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OIL REACTIVE/SOLUBLE MODIFIED PHENOLICS — I

Curing shellac- castor oil type

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A 'Durophen' type of product which is soluble in xylene/toluene has been prepared from a shellac-castor oil combination and bisphenol-A—formaldehyde condensate. The product from lac-castor oil composition (50:50) and phenolic condensate (1:2 mole) in the ratio of 1:3 has been found most suitable for thermohardening type of surface coatings. The effect of reactivity of phenolic condensate on surface coating properties was studied. The baked films were hard, flexible and possess good adhesion but poor impact strength. Solvent and chemical resistance was also found to be satisfactory.

Introduction

FOR the preparation of synthetic phenolic resins for use in varnish making, the aryl substituted phenols are as important as the alkyl phenols. One such phenolic compound which has been used for this purpose is bisphenol-A (p-p dihydroxy diphenyl propane). It has been used in the manufacture of a series of oil reactive/soluble unmodified phenolic resins and also other modified resins. The resins obtained from bisphenol-A[1] have better colour retention, hardness, bodying and drying properties as compared to other phenolic resins.

Ordinary phenolic resins are brittle and require plasticization in order to produce surface coatings of desirable properties. Curing castor oil type phenolic resins 2,3 which are made from a butylated phenonolic resin and oil, is expected to be hard (due to the presence of phenolic resin) and possess sufficient flexibility and film forming properties (derived from the oil).

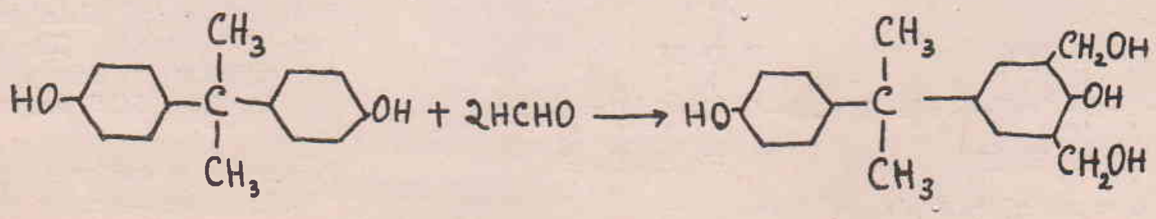
'Durophen'[2,4] is a plasticicized and thermohardening type of phenolic resin. It is obtained by the condensation of bisphenol-A with formaldehyde under alkaline condition. The condensation product thus obtained is butylated and plasticized with castor oil. The resulting product possesses good elasticity, high resistance to chemicals, enamel like hardness, good adhesion and also resistance to shock, impact and scratch.

Shellac which is a natural resin is a very good film former. It has several reactive groups[5] like carboxyl, aldehydic and hydroxyl. It can thus be modified by reactions with several chemicals and resins. The modification of shellac obtained from phenol and formaldehyde gave films which were water resistant but brittle. It has been claimed that acetylated shellac[7] modified with phenol and formaldehyde produces films of improved water resistance, elasticity and adhesion. The product thus obtained was found to be compatible with acids obtained from drying oils but insoluble in oil itself. Further it has been found that incorporation of spirit soluble phenolics[8] in shellac varnishes gave films of improved heat and water resistance but both the air dried and baked films possessed poor flexibility. The varnish prepared from maleinised tung oil[9] ammoniacal solution of shellac and water soluble phenolic resin has been claimed as suitable for coating metal surface.

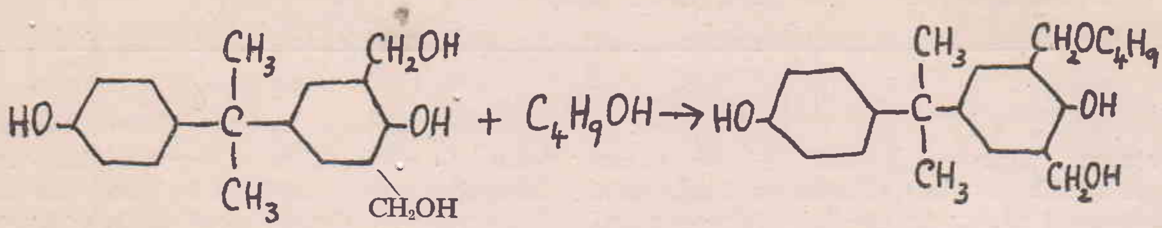
Shellac can be combined with various oils[10-13] (both drying and non-drying) in the presence of certain incorporating agents. Thus castor oil[14], a non-drying oil, can be combined with shellac in presence of a metallic oxide as incorporating agent. The resulting product was soluble in ketones, hydrocarbons and esters. The present work has been undertaken to prepare a 'Durophen' type of product which would be soluble in common hydrocarbon solvents like toluene and xylene.

