Laminating Resol Varnishes Made with Crude Multivalent Phenol

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SYNOPSIS

During the carbonization process of a lignite source available in the southern part of India, a very cheap byproduct, crude multivalent phenol, was obtained. This crude consisting of substituted phenols and carbonaceous pitch was distilled to get a pitchfree distillate of about 60% yield. The distillate mixture was used along with other phenols for synthesis of resol varnish using a base catalyst. The properties of the resols were evaluated and found to be similar to that of pure phenol (C_6H_5OH) resins. The resol varnishes prepared were used for making cotton paper phenolic laminates by hand impregnation and the compression-molding technique. The paper laminates have been evaluated for physical, chemical, mechanical, and electrical properties. The experimental investigations indicate that the distillate of multivalent phenol is a useful inexpensive substitute for conventionally used phenols in the manufacture of P_3 grade laminates. © 1993 John Wiley & Sons, Inc.

1.0. INTRODUCTION

Phenolic resins[1] find wide application in the manufacture of molded parts, impregnating varnishes, and laminated structures that are used in electrical equipment. Resol is a synthetic resin produced from phenol and aldehyde. These are usually made from phenol (phenol, cresols, resorcinol, cardanol) and formaldehyde mixtures, in which there is a molar excess of formaldehyde. This excess may be small or large according to the type of resin required. To catalyze the reaction, normally a base is employed. The product obtained from the first or A-stage of condensation[2] is designated as "resol." It might be a thick viscous liquid or meltable solid (55–85°C) and is soluble in alcohols and polar solvents.

On further heating at a temperature ranging from 110–140°C, the polymerization is continued into the B-stage with the formation of a resinous product generally referred to as "resitol." The resin at this stage is still fusible but is only sparingly soluble in polar liquids. On further supply of heat, the C-stage resin is formed, which is an insoluble 3D polymer referred to as "resite" or "Bakelite." In resite, the thermoset has the methylene bridge that is a thermodynamically stable cross-linkage.

Electrical laminates and castings need a neutral resin system for achieving good properties. Normally, the catalysts employed in preparation of resol are sodium hydroxide, lithium hydroxide, barium hydroxide, calcium oxide, triethanolamine, and ammonia. Ammonia is considered as the best catalyst employed in the preparation of resols as it ensures material free from electrolytically conducting salts. The mechanical and electrical properties of phenolic resins are considerably influenced by the moisture content and this is more so for components made from resins by incorporating fillers, plasticizers, and other ingredients. Ammonia-catalyzed resols are hydrophilic in nature and this qualifies them for impregnation of paper and cotton fabrics. The difficulties experienced in the dielectric applications of these resin compounds frequently arise because of water that is formed in the condensation reaction by which they are prepared or because of the molecular polarity that is introduced by the presence of hydroxyl groups in their composition. The presence of polar hydroxyl groups in the A- or resol state of the resin result in material with poor dielectric properties. When the polymerization[3] is carried to

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Table I Properties of Crude Multivalent Phenol

Properties	Values
Appearance	Thick black liquid
Specific gravity	1.17–1.18
Distillation range (°C)	215–280
Constituents	
Moisture	2% max
Catechol rich cut	25%
Low boilings	12%
Higher boilings	25–30%
Residue pitch	30–40%

the C-stage (resite), their effectiveness is substantially reduced and electrical resistivity increases to as high as 10^{14} ohms-cm and, also, the dissipation factor will be less than 0.01.

In the electrical field, the resin-laminated structures are formed from paper, cloth, asbestos, or glass. The particular type of resin used as a binding material is based on the requirement to which the assembled insulation will be subjected in commercial use. The laminated products are used in a wide variety of pressed forms, which include terminal strips, panel boards, slot wedges, transformer and switchgear parts, coil winding forms, and printed circuit boards.

2.0. EXPERIMENTAL

2.1. Raw Materials

(a) Phenol, *m*-cresol, cardanol, formalin, ammonia, methanol, gum rosin, and dioctylphthalate of technical grade were used for synthesis.

(b) Crude multivalent phenol obtained from Neyveli Lignite Corp. Tamil Nadu, India, was used after distillation. The properties of crude multivalent phenol[4] are given in Table I. The distillate of multivalent phenol (DMVP) contains the phenolic mixtures shown in Figure 1.

