance. Phenolic resins show better solder dip resistance in which the catalyst used for the reaction of formaldehyde and phenol takes part in the reaction and backbone structure of the resin, or as a chelate compound in the resin.

Peel strength is not affected by the existing state of catalyst in phenolic resin and shows almost the same value. Phenolic resins show almost the same good peel strength which have functionality for getting a three-dimensional structure by growth of the molecular chain due to heat condensation reaction. Phenolic resins show low peel strength which do not have sufficient functionality for heat curing, like resol synthesized below a F/P mole ratio of 1.5 and novolak.

References

1. N. A. Skow, *Mech. Eng.,* **75,** 709 (1953).
2. Y. Miura, T. Okuno, A. Kaneda, T. Kato, T. Aso, and T. Shikama, *Toshiba Review,* **13,** 1222 (1958).
3. D. K. Rider, *J. Appl. Poly. Sci.,* **6,** 166 (1962).
4. J. Williamson, *Trans. Inst. Metal Finishing,* **44,** 64 (1966).
5. S. M. Cohen, R. E. Kass, and E. Lavin, *Ind. Eng. Chem.,* **50,** 229 (1958).
6. T. Shono, *Kogyo Kagaku Zasshi,* **32,** 702 (1929).
7. A. Imoto, *Kogyo Kagaku Zasshi,* **52,** 185 (1949).
8. T. Shono and A. Takahashi, *Kogyo Kagaku Zasshi,* **56,** 375 (1953).
9. S. Seto and K. Ozaki, *Kogyo Kagaku Zasshi,* **57,** 687 (1954).
10. T. Shono and A. Takahashi, *Kogyo Kagaku Zasshi,* **56,** 422 (1953).
11. K. Hultzsch and W. Hesse, *Kunststoffe,* **53,** 166 (1963).
12. W. J. Burke and C. W. Stephens, *J. Amer. Chem. Soc.,* **71,** 609 (1949).
13. W. J. Burke and C. W. Stephens, *J. Amer. Chem. Soc.,* **72,** 409 (1950).
14. W. J. Burke and C. W. Stephens, *J. Amer. Chem. Soc.,* **74,** 1518 (1952).