

## PROPERTIES OF PAINTS BASED ON CARDANOL AND 3-PENTADECYLPHENOL, THE DERIVATIVES OF CASHEWNUIT SHELL LIQUID

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### ABSTRACT

Several paints based on cardanol and 3-pentadecylphenol (3-PDP) media were prepared and their characteristics determined. The effect of the modification of the media with alkyd resin was studied. All the paints were subjected to accelerated weathering for 1500 hours. The results indicated that 3-PDP media-based paints excelled in weathering performance over the cardanol varnish paints. Further improvement in weathering properties was also achieved with a partial blending of alkyds into the former paints showing thereby that 3-PDP media based paints with/without blending of alkyd were better than those based on cardanol varnish media.

### INTRODUCTION

A GOOD deal of literature has been available on the utilization of cashewnut shell liquid (CNSL) and its important derivatives like cardanol and 3-pentadecylphenol (3-PDP) in the preparation of resins and varnishes (Ramanujam, 1960; Sivasamban *et al.*, 1961; Anonymous, 1964; Agarwal *et al.*, 1966; Agarwal, 1967; Isaiah *et al.*, 1968), but not much work has been carried out so far on the preparation and evaluation of paints based on these CNSL derivatives. The advantages of these resins have been recognised in industrial finishings. We had recently reported that for internal coatings, cardanol-based paints could be used on par with the other phenolic resin based paints and that, as exterior coatings, they behaved better with alkyd modification (Madhusudan *et al.*, 1971). The present paper concerns itself with the preparation and evaluation of paints based on cardanol and 3-pentadecylphenol media with and without blending of alkyd resin.

### MATERIALS AND METHODS

The materials used in the study are listed in Table I.

(a) *Preparation of Media Based on Cardanol and its Blends with Pure Phenolics and Polymerised Cardanol*

(i) *Cardanol-DCO varnish (CD)*.—Cardanol was condensed with hexamine at a suitable temperature followed by the addition of mono-

meric DCO and continuing the heating till the varnish gave a string of about 45 cm length. The product was 'cut' with white spirit to 60% solids.

(ii) *Cardanol-styrene-DCO varnish (CSD)*.—To cardanol-hexamine condensate prepared as in (i), was added monomeric DCO varnish and was then styrenated under reflux by addition of styrene. The bodying and thinning of the product were done as earlier.

(iii) *Cardanol-p-tert. butyl phenol-linseed oil varnish*.—The oleoresinous varnish based on cardanol-phenol blend was prepared by the following two step method:

*1st step: Preparation of cardanol-phenol blend*.—Cardanol, *p*-tert. butyl phenol blend was reacted with formaldehyde (P/F: : 1/1.3) mole) in the presence of alkaline catalyst ammonia (maintaining at appropriate pH). After the reaction was complete, the condensate was freed from water firstly by heating at water-bath temperature under reduced pressure and then at 120–150°C till it gave a solid bead on cooling. Finally, it was allowed to set in shallow pan.

*2nd step: Preparation of varnish*.—The oleoresinous varnish was prepared by cooking together the phenolic resin prepared as above with alkali refined linseed oil at high temperatures till it gave a string of about 45 cm length. Finally, the product was 'cut' to 60% solids in white spirit.

(iv) *Pure phenolic-linseed oil varnish*.—The pure phenolic-linseed oil varnish was prepared as above by heating a 1:1 blend of Biolac-

TABLE I  
Source and characteristics of materials used

Material	Process/quality	Characteristics
(i) Cardanol	By distillation of CNSL	Iodine value (RK)* : 390 Hydroxyl value : 187 Viscosity centi- poises at 30°C : 55
(ii) 3-PDP	By catalytic hydrogenation of cardanol	Iodine value (RK)* : 258 Hydroxyl value : 185 Melting point (°C) : 51.5
(iii) DCO	Catalytic dehydration of castor oil	Iodine value (Wijs) : 130 Sap. value : 195 Viscosity poises at 30° C : 1.65
(iv) Alkali refined linseed oil	Commercial—from M/s. Gwalior Oil Mills, Bombay	Iodine value : 190 Sap. value : 188 Viscosity centipoises at 30°C : 65
(v) Styrene monomer	Commercial—from M/s. Polychem, Bombay	
(vi) Long oil linseed Penta alkyd, LP62 (Cent per cent solids)	M/s. Goodlass Nerolac Paints (P) Ltd., Bombay	Acid value : 8
(vii) Biolac 1071	Commercial—Pure Phenolic resin from M/s. Hard Castle Waud and Co., Bombay	
(viii) White spirit	Commercial—from M/s. Burmah Shell, India	Melting point (°C) : 82

\*(RK) = (Rosenmund—Kuhnenn).