(c) Paper for laminate preparation: Face prepregs—55 gsm cotton base paper was used for impregnation with prepared varnishes. Core prepregs—110 gsm cotton base paper was used for impregnation with varnishes prepared.

2.2. Synthesis of Resol/Laminating Varnish

A resol resin/varnish was synthesized using phenolic components 100 parts, formalin, 60–80 parts, ammonia, 2–5 parts, and gum rosin 0–10 parts charges in a three-necked flask fitted with stirrer, thermometer, and reflux condenser. The temperature of reaction mix was raised to the reflux temperature of formalin and maintained until the geltime of the sample by the hot plate method of 170°C dropped to 160–200 s. The refractive index was monitored and the reaction setup was changed to vacuum distillation. The desired amount of water was removed and digested at atmospheric pressure at 70–80°C until the geltime dropped to 120–160 s at 170°C. Solvent methanol and plasticizer dicotylphthalate was added and the resin was used for evaluation.

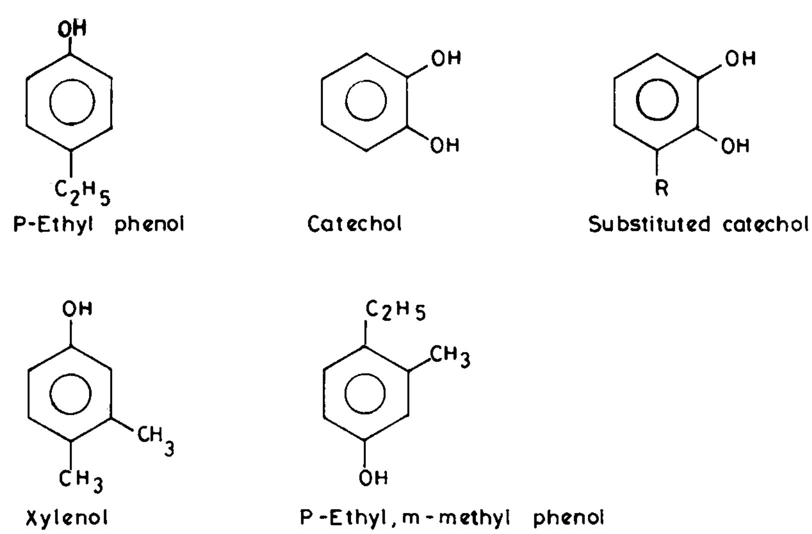

Figure 1 Constituents of distilled multivalent phenol.

2.3. Impregnation and Lamination

The cotton paper was dip-coated in varnish and passed between two adjustable squeeze rolls. The papers were air-dried at room temperature overnight and oven-dried (110°C) to obtain prepreg material of the desired resin and volatile content.

Several layers of prepreg materials were arranged in between stainless-steel plates and compression-molded at 150°C to a dial pressure at 4940 psi for 1 h. This pressure corresponds to 1000 psi. The laminates formed were cooled under pressure and removed when room temperature was attained.

2.4. Evaluation

1. Chemical and physical (resin): Density, viscosity, geltime, and volatile content were evaluated as per standard procedures. (Laminate): Density and water absorption were evaluated as per IS-1998/BS-2782 specifications.
2. Mechanical (laminate): Tensile strength, impact strength, and cross-breaking strength were evaluated as per BS-2782 specifications.
3. Electrical (laminate): Dissipation factor, capacitance, permittivity, insulation resistance, and breakdown voltage as per IS-1998 specifications.
4. Thermal (cured resin): Thermogravimetric analysis was carried out using Mettler TAHE-20.
5. Resistance to chemicals (laminates): Chemical resistance of laminates were evaluated as per ASTM D-543 (1978).

