S. N. 113

WATER-BASED SHELLAC COATINGS — PART I.

Lac-Tung Oil-Phenolic Resin

By

P. K. KUNDU and SHRAVAN KUMAR,
Indian Lac Research Institute Namkum, Ranchi.

Incorporation of suitable proportions of water-soluble tung oil and water-soluble phenolic resin into ammoniacal solution of shellac produces a water-based varnish suitable for coating on metal surface. The best performance is obtained when 14 pts of phenolic resin and 57 pts. of tung oil are incorporated to 29 pts. of shellac. This varnish remains clear on dilution with water and the films produced after baking at 150°C for 30 minutes are hard, smooth, glossy and highly flexible. Their resistance to water, chemicals and solvents is very good. In conjunction with red oxide of iron, it produces a baking type of primer which shows excellent adhesion and flexibility and possesses satisfactory resistance to corrosion.

In view of its excellent anticorrosive properties and baking schedule normally practised in the industry, the use of this primer for coating of ferrous metals is indicated.

Introduction

One of the major problems currently under intensive research and development in the surface coating industry is the elimination or reduction in the use of organic solvents. In recent years, a great deal of interest is being shown in stoving finishes which are partly or completely thinned with water. These water-thinned finishes have added advantages over the conventional systems. In these finishes, the risk of fire and the pollution of atmosphere by the toxic vapours of the solvents is completely eliminated. These water-thinned finishes[1] produce hard, smooth and glossy films on stoving and in general performance they compare quite favourably with solvent systems.

Water-thinned coatings are essentially of two types, one in which the media is dispersed in water and the other where the media is soluble in water. The first type is commonly known as 'emulsion type' and the other as 'water-soluble type'.

In water-soluble systems, the vehicle exists as clear liquid and remains clear[2] even when diluted with water. In these finishes the media consists of some water-soluble resin, water-soluble oil etc. Water-soluble resins used for such coatings are usually of low molecular weight. As these water-soluble finishes do not contain any wetting agent, emulsifier, stabilizer etc., they show good resistance to water and other chemicals.

Water-solubility of resins is normally achieved by introducing more polar groups into the molecule which makes the resins water-soluble on their own rights; or by introducing a carboxyl group in the molecule which, when treated with an alkali, solubilises the resin. Drying oils are normally made water-soluble by the maleinization process i.e. by adding maleic anhydride at the double bond and neutralising the introduced carboxyl groups in the oil with an alkali.

A good number of synthetic resins and drying oils have already been exploited in the manufacture of these finishes in the more advanced countries. In our country however, these water-thinned finishes are almost in their infancy.

So far, among natural resins, only shellac has been used in the production of water-soluble lacquers and primers. Chemical structure of this natural resin shows a close parlance with the structure and mechanism of the present day water-soluble resins[2]. Owing to the presence of one free carboxyl

Reprinted from PAINTINDIA, Sep., 1966.

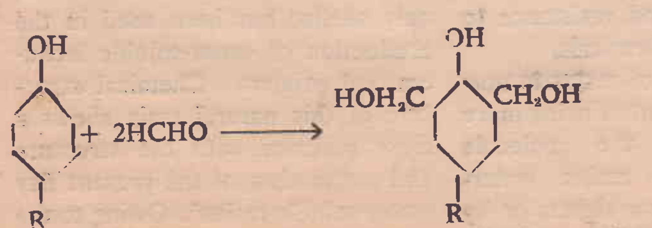
group in the molecule, it dissolves freely in aqueous alkalis to form clear solutions[3]. These aqueous varnishes do not adhere well on metals but when blended with water-soluble drying oils such as linseed[4] and tung oils[5], they form highly adherent, hard, smooth and glossy films on various substrates.

In order to further improve upon the properties of these varnishes, it was thought to incorporate a curing agent — a thermosetting resin in the above varnish compositions. These thermosetting resins by virtue of forming a cross-linked structure with the functional groups of the same or other resins show much improved performance in regard to water, chemical, solvent and mechanical resistant properties.

