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Effect of Adding Cardanol to Unsaturated Polyester Resins

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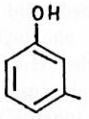
Effect of adding cardanol on the curing behaviour of general purpose, isophthalic-based and bisphenol-based unsaturated polyester resins has been studied. Inhibitive action of cardanol was compared with that of other well-known inhibitors. Cardanol addition provides resins of extended pot life, low exotherms and crack-free thick castings. Cardanol is several times cheaper than other well-known inhibitors for polyester resins.

Unsaturated polyester resins are widely used for making glass fibre reinforced sheets for sky-lights, green houses, windows of industrial buildings, walls, partitions and similar applications. The polyester resins discussed in this paper are the unsaturated polyesters dissolved in a monomer usually styrene.

Little has been published on inhibitor systems and low exotherm resins outside the patent literature. Noller *et al.*[1] have studied gelation and cure characteristics of organic peroxide-accelerator-inhibitor systems in a standard unsaturated polyester resin at both elevated and room temperatures. Parker[2] determined tank life and gel time of polyester resins inhibited by hydroquinone, 4,4-dihydroxybiphenyl, catechols and substituted catechols which were found to have considerable merit as inhibitors. Foster and Miller[3] studied hydroquinones and *p*-benzoquinones inhibitors for their relative suitability in different stages of polyester manufacture and application namely esterification, blending, storage and processing. Brinkman *et al.*[4] presented data on the behaviour of cobalt, manganese and vanadium salts, tertiary amines, and quaternary ammonium bases as accelerators for ketone and diacyl peroxides. Litwin and Beacham[5] studied catalysis and inhibition of diallyl phthalate polyesters. Conventional inhibiting substances such as quinones and hydroquinones tend to retard gel rate and suppress final cure of these polyesters.

Jain and Asthana[6] have studied the effect of addition of cardanol on peroxide curing of polyester resins. They found that cardanol acted as an inhibitor and that the gel time and cure time of cardanol-added polyesters were increased. In this study the inhibiting action of cardanol has been compared with other well-known inhibitors in isophthalic based and bisphenol based resins in addition to general purpose resins. These resins are commercial grade polyesters containing 0.3% hydroquinone/*tert*-butylcatechol. Important characteristics were determined as per IS: 6746-1972 specification for unsaturated polyester resin systems for low pressure fibre reinforced plastics and are summarised in Table 1.

Cardanol is a distillation product of cashewnut shell liquid and is a mixture of monohydroxy phenols with a 15-carbon chain substituted in the *meta*-position. It is generally represented by the following formula having unsaturation equivalent to two double bonds in the side chain.



$(CH_2)_7\ CH:CHCH_2CH:\ CH(CH_2)_2\ CH_3$

Characteristics of Cardanol were determined according to IS:840 Indian Standard Specification for CNSL and are reported in Table 2.

Table 1—Characteristics of Resins

	Characteristics	General Purpose (GP)	Isophthalic based (IP)	Bisphenol based (BPh)
1	Viscosity at 25°C, in cs	200	600	550
2	Specific gravity (25°C)	1.11	1.12	1.08
3	Acid value (mg. KOH/g)	25	12	8
4	Volatiles, %	36	40	50
5	Water absorption of cast resin at 25°C in 24 hr, %	0.13	0.10	0.03
6	Temp. of deflection under 18.5 kg/cm² load of cast resin, °C	75	100	125
7	Gel time* at 27°C, min	65	35	18†

*With 1% MEKP+2% Co naphthenate
†1% promotor also added

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SPI gel characteristics were studied as follows: 10 g resin was mixed with 1 % benzoyl peroxide and wetted by two or three drops of styrene. A copper constantan thermocouple junction was then inserted into each resin sample at its centre and the samples were maintained at 82 ± 1°C in a water bath. The temperature rise in the resin sample was recorded using a dc microvoltmeter. Cardanol and other inhibitors like hydroquinone (HQ), 2,5 ditertiarybutylhydroquinone (2,5 DTBHQ), quinone (Q), and 2,4-dihydroxybenzophenone (2,4 DHBP) were mixed with the resin sample and SPI gel characteristics were determined. Graphs were plotted between the temperature rise and time. Gel and Cure time were measured by standard SPI procedure according to which gel time is the time required for temperature to rise from 67.5 to 87.7°C.