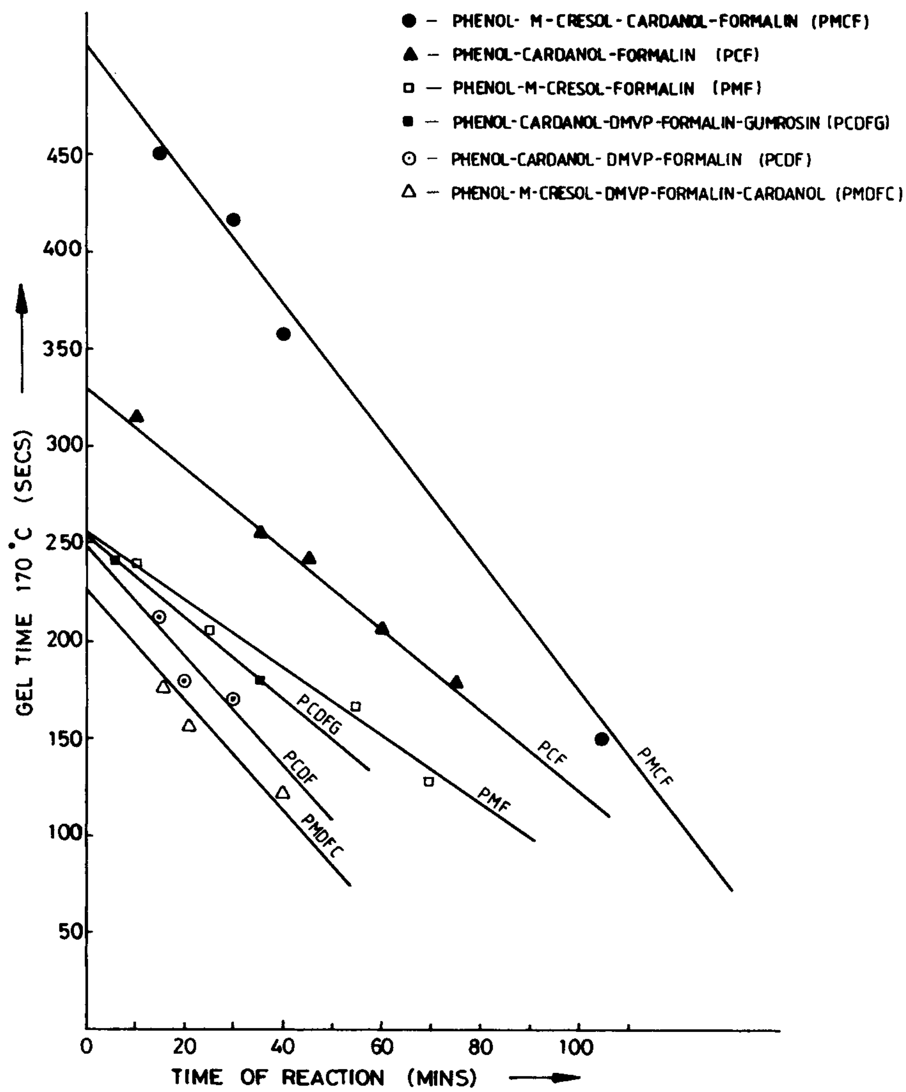

Figure 2 Variation of geltime with reaction time.