Water-soluble thermosetting resins such as ureas, phenolics and melamine are the most widely used curing resins[6]. These resins because of their poor film forming characteristics are normally used in conjunction with a good film former.

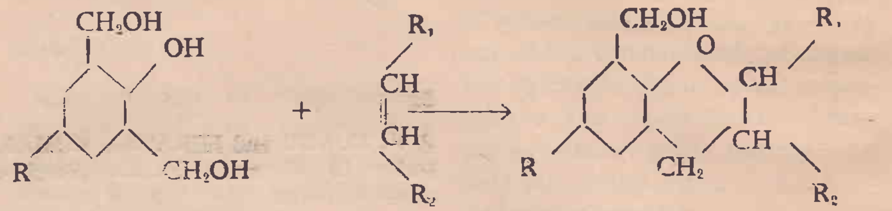
In the present work, lac-drying oil varnish has been used as the film former while phenolic resin is used as the curing agent.

Modified phenolic alcohols with little or no condensation are generally used for curing purposes. To obtain water-soluble products, the functionality of phenol is reduced by blocking off the ortho- or para-position with alkyl group and then reacting with formaldehyde at 30°-60°C under alkaline conditions.

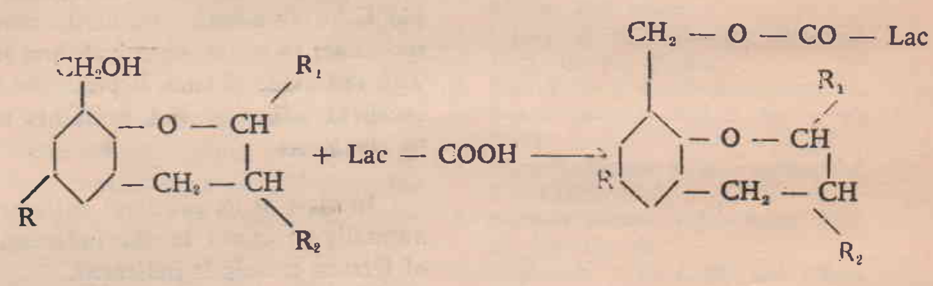


p-alkyl phenol   Dimethylol p-alkyl phenol

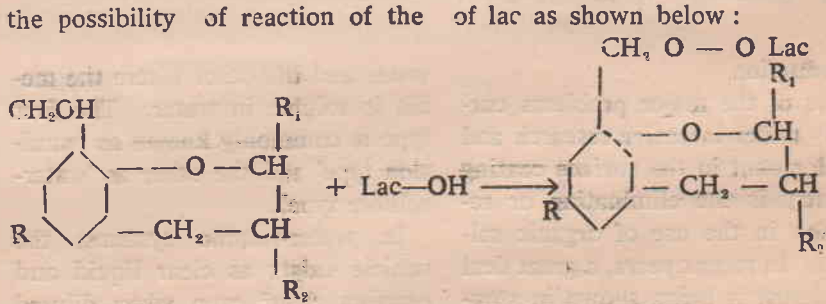
This dimethylol p-alkyl phenol reacts with drying oils to form a condensation product as shown below.



In the above reaction, one methylol group is left free which can be further reacted with the carboxyl or hydroxyl of lac. Kumar[7] has recently observed on the basis of his experiments on lac-urea and lac-melamine resin varnishes that it is the carboxyl group of lac which is more reactive than OH groups and therefore we may have the following type of reaction product.



However this does not score out the possibility of reaction of the methylol groups with the hydroxyl of lac as shown below :



Experimental

Aqueous lac-tung oil-phenolic resin varnishes were prepared by blending together water-soluble lac, tung oil and phenolic resins in appropriate proportions. It has been found that incorporation of phenolic resin into lac-tung oil varnishes resulted in clear homogeneous blends which could be further diluted with water. A little proportion (5%) of organic solvents such as butyl cellosolve (on wt. of varnish) or alcohol was also added to reduce viscosity and increase compatibility of the resin. These varnishes were then studied for their viscosity and solid content.