In order to study SPI exotherm curves at room temperature (30°C), the resin samples were maintained at room temperature. 2 % of accelerator and 1 % of catalyst were added in place of 1 % benzoyl peroxide. The catalyst used was methyl-ethyl-ketone peroxide and the accelerator was a cobalt salt dissolved in 30 % styrene. Exotherm curves were plotted between temperature and time as in the case of standard SPI

Table 2—Characteristics of Cardanol

1	Colour	Pale yellow
2	Specific gravity	0.935
3	Viscosity, cp (Brookfield spindle No 1, rpm 10)	110
4	Acid value mg KOH/g	1.67
5	Iodine value (wijs)	317
6	Ash content	Nil
7	Moisture content, %	0.2
8	Matter insoluble in toulene, %	0.002

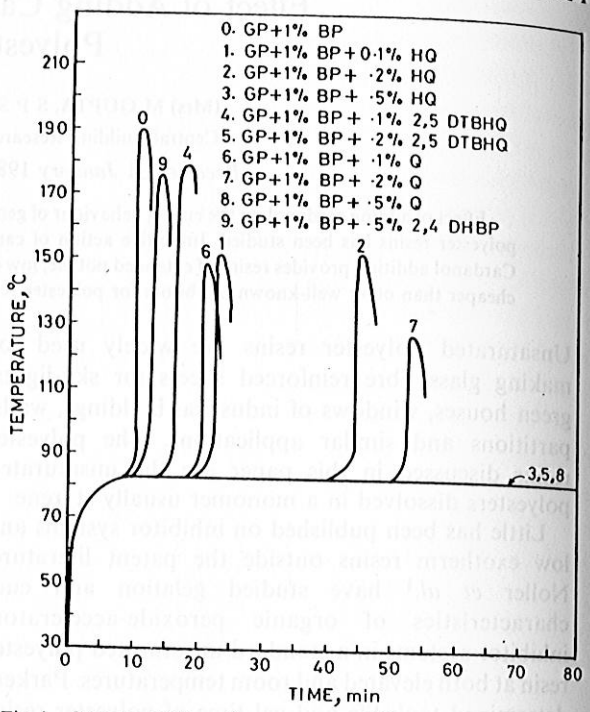

Fig. 1—Standard SPI exotherm curves at different concentrations of different inhibitors for GP resin

Table 3—Cure Characteristics of General Purpose Resin with Different Inhibitors with 1 % Benzoyl Peroxide at 82°C

Inhibitor, %		Gel time, min	Curing time, min	Kick off Temp, °C	Exotherm peak, °C
	Control	8	11	85	190
Hydroquinone	0.05	14	17	87	152
	0.1	20	23	88	152
	0.2	41.5	45	89	152
	0.5	>24 hr	Nil	Nil	No peak
2,5 Ditertiarybutyl hydroquinone	0.05	12	15	87	190
	0.1	15	18	88	183
	0.2	17	Nil	Nil	No peak
Quinone	0.05	14	17	86	183
	0.1	18.5	21	87	149
	0.2	50.5	53	89	127
	0.5	>20 days	Nil	Nil	No peak
2,4 Dihydroxy benzophenone	0.1	10	13	86	183
	0.5	11	14	87	176
Cardanol	0.1	13.5	16	86	165
	0.5	16.5	19	87	134
	1	18.5	21	88	134
	2	22.5	25	88	134
	3	37.5	41	89	134
	4	45.0	49	89	100
	4.5	62	Nil	Nil	No peak

Table 4—Cure Characteristics of Isophthalic Resin with Different Inhibitors with 1% Benzoyl Peroxide at 82°C