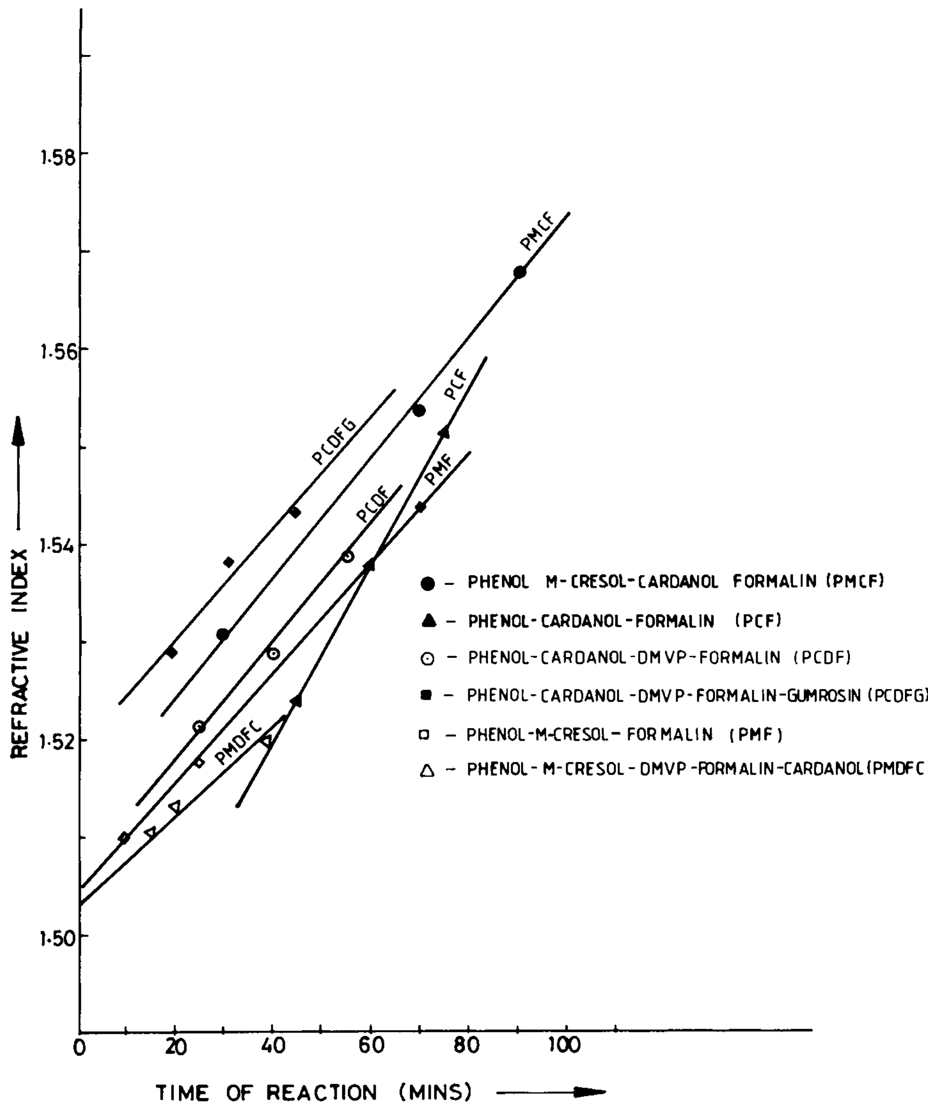

Figure 3 Variation of refractive index with time.

6. Infrared spectra of varnish were taken by Bomem's FTIR spectrophotometer.

3.0. RESULTS AND DISCUSSION

3.1. Reactivity of Distilled Multivalent Phenol (DMVP)

To establish the reactivity, various reactions, viz., phenol-*m*-cresol-cardanol-formalin (PMCF), phenol-cardanol-formalin (PCF), phenol-*m*-cresol-formalin (PMF), phenol-cardanol-DMVP-formalin (PCDF), phenol-cardanol-DMVP-gum rosin-formalin (PCDGF), and phenol-*m*-cresol-DMVP-cardanol-formalin (PMDCF) were carried out using ammonia as catalyst. During the course of reaction, geltime and refractive index were monitored periodically, and the data obtained are shown in Figures 2 and 3. As DMVP contains dihydroxy benzene compound, of the order of 40%, the reactions are faster compared to other monohydroxyphenols.

From Figures 2 and 3, the rate of polymerization follows the order

PMDCF > PCDGF > PMF > PCF > PMCF

As the reaction with DMVP was very fast, the reactions were not controllable in order to get desired

Table II Process Control Parameters

Resin Type	Reflux Time (min)	Refractive Index	Geltime before Vacuum Distillation 170°C (s)	Final Geltime 170°C (s)	Resin Content (%)	Viscosity Fordcup No. 4 (s)
PMF	70	1.544	130	120	52.30	35
PMCF	45	1.563	160	109	54.27	40
PCF	45	1.547	180	109	53.82	40
PCDF						
20 DMVP parts	75	1.540	175	120	51.30	39
40 DMVP parts	60	1.529	172	120	52.40	25
PCDFG						
20 DMVP parts	60	1.548	180	114	60.35	45
40 DMVP parts	60	1.529	172	120	64.97	41
60 DMVP parts	60	1.536	180	120	62.40	40

Higher resin content of 60–64% has been obtained for system with gum rosin formulation as it is a solid that increases the solids content of varnish.

final geltime. Gum rosin[5] (rosin or colophony is a thermoplastic acidic product isolated from exudates of living pine trees. It has the ability to impart or improve singly or in combination properties of adhesion, water resistance, plasticizer, etc.) incorporation into the resin system helped to slow down the rate of reaction.

Table II lists the process parameters observed and also the properties of the varnish.