1071 and alkali refined linseed oil till a 45 cm long string was obtained.

(v) *Cardanol resole-linseed oil varnish*.—The method of preparation of this varnish is similar to the one described under (iv). The ratio of cardanol resole-lined oil varnish was 1:2.

(vi) *Polymerised cardanol-linseed oil varnish*.—Cardanol was first polymerised by heating it in the presence of a catalyst, till a viscosity of about 120 poises was obtained. Then the polymerised cardanol (Polycol) was heated with linseed oil till a string of 45 cm was obtained.

(b) *Preparation of Media Based on 3-pentadecylphenol (3-PDP)*

(1) *3-PDP resole-linseed oil varnish (1:1) in situ varnish*.—3-PDP was reacted with formaldehyde (P/F: : 10/1.3 mole) for about 4 hr in presence of ammonia. After completion of the reaction and freeing the resin from moisture, the *in situ* varnish was prepared by heating it with linseed oil in 1:1 ratio till a string of 45 cm could be obtained. The varnish was thinned to 60% solids with white spirit.

(2) *3-PDP-resole-linseed oil varnish (1:2)*.—The preparation of this varnish is just similar to the one described in (b 1) above except that the ratio of 3-PDP-resole to linseed oil was increased to 1:2. The thinning of the product was done as usual.

(3) *3-PDP-novolac-linseed oil varnish (1:2)*.—The novolac was prepared by condensing 3-PDP with formaldehyde in the mole ratio of P/F: : 1/0.8. The moisture-freed resin was heated with linseed oil till the product gave a string of 45 cm length. It was 'cut' to 60% solids in white spirit.

(4) *3-PDP-hexamine-linseed oil varnish (1:2)*.—The 3-PDP was first condensed with hexamine and then heated with linseed oil till a string of 45 cm length could be obtained. The 3-PDP-linseed oil varnish was 'cut' to 60% solids in white spirit.

(5) *3-PDP-hexamine-linseed oil-modified phenolic varnish*.—To the 3-PDP-hexamine condensate prepared under (b 4) was added linseed oil followed by a slow and careful addition of modified phenolic resin (biolac 1226). Finally, the whole reaction mass was cooked at top temperatures till a 45 cm long string was

obtained. The product was thinned with white spirit in the usual way.

(c) *Preparation of Media Modified with Alkyd*

The above media based on cardanol, polycol, and 3-PDP were modified by blending them in a 1:1 ratio with the commercially available long oil penta linseed oil alkyd (L.P. 62).

These blends were specially prepared in order to assess the performance of the media blended with alkyds in the accelerated weathering.

(d) *Media for Control*

The pure phenolic-linseed oil varnish and varnish and long penta linseed oil alkyd (commercial variety) were taken as standards for comparison.

(e) *Preparation of Paints Based on the Above Media*

Several paints prepared by the usual paint preparation technique from the above media at 20% PVC and P: B ratio 1:1 had the following composition:

	Parts by weight
Medium	.. 100
TiO <sub>2</sub> (Anatase)	.. 30
ZnO	.. 30
Sb <sub>2</sub> O <sub>3</sub>	.. 20
Barytes	.. 10
Talc	.. 10
Carbon black	.. 2
White spirit	.. 100

Driers Co (0.05%), Mn (0.02%) and Pb (0.5%) as metal on varnish solids were added.

(f) *Application and Testing of the Paints*

The mild steel panels of size 150.0 × 10.0 cm were first given two coats on one side with zinc chrome-iron oxide primer based on linseed stand oil modified phenolic resin varnish (2:1) according to IS: 2074 and a single coat on the other side and allowed to air dry for 48 hr. Two coats of the paints under test were then applied on to the single coated side of primer in an air conditioned room, each coat having a film thickness of 1.5 mils.