The oil reactive phenolic resin[15] (resole type), prepared with high formaldehyde/phenol ratio and an alkaline catalyst, has orthomethylol structure and combines chemically with the unsaturated centres in the oil molecule and with the ester links. The ortho methylol phenol structure adds to the double bond and forms chroman type compounds.

Bisphenol-A with 2 moles of formaldehyde may form the following condensate in presence of an alkaline catalyst. The addition takes place at any two of the four reactive ortho positions with respect to the hydroxyls.



On butylation of this phenolic condensate with one equivalent of n-butanol, the reaction product would have one methylol group in unreacted condition.



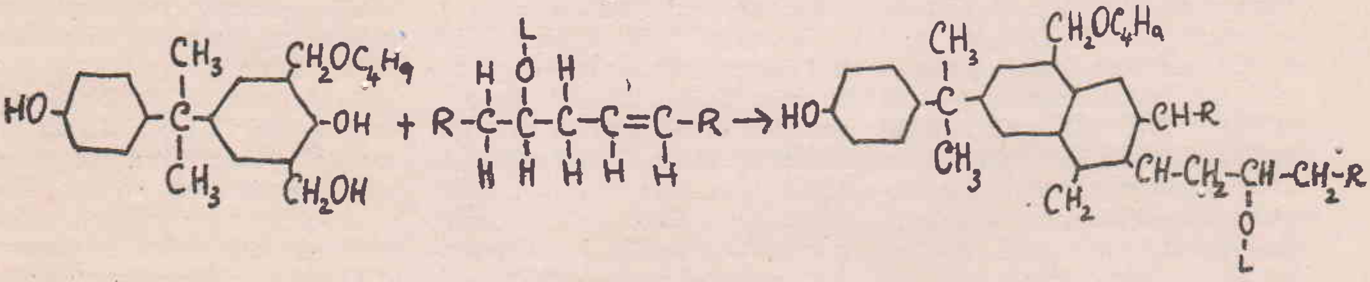
When shellac and castor oil are incorporated in equal proportion, it was observed[14] that the hydroxyl value becomes lower but the carboxyl value remains practically constant. Three possibilities may be put forward explaining this lowering of hydroxyl value viz. formation of acetals by reaction between —OH of the castor oil with the —CHO of shellac or etherification between —OH of shellac and —OH of castor oil or formation of double bond (unsaturation) in oil molecule by reaction between adjacent —H and —OH.

Taking into consideration the procedure adopted and catalyst used for the preparation of lac-castor oil combination, the possibility of the first and the last reactions enumerated above would be rare. Thus the only explanation that suggests itself is the possibility of etherification which may occur as follows:-

$$R-\underset{H}{C}-\underset{\underset{H}{|}}{\overset{OH}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{C}=\underset{H}{C}-R + L-OH \rightarrow R-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{O-L}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{C}=\underset{H}{C}-R$$

Where, L = rest of the shellac molecule

This lac-castor oil composition when reacted with above butylated phenolic condensate possibly will form a chroman type compound. The chroman (1) or (2) may be formed as a result of addition to either end of the double bond.



(1)

(2)

A shellac castor oil combination has been reacted with a bisphenol A-formaldehyde condensate and butanol and the resulting product dissolved in a suitable hydrocarbon. The film properties of the varnishes thus obtained have been studied and evaluted.