Infrared Spectral Study

From Figure 4, it can be seen that MVP resol compares well with that of the standard resol presently used for making P_3 grade laminates.

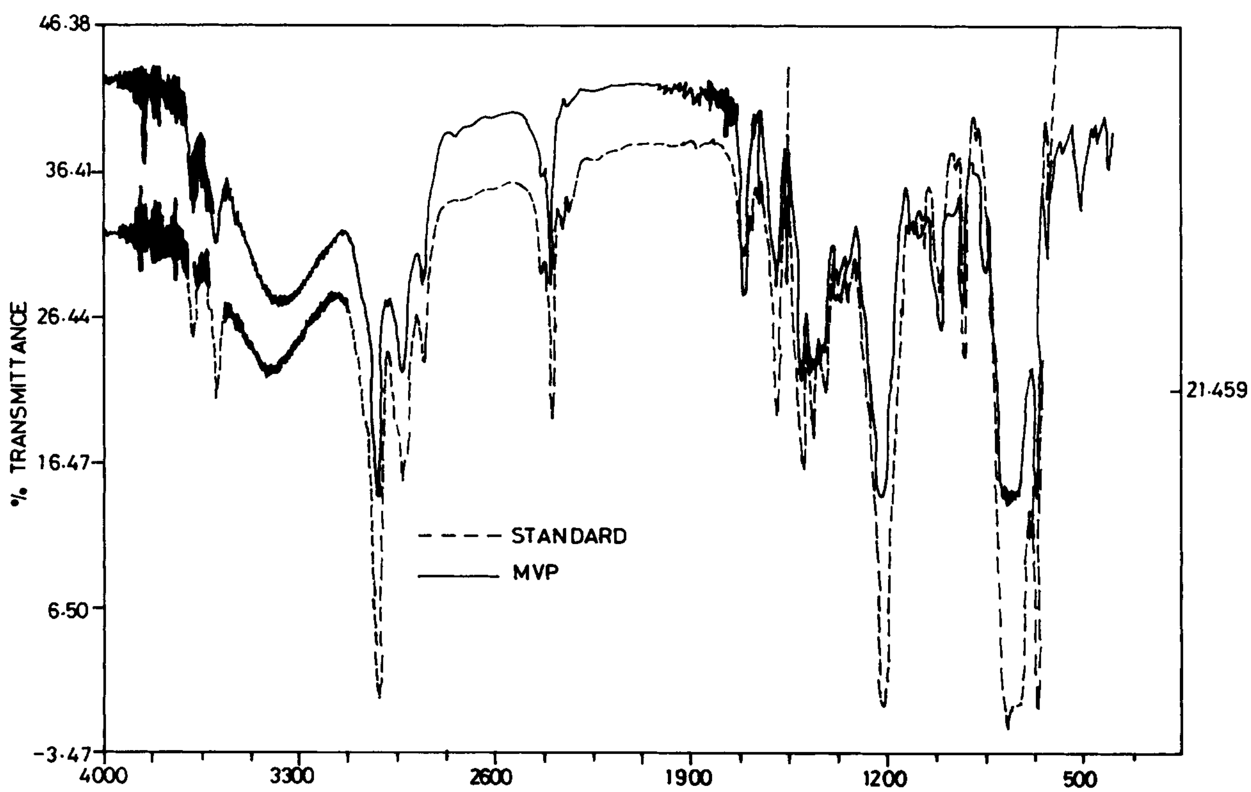

Figure 4 IR spectra of standard resol and MVP resol.

Table III Physical, Mechanical and Electrical Properties

A. Physical and Mechanical Properties

Formulation	Density	Water Absorption (mg)	Tensile Strength (kg/cm^2)	Cross-breaking (kg/cm^2)	Impact Strength (kg-cm)
PMF	1.3679	65	750.27	752.53	17
PMCF	1.2974	38	747.5	752.33	17.5
PCDF					
20 DMVP parts	1.2974	33	1188.38	661.18	16.25
40 DMVP parts	1.2332	40.7	772.06	729.88	16
PCDFG					
20 DMVP parts	1.2845	16	579.2	709.9	13
40 DMVP parts	1.2384	16.5	473.7	541.9	10
60 DMVP parts	1.2472	17	588.3	661.2	16.3