Inhibitor, %		Gel time, min	Curing time, min	Kick off temp., °C	Exotherm peak, °C
	Control	11.5	14.5	87	205
Hydroquinone	0.05	15	18.5	89	191
	0.1	16.5	19.5	90	190
	0.2	43.5	46.4	90	156
	0.3	>48 hr	Nil	Nil	No peak
2,5 Ditertiary butyl hydroquinone	0.05	15	Nil	Nil	No peak
Quinone	0.05	17	20	89	180
	0.1	20	23	90	156
	0.2	38.5	42	92	141
	0.3	>72 hr	Nil	Nil	No peak
2,4 Dihydroxy benzophenone	0.05	12.5	15	87	178
	0.1	12.5	15	87	178
Cardanol	0.1	15.5	18.5	89	190
	0.5	18.5	23.5	91	170
	1	19.5	24.5	93	167
	2	28.5	32	94	162
	5	96	Nil	Nil	No peak

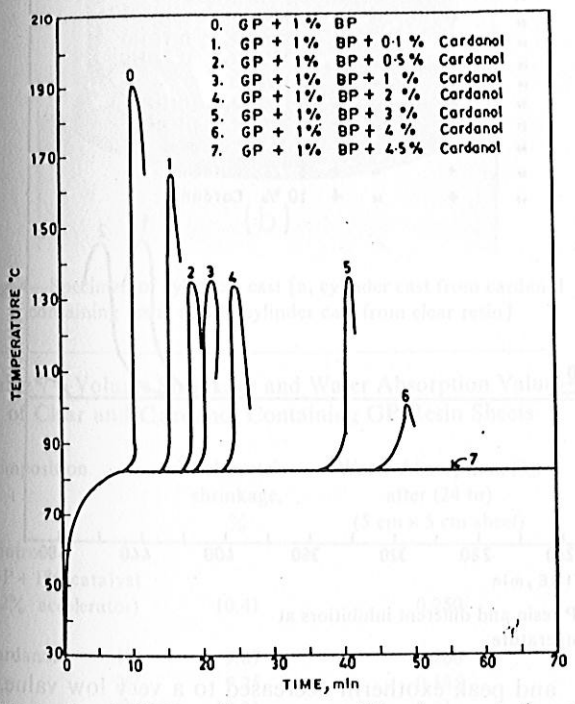

Fig. 2—Standard SPI exotherm curves at different concentrations of cardanol for GP resin

curves. Gel time was observed visually and peak temperature was noted from the curves in all cases.

SPI exotherm curves at 82°C for GP resin with different concentrations of various inhibitors are given in Figs 1 and 2. Gel time, cure time, kick off temperature and peak exotherm for these systems are given in Table 3. It would be seen from the results that as the concentration of an inhibitor increases, gel time, cure time and kick off temperature increase while peak

Table 5—Gel Time and Exotherm Peak Values of General Purpose Resin with Different Inhibitors at Room Temperature (30°C)

Inhibitor, %		Gel time, min	Exotherm peak, °C
	Control	30	145
Hydroquinone	0.1	285	71
	0.2	288	70
2,5 Ditertiary	0.1	40	42
butyl hydroquinone	0.2	102	38
Quinone	0.1	495	No peak
2,4 Dihydroxy	0.1	22	140
benzophenone	0.2	30	140
Cardanol	1	85	42
	2	115	42
	5	175	36
	10	185	36

exotherm decreases. At a particular concentration of inhibitor in each case no peak exotherm is obtained, and the gel time increased appreciably.

However, with inhibitor 2,4 DHBP even at 0.5% concentration the increase in gel time and cure time was only marginal and so also the reduction in peak exotherm. Inhibitors HQ and Q gave no peak exotherm at 0.5% concentration but the gel time increased to > 24 hr and > 20 days respectively which is not a desirable feature. Inhibitor 2,5 DT BHQ gave no peak exotherm at 0.2% concentration but its gel time did not increase significantly either. With cardanol at 4.5% no peak exotherm was obtained but gel time increased appreciably to 62 min compared to 8 min for the control. Polyester systems with no peak exotherm and appreciably longer gel time as obtained with cardanol addition are considered to be suitable for