EXPERIMENTAL

Preparation of shellac — castor oil compositions

Different compositions of shellac (dewaxed lemon) and castor oil (B.P.) have been prepared (Table I) in the presence of calcium hydroxide (B.D.H.) (5% on the weight of shellac) as incorporating agent as per method of Mani, Tripathi and Misra.[14]

Preparation of phenolic condensate

Bisphenol-A (1 mole) was dissolved in sodium hydroxide (2 moles) solution in water and formaldehyde (37% w/v) was added slowly under stirring. The temperature was maintained below 40°C throughout the reaction. After adding all the formaldehyde (1-4 moles) the temperature was increased to 50-60°C and maintained at this temperature for about 6 hrs. The product was cooled to room-temperature and neutralised with the calculated amount of dilute sulphuric acid pH-5 (approx). The product was washed several times with water till free from SO_4^{11} and vaccum dried.

Preparation of coating composition

Different lac — castor oil compositions were mixed with different proportions of phenolic condensate dissolved in equal weight of n-butanol (Table I and II). The mixing was done at 130-140°C. This resin was then dissolved in toluene (L.R.) or xylene (L.R.) and film properties studied.

RESULTS AND DISCUSSIONS

Surface coating properties

The surface coating properties of three different compositions prepared from shellac-castor oil combinations and the phenolic condensate by mixing the two in different proportions have been studied and are summarised in Table I. All the observations have been taken under identical conditions. The film was prepared on tin plate panels and baked for 30 minutes at 150°C in an air oven. Hardness, flexibility and impact resistance were determined using standard methods.

All the lac — castor oil compositions were quite compatible with phenolic condensates and were soluble in xylene and toluene. The hardness of the film increased with increase in the proportion of the phenolic resin. The flexibility, however, decreased proportionately (Table I). The films have good adhesion but poor impact strength.

As far as film properties were concerned the optimum ratio of lac — castor oil composition (50:50) and phenolic condensate (1:1) was found to be in the ratio of 1:3.

Effect of methylol groups

Bisphenol-A has a potential functionality of four and has good reactivity because formaldehyde can add to the two ortho positions in each ring. Hence the four different phenolic condensates were prepared with bisphenol-A and formaldehyde in the mole ratios ranging from 1 to 4. All condensates were alkali catalysed and were of resole type. In this way condensates having different number of methylol groups ranging from 1 to 4 were obtained.

Lac — castor oil composition (50:50) was reacted with phenolic condensation having different reactivities i.e. different number of methylol groups (Table II). It has been observed that phenolic condensate upto mole ratio 1:2 reacted well and was quite compatible with lac — castor oil composition. But condensates of mole ratios 1:2 and 1:3 were not compatible and also the coating compositions were not found homogeneous in xylene or toluene. Further it has been observed that if the mole ratio of formaldehyde in phenolic condensate is increased the same product gives better film performance with regard to hardness and flexibility.

As far as the surface coating properties were concerned the optimum mole ratio of formaldehyde in phenolic condensate was found to be 152. Furtehr the most suitable ratio of lac — castor oil composition (50:50) and phenolic condensate (1:2) was found to be 1:3.

Chemical & solvent resistance and colour

The chemical and solvent resistance of different compositions of shellac — castor oil (50:50) and phenolic condensates was studied (Table III). The films were prepared on glass slides and baked for ½ hr. at 150°C in air oven and observation were taken.

It was observed that the increased proportion of phenolic condensate in compositions favoured water and dilute alkali resistance. Most of the compositions were found to be resistant to dilute, acid, benzene, white spirit, xylene, lubricants and methylated spirit on immersion upto 7 days. This might be due to cross-linking as a result of baking. Only compositions having lower phenolic contents were found to be soft even after continuous immersion in methylated spirit for 7 days. These films, however, recovered completely after an hour.

The solvent and chemical resistance, of lac-castor oil composition

TABLE I: CHARACTERISTICS OF LAC — CASTOR OIL PHENOLIC RESIN VARNISHES.