B. Electrical Properties

	Tan Delta 1/10/30 (MC/sec)	Permitivity 1/10/30 (MC/sec)	Cap. pF	IR (M ohms)		BDV (kV/mm)
				Dry	Wet	
PMF	0.019/ 0.021/ 0.019	3.345/ 3.166/ 3.166	24	0.98×10^3	0.5×10^3	17.5
PMCF	0.0258/ 0.0359 0.035	3.98/ 3.79/ 3.74	8.62	0.35×10^6	0.5×10^3	18.4
PCDF						
20 DMVP parts	0.0268/ 0.018 0.025	3.58/ 3.45/ 3.51	10.14	1.4×10^5	1.4×10^3	18
40 DMVP parts	0.0238/ 0.025/ 0.030	3.54/ 3.54/ 3.34	9.92	1.3×10^5	0.9×10^3	20
PCDFG						
20 DMVP parts	0.0229/ 0.022/ 0.02	3.88/ 3.14/ 3.41	9.86	2.1×10^4	1.0×10^2	18.5
40 DMVP parts	0.019/ 0.021/ 0.02	3.34/ 3.16/ 3.16	10.84	1.5×10^4	5.5×10^3	18.1
60 DMVP parts	0.018/ 0.02/ 0.022	3.85/ 3.14/ 3.42	9.86	0.7×10^5	1.6×10^3	21.3

3.2. Laminate Evaluation

The results of physical, mechanical, and electrical tests conducted on laminates are presented in Table IIIA and B, which lists the physical, mechanical, and electrical properties of the laminates prepared from different types of resin. It is evident that properties of the DMVP-incorporated resins are comparable to that of standard phenol, *m*-cresol (PMF), as well as phenol–*m*-cresol–cardanol (PMCF) res-

Table IV Comparative Thermogravimetric Properties of Crude MVP Resols with Standard Resol

% Weight Loss	Temperature (°C)			
	Standard	20 DMVP	40 DMVP	60 DMVP
5	225	237	248	253
10	275	258	287	270
30	315	308	330	314

ins. Insulation resistance values after immersion in water for 24 h for the DMVP system are better (0.5×10^3 for PMF/PMCF, $1.6/5.5 \times 10^3$ for PCDGF). The insulation resistance is very critical for all the applications of P_3 grade laminates. Cross-breaking strengths, in general, for all the formulations are lower due to small size of the samples used.

3.3. Thermal Behavior

The thermal rating of insulating material is an important parameter that has to be established or known prior to actual use in electrical equipment. The thermogravimetric analysis[6] technique where the weight of the sample of the material is continuously recorded as a function of time and temperature when subjected to a programmed temperature rise was used. The cured laminates were examined by using the Mettler TAHE-20 balance, 94006 temperature programmer, and other relevant accessories.

Table IV and Figure 5 show the comparison of DMVP resins with respect to a reference standard