Viscosity was determined by No. 4 Ford cup and the solid content by evaporating the solvent at 105°C to constant weight. It was

TABLE 1

Composition of the varnishes : (Calculated on solid basis)

Composition no.	Water-soluble phenolic resin w. in gms.	(%)	Water-soluble oil w. in gms.	(%)	Water-soluble lac w in gms.	(%)
1.	19.8	17.50	50.0	44.2	43	38.50
2.	20.0	17.70	43.0	38.6	50	44.30
3.	15.0	14.01	60.0	57.0	30	28.51
4	10.0	5.01	132.0	65.0	60	30.01
5	15.0	7.20	132.0	63.0	60	29.00
*6.	20.0	12.00	66.5	40.0	80	48.00
7.	50.0	100.00	—	—	—	—
8.	—	—	50.0	100.0	—	—
9.	—	—	—	—	50	100.00

* With p-tert butyl phenolic resin

noted that after standing for some weeks, the viscosity of these blends was reduced but the film properties did not change.

Water-soluble lac solution used in the preparation of above varnishes was prepared by dissolving ammoniated lac in warm water. Maleinised tung oil was prepared by reacting tung oil with maleic acid or anhydride at 80°C for 2 hours. The product so obtained was washed thoroughly with water and then dissolved in requisite amount of ammonia to give a clear solution.

Water-soluble phenolic resin was prepared by reacting 100 parts phenol, 120 parts formalin and 3 gms. of sodium hydroxide (dissolved in minimum quantity of water) for 20-30 minutes. The product was then cooled and diluted with water to 25% solids. The pH of the solution was maintained at 7.5-8.

Film properties

These water-thinned varnishes produced hard, smooth and glossy film on various substrates when applied by flowing process. They showed excellent flexibility and good adhesion on metals and other like substrates.

Both baked as well as air-dried films (in the presence of cobalt as drier) were studied. But since air-dried films did not show any appreciable improvement in the film properties over the parent lac, further experiments were restricted to the baked films only. Different schedules of time and temperature of baking were studied and it was found that baking at 150°-160°C for 30 minutes serves the best. Baking of the film for less time did not give adequate resistance to water and chemicals. Also baking for prolonged period made the film darker and comparatively brittle.

TABLE 2

Characteristics of lac - tung oil - phenolic resin varnishes (stoving type)

Expt. Nos. w.r.t. previous composition nos.	Drying time: Surface dry (hrs.)	Drying time: Hard dry	Stoving schedule: Temp. °C	Stoving schedule: Time in mins.	Scratch hardness (g)	Bend test (1/8" mandrel)	Flexibility & adhesion	Viscosity in seconds at 22°C (N0.4 Ford cup)	Solid content (Percentage)
1.	15	>7 days	150	30	700	no cracks	good	25	30.0
2.	15	>7 days	150	30	500	fine cracks	not good	45	32.0
3.	15	>7 days	150	30	900	no cracks	very good	65	32.5
4.	17	>7 days	150	30	1100	no cracks	very good	75	33.0
5	17	>7 days	160	40	900	no cracks	very good	24	30.0
6.	4	20 hrs.	150	30	500	cracks	very bad	90	30.0
7.	—	—	—	—	—	—		—	50.0
8.	8	48 hrs.	150	30	100	fine cracks	not good	65	30.0
9.	0.66	1 hr.	150	30	800	fine cracks	not good	23	24.0

Film properties such as hardness, flexibility and resistance to water, chemicals etc. were determined and it was noted that varnishes containing more of oil showed better flexibility but poor hardness.

As regards solvents and chemical resistant properties, compositions containing more of phenolic resin gave better performance.