S.No.		Lac : castor oil (by wt).	L.C. : P.C (by wt).	Compatibility	Baking schedule Temp °C	Baking schedule Duration minutes	Scratch hardness (in kg)	Flexibility round a conical mandrel (min. dia 3 mm).	Elasticity condition of the film on bending double	Impact resistance (falling block type)
1		2	3	4	5	6	7	8	9	10
	1	45:55	1:2	Compatible	150	30	1.1	N.C.	N.C.	Fails
A	2	,,	1:3	,,	,,	,,	1.1	,,	,,	,,
	3	,,	1:4	,,	,,	,,	1.0	,,	,,	,,
	1	50:50	1:2	,,	,,	,,	1.1	,,	FC	,,
B	2	,,	1:3	,,	,,	,,	1.2	,,	NC	,,
	3	,,	1:4	,,	,,	,,	1.1	,,	,,	,,
	1	55:45	1:2	,,	,,	,,	1.0	C	C	,,
C	2	,,	1:3	,,	,,	,,	1.2	N.C.	V.F.C.	,,
	3	,,	1:4	,,	,,	,,	1.1	,,	NC	,,

LC = Lac-castor oil.
PC = Phenolic condensate (bisphenol- A : Formaldehyde = 1:1)
NC = No crack
C = Cracks
FC = Fine cracks
VFC = Very fine cracks.

TABLE II: EFFECT OF METHYLOL GROUPS ON SURFACE COATING PROPERTIES OF LAC-CASTOR OIL-PHENOLIC RESIN

S. No.	Lac castor oil (wt)	Mole ratio bisphenol A: formaldehyde (in phenolic condensate).	LC:PC (by wt)	Compatibility	Baking schdule Temp. °C	Baking schdule Durn minute	Scratch hardness (in kg)	Flexibility (round a conical mandrel) (min. dia. 3 mm)	Elasticity condition of the films on bending double	Impact resistance (falling block type)
1	2	3	4	5	6	7	8	9	10	11
A 1	50:50	1:1	1:2	Compatible	150	20	1.1	NC	FC	Fails
A 2	"	"	1:3	"	"	"	1.2	"	NC	"
A 3	"	"	1:4	"	"	"	1.1	"	"	"
B 1	"	1:2	1:2	"	"	"	1.2	"	"	"
B 2	"	"	1:3	"	"	"	1.4	"	"	"
B 3	"	"	1:4	"	"	"	1.2	"	"	"
C 1	"	1:3	1:2	non-compatible						
C 2	"	"	1:3	"	Nil	Nil	Nil	Nil	Nil	Nil
C 3	"	"	1:4	"						
D 1	"	1:4	1:2	"						
D 2	"	"	1:3	"	Nil	Nil	Nil	Nil	Nil	Nil
D 3	"	"	1:4	"						

NC = No crack FC = Fine cracks LC = Lac-castor oil PC = Phenolic condensate

TABLE III: SOLVENT AND CHEMICAL RESISTANCE OF LAC CASTOR OIL PHENOLIC RESIN

S.No. (as Table II)	Water resistance (in days)	Alkali resistance (3% w/v Na_2CO_3) (in days)	Acid resistance (6N H_2SO_4) (in 7 days)	Benzene (in 7 days)	White spirit (in 7 days)	Xylene (in 7 days)	Methylated spirit (95%) (in 7 days)	Lubricants (Mobile oil) (in 7 days)
A 1	NE(7)	NE(7)	NE	NE	NE	NE	NE	NE
A 2	NE(3)	Soft(7)	"	"	"	"	"	"
A 3	NE(1)	Soft(1)	"	"	"	"	SS	"
B 1	NE(7)	NE(7)	"	"	"	"	NE	"
B 2	NE(7)	NE(7)	"	"	"	"	"	"
B 3	NE(3)	Soft(2)	"	"	"			
—						"	VSS	"
C 1								
C 2								
C 3				Nil				
D 1								
D 2								
D 3				Nil				

NE = No effect SS = Slight softening VSS = Very slight softening.

(50:50) and phenolic condensate (1:2) when mixed in the ratio of 1:3, was also found to be satisfactory. The colour of this varnish was also measured with Lovibond Tintometer. The matching standard with 13 M.M. cell was found as Red -8, yellow -13.0 and Blue 9.9 and with 5 M.M. cell was found as Red -12, yellow -8 and Blue -6.

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