The general characteristics of all the paints, such as drying time, scratch hardness, and flexibility, were determined and their results are given in Table II. In all the paints with and without alkyd modification, properties such as resistance to water, acid, alkali, and white spirit were found to be satisfactory.

(g) *Accelerated Weathering*

All the painted panels in duplicate were subjected to accelerated weathering test in a Marr Weatherometer equipped with two carbon arc lamps. They were exposed to weathering for 1,500 hr at the rate of 20 hr day which included a 4 hr exposure to water spray working at a nozzle pressure of 2.0-2.5 kg/cm<sup>2</sup> at 40° C. Periodically, the panels were turned upside down with their position changed in the rows. No other types of deterioration in film properties were noticed except chalking and loss of gloss. The results of these tests are incorporated in Table III.

## DISCUSSION

*Film properties.*—The slow drying and low scratch hardness of 3-PDP varnish paints as compared to those prepared from cardanol (Table I) are perhaps due to the loss on saturation of cardanol during the hydrogenation process which prevents oxidative polymerisation reactions. However, a considerable improvement in drying time and hardness of the former is achieved by the addition of linseed penta-alkyd or modified phenolic resin. In this respect, polymerised cardanol (polycol) which alkyd modification showed better drying time and scratch hardness (990 g) and also close resemblance to the paint prepared from 3-PDP-hexamine-linseed oil-modified phenolic resin, indicating thereby that polymerised cardanol (polycol) may be advantageously used in certain types of industrial finishes.

*Accelerated weathering properties.*—The chalking resistance of paints based on 3-PDP varnishes is comparatively higher than those based on cardanol. An improvement in weathering resistance of the latter is noticed when *p*-tert. butyl phenol is added to it in the preparation of phenolic resin composition. Paints based on polycol varnish have shown equally good weathering properties. Among the paints based on 3-PDP varnishes, that based on novolac have shown better resistance

TABLE II

*Some characteristics of paints used in the study*

Sl. No.	Paints based on media	Paints without alkyd modification			Paints with alkyd modification		
		Drying time hr	Scratch hardness g	Flexibility	Drying time hr	Scratch hardness g	Flexibility
1.	Cardanol-DCO varnish (1 : 2) (CD)	6	500	Satisfactory	5	600	Satisfactory
2.	Cardanol-styrene-DCO varnish (CSD)	5	600	do	5	600	do
3.	Cardanol-p-tert. butyl phenol-linseed oil varnish	4	400	do	4	550	do
4.	Pure phenolic-linseed oil varnish (1 : 2)	5	400	do	5	700	do
5.	Cardanol-resole-linseed oil (1 : 2)	4	400	do	4	500	do
6.	Polymerised cardanol + Linseed oil (1 : 2)	9	700	do	6	900	do
7.	3-PDP-resole-linseed oil (1 : 1)	12	300	do	8	500	do
8.	3-PDP-resole-linseed oil (1 : 2)	12	300	do	8	500	do
9.	3-PDP-novolac-linseed oil (1 : 2)	12	250	do	8	450	do
10.	3-PDP-Hexa-cond. + linseed oil (1 : 2)	10	350	do	6	600	do
11.	3-PDP-Hexa-cond. + linseed oil + Mod. phenolic resin (1 : 1 : 1)	6	550	do	5	900	do
12.	Long oil penta linseed oil alkyd (LP 62)	4	800	do	..	..	..