In view of good adhesion, excellent flexibility and satisfactory solvent and chemical resistant properties, these varnishes were evaluated as vehicle for inhibitive primers.

Red oxide primers

Red oxide primers were prepared by grinding together appropriate proportion of the varnish and red oxide of iron (35% P.V.C.) in a ball mill for 18-20 hrs. The primers so obtained could be applied satisfactorily by any of the conventional techniques viz. brushing, dipping or spraying.

These coated panels air-dried rapidly and could be baked after a flash off period of 5-7 minutes. The films so obtained possessed a typical matt-primer finish.

These coated panels were studied for their water, solvent and corrosion resistant properties as specified under IS :101-1961. It was noted that baked films showed excellent resistance to water and did not show any blushing or lifting of the film when immersed in water continuously for 15 days. They also showed good resistance to various solvents and chemicals. These baked films showed excellent wetting and hold out to various types of top coats such as synthetic enamels, nitro-cellulose lacquers and oil paints and did not show any tendency to bleed into any of these finish coats or to lift. These finish coats could be applied immediately after baking of the primer coat.

Corrosion resistant properties of these primers were studied by salt droplet test. Mild steel panels passivated by dipping for one minute in 50% phosphoric acid, were coated with the primers by all the three conventional methods viz., by dipping, spraying and brushing. One set was allowed to air-dry for 24 hrs. when on some of them nitrocellulose and synthetic enamel finishing coats were applied.

TABLE 3

Solvent and chemical resistant properties of lac - tung oil - phenolic resin varnishes (stoving type) — resistance to —

Expt. nos. w.r.t. previous composition nos.	Water (hrs.)	Alkali (3% Na_2CO_3 hrs.)	Acid H_2SO_4 (10%) hrs.	10% acetic acid (hrs.)	10% acid HCl (hrs.)	Spirit 50 rubs	Acetone 30 rubs	Lubricating oil at 50°C
1.	NE	48	NE	NE	NE	NE	NE	NE
2.	NE	72	NE	NE	NE	NE	NE	NE
3	NE	48 (F.S.)	NE	NE	NE	NE	NE	NE
4.	NE	48 (F.S.)	NE	NE	NE	NE	NE	NE
5.	NE	12	NE	NE	NE	NE	NE	NE
6	NE	12	B (72 hrs.)	B (72 hrs.)	B (72 hrs.)	NE	NE	NE
7	—	—						
8.	B(6)	S.B.(2)	F.S. (2/3/4)	B(3)	F.S. (2/3/4)	NE		
9	NE	F.S. (6)	NE	B (2 days)	NE	F.R. (40 rubs)	FR(4)	NE

N.B. F.S. — Film softens
NE — No effect
FR — Film removed
B — Blushing
SB — Slight blush

TABLE 4

Air-drying properties of lac - tung oil - phenolic resin varnishes in presence of cobalt acetate as drier

Expt. nos. w.r.t. previous composition nos.	Drying time: Surface dry (hrs.)	Drying time: Hard dry (hrs.)	Scratch hardness (gm.)	Bend test ($\frac{1}{8}$" mandrel)	Flexibility & adhesion	Resistance to water (initial blushing time minutes)	3% sodium carbonate solution (initial blushing time) minutes
1.	6	72	400	cracks	not good	30	15
2.	6	72	400	fine cracks	good	30	20
3.	6	48	400	no cracks	very good	60	30
4	2	24	1000	no cracks	very good	60	40
5.	2	24-48	500	no cracks	good	30	20
6	1.5	15	200	cracks	not good	20	20

Expt. nos.	Resistance to 10% acid sulphuric (hrs.)	10% acid hydrochloric initial blushing time (hrs.)	Spirit (dipped) initial softening time (minutes)
1	8	8	30
2	8	8	30
3.	10	8	30
4.	15	15.	60
5.	15	15	60
6.	8	8	10