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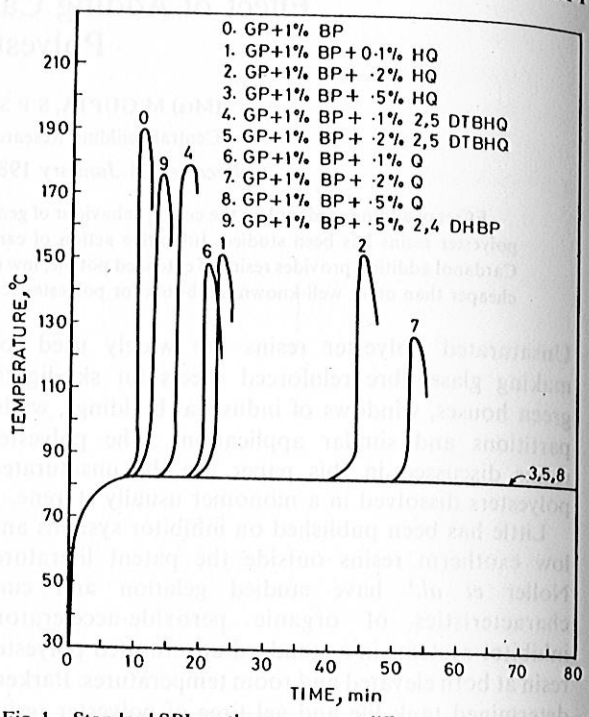

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	0.5	>20 days	Nil	Nil	No peak
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	0.5	16.5	19	87	134
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	2	22.5	25	88	134
	3	37.5	41	89	134
	4	45.0	49	89	100
	4.5	62	Nil	Nil	No peak

Table 4—Cure Characteristics of Isophthalic Resin with Different Inhibitors with 1% Benzoyl Peroxide at 82°C

Inhibitor, %		Gel time, min	Curing time, min	Kick off temp., °C	Exotherm peak, °C
	Control	11.5	14.5	87	205
Hydroquinone	0.05	15	18.5	89	191
	0.1	16.5	19.5	90	190
	0.2	43.5	46.4	90	156
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Quinone	0.05	17	20	89	180
	0.1	20	23	90	156
	0.2	38.5	42	92	141
	0.3	>72 hr	Nil	Nil	No peak
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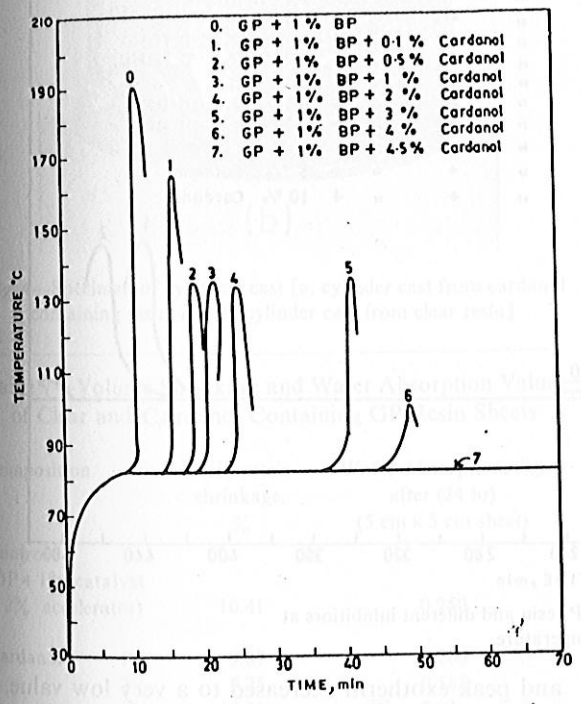
Cardanol	0.1	15.5	18.5	89	190
	0.5	18.5	23.5	91	170
	1	19.5	24.5	93	167
	2	28.5	32	94	162
	5	96	Nil	Nil	No peak



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benzophenone	0.2	30	140
Cardanol	1	85	42
	2	115	42
	5	175	36
	10	185	36

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Table 6—Cure Characteristics of Bisphenol Resin with Different Inhibitors with 1% Benzoyl Peroxide at 82°C