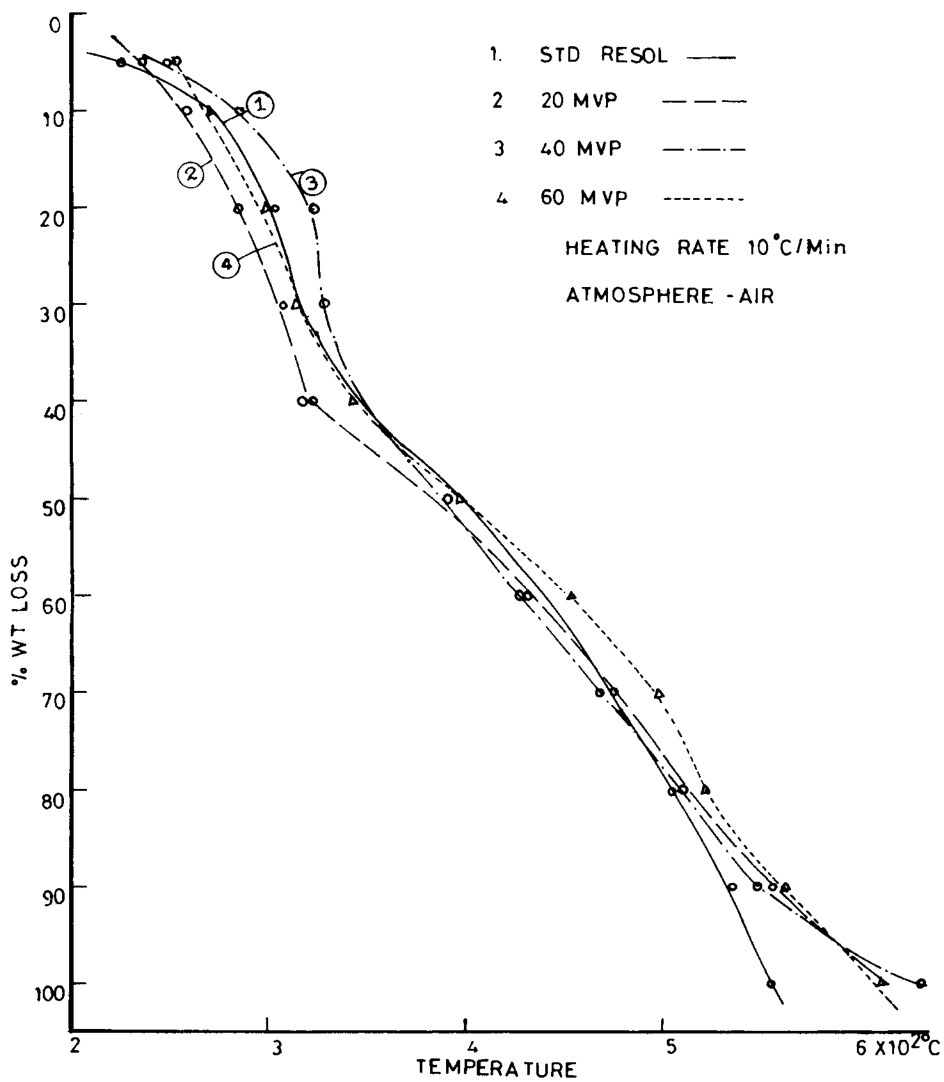

Figure 5 Wt loss curve with temp rise for standard DMVP system.

Table V Chemical Resistance of 60 Parts DMVP Resol–Cotton Paper Laminate Sheet

Property	3% H_2SO_4	10% HCl	10% HNO_3	5% CH_3COOH	CCl_4	$(CH_3)_2CO$	CH_3OH	$C_6H_5NH_2$	25% NH_3
Appearance	No change	No change	No change	No change	Loss in gloss	Loss in gloss	No change	Slight change in gloss	Slight change in gloss
Average thickness change (mm)	0.023	0.003	0.013	0.016	0.003	0.096	0.010	0.013	0.020
% Absorption	0.963	0.635	1.145	1.114	1.131	2.615	2.431	0.706	1.293

phenolic resol. As the concentration of DMVP in the resin system increased, the decomposition temperature at 5% weight loss increased, showing that DMVP addition has bettered the thermal resistance of the laminate. At higher percentages of decomposition, the DMVP laminates have shown more or less similar behavior to the standard system.

The substituents present in DMVP, namely, alkyl and hydroxyl, probably enhance the reaction rate of the system and give rise to a highly cross-linked cured product that is better than standard phenol.

3.4. Chemical Resistance

The laminate specimens of 60 parts DMVP formulation were placed in appropriate containers for the reagents used and the specimens were totally immersed in fresh reagent for 7 days in the standard laboratory atmosphere. After 7 days, the specimens were removed from the reagent and washed with running water for samples removed from the acid and alkali. The wet samples were dried using tissue paper and immediately taken for analysis.

Table V gives the data of appearance, thickness swelling, and percentage absorption in acidic, basic, and neutral media. It is evident that the laminate is not affected by dilute and strong acids or by bases.

4.0. ECONOMIC ASPECTS

The price of crude multivalent phenol is about 10% of the price of standard phenol. With the yield being 60% and after adding the relevant cost of processing, etc., it has been estimated that resol resins made out of DMVP would cost at least 20% less than standard resol presently employed in the electrical laminate industry. The resulting properties, as discussed earlier, are similar to the ones obtained with standard resol.

5.0. CONCLUSIONS

Several resol resins from distilled multivalent phenol have been synthesized and their use for making electrical-grade laminate has been established on a laboratory scale. The raw material-distilled multivalent phenol, being inexpensive, would be beneficial for resin manufacturers and laminate industries.

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