TABLE 5

Characteristics of red oxide primer

	Primer no. 1 (baking type) (containing varnish no. 3)	Primer no. 2 (baking type) (containing varnish no. 4)	Primer no. 3 (air-drying type) using catalyst (containing varnish no. 4)
1. Drying time (hard dry)	150°C at 30 mts.	150°C (30 mts.)	48 hrs. at room temp.
2. Consistency (No. 4 Ford cup at 22°C)	29 sec	28 secs.	25 sec.
3. Finish	egg shell	egg shell	egg shell
4. Colour	That of red oxide	that of red oxide	that of red oxide
5. Scratch hardness (gms)	1400	1500	900
6. Flexibility and adhesion (after 48 hours)	no cracks (good adhesion)	no cracks (v. good adhesion)	no cracks (good adhesion)
7. Protection against corrosion			
(a) jar sulphur dioxide exposure	satisfactory (96 hrs.)	satisfactory (96 hrs.)	—
(b) salt droplet test (4 days)	satisfactory (96 hrs.)	satisfactory (96 hrs.)	satisfactory (72 hrs.)
8. Weight of 10 litres of the product	13.61 kg.	13.13 kg.	13.35 kg.
9. Film thickness (mils)	2 mil	2 mil	2 mil.
10 With 1% detergent solution rubbed upto 2000 times	nothing happened	nothing happened	satisfactory

Another set was baked after a flash off period of 7 minutes at 150°C for 30 mits. and to few of these industrial enamel of the baking type was applied and again baked at the same temperature.

Air-dried films after 7 days and the baked ones after 24 hours were subjected to salt droplet test for 4 days (as specified by IS : 101-1961) This exposure did not produce any rust spots on baked panels however, a few rust spots were seen on the air-dried panels. The primers coated, were also subjected to sulphur dioxide exposure test. No corrosion could be noticed upto 4 days.

The films were next subjected to impact resistance test (of the falling block type). No flaking off of the primer film was noticed in both the compositions. Natural weathering experiments were also conducted. Mild steel panels 10" x 12" coated with the primer and baked were exposed for three months on the roof of the laboratory. At the end of three months, all the panels carrying finish coats and the panels containing primer alone remained perfectly unaffected.

Conclusions

Incorporation of water-soluble phenolic resin into aqueous lac-tung oil varnishes results in considerable improvement in the properties of the baked film. As the quantity of the phenolic resin in the above composition increases, hardness and solvent and weather resistant properties show an increasing trend but flexibility deteriorates. On the other hand, if the phenolic resin content is reduced beyond a certain limit, the films did not show adequate resistance to solvents and chemicals. With all these considerations, the composition containing about 14% of the phenolic resin is considered to be the best. This composition produces hard, smooth and glossy films on baking, which shows good adhesion and flexibility and possesses good resistance to water, chemicals and solvents etc.

In conjunction with red oxide as pigment, it produces a baking type of primer which can be applied by any of the conventional techniques viz. by brush, dip or spray, to produce a fine matt finish. These primers show good wetting and hold out to top coats.

Acknowledgements

The authors are grateful to Dr. G. S. Misra, Director for his valuable suggestions and encouragement

References

1. Farrow, E. L., **Paint Tech., 1960, 24** No. 273, 19-21.
2. Letsky, B. M., **Product Finishing,** 1963, **16,** No. 2, 63.
3. Rao, V. S. & Sankaranarayanan, Y., **Res. & Industry,** Vol. **5, No. 4, '60,** 87-89.
4. Shravan Kumar et al, Indian Pat. No. 88878, 1965.
5. Shravan Kumar, **Paint Tech.,** 1965, **29** No. 12, 15.
6. Hopwood, J. J., **J. Oil Col. Chem. Assn.,** 1965, Vol. **48, No. 2, 157.**
7. Shravan Kumar, **Paint Tech., 1966,** Vol. **30, No. 2, 16.**