Inhibitor, %		Gel time, min	Curing time, min	Kick off temp., °C	Exotherm, °C
	Control	19	22	85	180
Hydroquinone	0.05	41.5	45	88	176
	0.1	52	56	89	156
	0.2	>24 hr	Nil	Nil	No peak
2,5 Ditertiary butyl hydroquinone	0.05	20	Nil	Nil	No peak
Quinone	0.05	36	39	89	154
	0.1	51	55	91	154
	0.2	>48 hr	Nil	Nil	No peak
2,4 Dihydroxy benzophenone	0.05	21.5	24	85	180
	0.1	21.5	24	85	180
Cardanol	0.1	23.5	26	86	177
	0.5	32.5	36	89	160
	1	35	39.5	90.5	160
	2	53	Nil	Nil	No peak

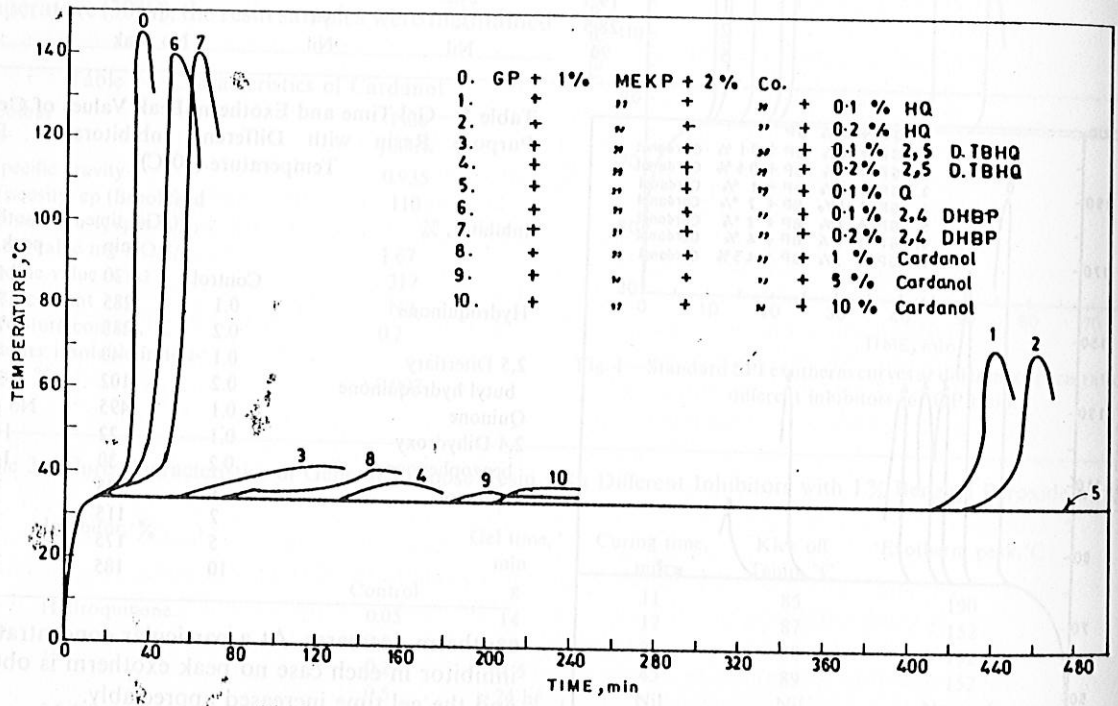

Fig. 3—Exotherm curves with GP resin and different inhibitiors at room temperature

various applications as extended pot life, low exotherm and potting resins. Gel time, cure time, kick off temperature and peak exotherm for isophthalic and bisphenol resins with different inhibitors are given in Tables 4 and 6 respectively. The cure characteristics in case of isophthalic and bisphenol resin systems with different inhibitors have been observed to be more or less the same as in the case of GP resin systems.

Exotherm curves obtained at 30°C for GP resin and different inhibitors are given in Fig. 3. Gel time and peak exotherm values are reported in Table 5. Gel time increased with the increase in quantity of inhibitors and peak exotherm decreased to a very low value. It would be seen that in case of cardanol and DTBHQ the peak exotherm does not increase beyond a few degrees above room temperature and gel time is appreciably prolonged. Thus cardanol added resins may be termed suitable as extended pot life and low exotherm resins.