TABLE III

*Accelerated weathering data of paints used in the study*

Expt. No.	Paints based on media				Paints without alkyd modification				Paints with alkyd modification			
	Chalking		Loss of gloss		Chalking		Loss of gloss		Chalking		Loss of gloss	
	hr	Grading	hr	Grading	hr	Grading	hr	Grading	hr	Grading	hr	Grading
1.	Cardanol-DCO varnish (CD) 1 : 2	300	1	200	1	500	1	300	1	600	4	4
	Cardanol-styrene-DCO varnish (CSD)	600	4	400	4	800	4	600	4	1000	4	4
2.	Cardanol-p-tert. butyl phenol-linseed oil varnish	250	1	200	1	700	1	300	1	800	1	1
	Pure phenolic-linseed oil varnish (1 : 2)	500	4	400	4	1000	4	600	4	800	4	4
3.	Cardanol-resole-linseed oil (1 : 2)	400	1	300	1	800	1	400	1	400	1	1
	Polymerised cardanol + Linseed oil (1 : 2)	800	4	500	4	1200	4	600	4	400	4	4
4.	3-PDP-resole-linseed oil (1 : 1)	400	1	300	1	800	1	400	1	400	1	1
	3-PDP-resole-linseed oil (1 : 2)	800	4	500	4	1200	4	800	4	800	4	4
5.	3-PDP-novolac-linseed oil (1 : 2)	250	2	200	2	300	Nil	200	1	400	4	4
	3-PDP-Hexa cond-linseed oil (1 : 2)	400	4	250	4	675	4	400	4	400	4	4
6.	3-PDP-Hexa cond-linseed oil-modified phenolic resin (1 : : 1)	300	1	300	1	400	1	400	1	400	1	1
	Long oil penta linseed oil alkyd (LP62)	1000	4	600	4	1500	4	1000	4	1500	4	4
7.	3-PDP-resole-linseed oil (1 : 1)	300	1	300	1	600	1	500	1	1500	3	3
	3-PDP-resole-linseed oil (1 : 2)	900	4	600	4	1500	2	1500	2	1500	3	3
8.	3-PDP-novolac-linseed oil (1 : 2)	500	1	450	1	600	1	500	1	1500	1	1
	3-PDP-Hexa cond-linseed oil (1 : 2)	1000	4	700	4	1500	1	1500	1	1500	2	2
9.	3-PDP-Hexa cond-linseed oil (1 : 2)	600	1	500	1	900	1	600	1	1500	1	1
	3-PDP-Hexa cond-linseed oil (1 : 2)	1000	4	700	4	1500	1	1500	1	1500	2	2
10.	3-PDP-Hexa cond-linseed oil (1 : 2)	500	1	450	1	700	1	500	1	1500	1	1
	3-PDP-Hexa cond-linseed oil (1 : 2)	900	4	700	4	1500	2	1500	2	1500	2	2
11.	3-PDP-Hexa cond-linseed oil-modified phenolic resin (1 : : 1)	400	1	300	1	1400	1	1200	1	1500	1	1
	Long oil penta linseed oil alkyd (LP62)	900	4	650	4	1500	1	1500	1	1500	2	2
12.	Long oil penta linseed oil alkyd (LP62)	1500	Nil	1000	1	..	..	..	..	..	..	..
	Long oil penta linseed oil alkyd (LP62)	..	..	1500	2	..	..	..	..	..	..	..

Key to grading : Nil—no change; 1—very slight; 2—slight; 3—definite; 4—bad.

to chalking (upto 600 hr exposure) than those based on resole.

Incorporation of long oil linseed penta-alkyd brings about an overall improvement in weathering properties. It is interesting that styrene, while increasing the hardness of paint (Table II), does not improve the weathering property. Paints based on 3-PDP novolac showed initial chalking after 900 hr exposure as against 600 hr in the case of cardanol-resole type paints. In all the cases, loss of gloss is evidenced over a wide range of exposure time (300-1,200 hr). The paints based on 3-PDP, have shown better gloss retention (500 hr). The alkyd modified paint based on 3-PDP-hexamine-linseed-modified phenolic resin media is by far the best in both gloss retention and resistance to chalking. These results compare well with that of control alkyd.

#### CONCLUSION

Cardanol-based paints are on par with the other phenolic resin-based paints. Alkyd modified styrenated cardanol paint can also be used for exterior coatings, while the unmodified one is suitable for interior coating with the added advantage of hardness. Paints based on polycol may possibly replace some of the commercially available costlier phenolic resins in paint formulations. The paints based on 3-PDP varnish have shown better

weathering resistance as compared to cardanol-based paints. In general, alkyd modification of the paint media based on 3-PDP conferred better weathering resistance than those based on cardanol. The paints based on 3-PDP hexamine possesses properties in that the preparation of the former media is easier and cheaper than the latter.

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