Samples of cylinders of size approx. 50 mm dia and 25 mm length were cast from GP resin with and without cardanol and their volumetric shrinkage was measured. Water absorption was measured on sheets of size 50 mm × 50 mm × 3 mm on 24 hr immersion in water. The results are reported in Table 7. It would be

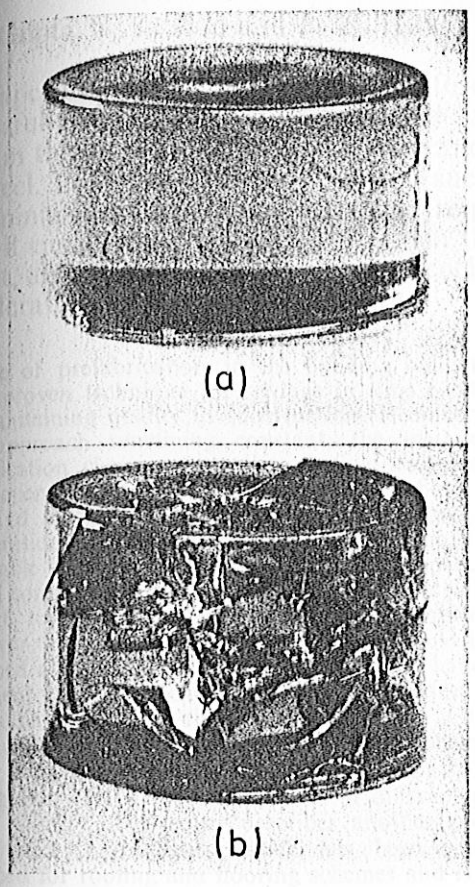

Fig. 4—Specimen of cylinders cast [a, cylinder cast from cardanol containing resin; and b, cylinder cast from clear resin]

Table 7—Volume Shrinkage and Water Absorption Values of Clear and Cardanol Containing GP Resin Sheets

Composition		Volumetric shrinkage, %	Water Absorption, (%) after (24 hr) (5 cm × 5 cm sheet)
Control (GP + 1% catalyst +2% accelerator)		10.41	0.250
Cardanol	1%	9.87	0.200
	2%	9.75	0.185
	5%	10.21	0.21

seen that the shrinkage and water absorption of cardanol added sheets are marginally reduced. A significant observation was that cylinders cast from clear resin were all cracked due to exothermic heat evolved during curing whereas no cylinder cast from cardanol containing resin cracked on curing (Fig. 4).

Table 8—Flexural Strength of Clear and Cardanol Containing GP Resin Sheets

Composition, %	Flexural strength, kg/cm²	
GP + 1% catalyst + 2% accelerator	Control	648.29
Cardanol	0.1	743.54
	0.5	697.97
	1	563.99
	2	445.24
	5	365.95

Flexural strength of clear resin and cardanol containing sheets (3 mm thick) were measured on a sample size 75 mm × 25 mm. The results are reported in Table 8. At lower concentration of cardanol there is an increase in flexural strength but as the cardanol concentration increases flexural strength goes down. Cardanol containing sheets were also subjected to benzene immersion test. A 50 mm × 50 mm size sample was weighed and immersed in benzene. These samples were taken out after 24 hr and reweighed. There was no change in the weight of clear as well as cardanol containing sheets which suggests that cardanol is taking part in the copolymerization reaction.

Conclusion

Effect of addition of cardanol on the curing characteristics of different polyesters namely general purpose, isophthalic-based and bisphenol-based has been studied. Cardanol, when added in small proportions, inhibits the curing of polyesters and provides resins of extended pot life with very low peak exotherms. Inhibiting action of cardanol has been compared with other known inhibitors.

Low exotherm and extended pot life resins obtained as a result of addition of cardanol are suitable in castings in thick sections and potting resins for electrical components. A significant feature of cardanol addition is that thick castings are free from cracks even when very small amount of cardanol say 0.1 % is added to the system.

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