Surface coatings based on lac-linseed oil combinations

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INTRODUCTION

SHELLAC is one of the most valuable natural resin used in the field of surface coatings from very early times. This resin is particularly valued for the hardness, gloss and toughness of its films and its excellent adhesion to a wide variety of surfaces such as wood, metal, paper fabric etc. Its inertness towards acids and hydrocarbon solvents and its excellent electrical properties make it a still more valuable resin.

Though shellac finds considerable use in the coating and finishing industry as a spirit or aqueous varnish, its use in oil varnishes has so far been extremely limited due its incompatibility with drying oils and its insolubility is cheaper aromatic hydrocarbon solvents.

Attempts were made[1–8] to combine shellac with drying and non-drying oils inorder to combine the film forming characteristics of the former with the elasticity and weather resistance of the later. As a result of sustained efforts made by groups of research scientists lac-oil varnishes soluble in cheaper aromatic hydrocarbon solvents could be prepared by reacting lac with drying oil in presence of a metallic oxide[5] such as CaO, ZnO, PbO etc. Lac-oil varnishes were also prepared by incorporating lac with drying oils in the presence of glycerol[6]. These lac-oil varnishes showed good solubility in cheaper aromatic hydrocarbon solvents like white spirit, M.T.O. and on application by brush/ffow produced smooth and glossy films having good flexibility and improved electrical insulating properties. However, even in the presence of drier these varnishes did not dry to a hard film and showed tackiness for a longer time. These films also showed poor resistance to water and to natural weathering. Because of these shortcomings lac-oil varnishes developed earlier could not make out its way in paint and varnish industry.

The present study was, therefore, undertaken with a view to develop lac-oil varnishes and paints which may be free from the defects which persisted in the earlier compositions.

EXPERIMENTAL

The process for the preparation of lac-linseed oil varnish was re-examined. Based on the theoretical possibilities the reaction of lac with linseed oil was studied under different conditions of time, temperature and the quantity of reactants. The products obtained at different stages of chemical reaction were examined for their acid and hydroxyl values and also for their solubility in hydrocarbon solvents. The data so obtained are given in Table I.

TABLE — 1
PHYSICO-CHEMICAL PROPERTIES OF LAC-OIL VARNISHES AT DIFFERENT STAGES OF REACTION

Time of reaction minutes at 290°C	Acid value	Hydroxyl value	Solubility in white spirit
5	33.5	87.5	Insoluble
10	30.6	87.0	Partly soluble
20	28.6	86.5	Soluble
35	28.0	86.0	Soluble

It was observed that when the quantity of lac used in the experiment was increased to 60% homogeneous varnishes could be obtained but when the same was increased beyond 60% gelling took place. Further when the temperature of reaction was raised to 290°C the reaction product remained homogeneous but when the temperature was raised further the varnish gelled. It was further observed that the solubility of the resultant product gradually increased as the reaction proceeded and after 20 minutes the product became fully soluble in hydrocarbon solvents indicating completion of reaction between lac and oil. Chemical properties such as OH and COOH values of the resultant product also supported the above view.

The best performance was obtained when 60 grams of lac was reacted with 100 grams of linseed oil at 290°C for 20 minutes.

The detailed procedure for the preparation of lac-linseed oil varnish is described below.

In a three necked flask 200 gm. of double boiled linseed oil was heated with efficient stirring and the temperature was raised to 170°C. At this stage 6 gm litharge and 3 gm lime were added and the temperature was further raised to 250°C and the heating was continued for 10-15 minutes till a clear transparent liquid was obtained. The product was then cooled to 240°C and shellac (120 g) powder (40 mesh) was added in small lots. After completion of addition of shellac the temperature was quickly raised to 290°C when characteristic frothing was noticed and shellac went into solution giving a clear melt. The cooking was continued for 20 minutes for completion of reaction. The product was then cooled down to 170°C, thinned with white spirit (400 ml) and filtered. One percent cobalt naphthenate (on the weight of the varnish) was added to it as drier.

The effect of using different varieties of lac and oil in the above formulation was also studied. The varnishes so obtained were tested for their film properties. Standard methods of testing film properties as prescribed in ISS — 101/1964 were followed. The data are presented in Table II.

The performance of the lac-oil varnish obtained by the unmodified process[9] was also studied side by side. The results are given in Table II.

RESULTS AND DISCUSSIONS

The lac-oil varnishes obtained by the modified process were clear, transparent and pale yellow in colour. These varnishes showed very good drying characteristics and produced films which were hard, smooth, glossy and ffexible. These films did not show any persistant tackiness. Further the air dried films of these varnishes showed better hardness to scratch test and improved resistance to water. The best film performance was shown by the varnish based on double boiled linseed oil.

TABLE — 2 FILM PROPERTIES OF LAC-OIL VARNISHES

Properties	Varnish obtained by the un-modified process	Varnish obtained by the modified process	
		By using alkali refined linseed oil	By using doubled boiled linseed oil
Appearance of the film	Smooth, uniform but dull	Smooth, uniform & glossy	Smooth, uniform & glossy
Drying time			
i) Tack free time	Tackiness persists even after 70 hours of air drying	2.5-3 hours	2-2.5 hours
ii) Hard dry time	Does not arise	18 hours	14 hours
Hardness (Load in gram on 1 mm steel ball)	—	700	900
Flexibility (film bent over 1/8" mandrel)	—	Good	Good
Water resistance (film immersed in water for 24 hours)	Blushed in 30 minutes	Blushed in one hour	No blushing upto 24 hours
Resistance to white spirit	Poor	Poor	Good
Resistance to dilute acids	Good	Good	Good
Dielectric strength (of baked film)	1-3 KV/mil	1.7 KV/mil	2.2 KV/mil

Further improvement in the film properties was obtained when they were baked at 100°C for one hour or at 150°C for 30 minutes. Baked films were found to possess most of the desirable properties of baking type insulating varnish such as high dielectric strength, good flexibility, improved resistance to temperature and to the action of transformer oil.

Chemical reactions involved in the formation of lac-oil varnishes

The mechanism involved in incorporating lac in drying oils has been studied by a number of workers but the conclusions drawn by different workers vary widely.

In the preparation of lac-oil varnishes lead acts as glycerolysis agent[2]. In its presence the oil is hydrolysed into a mixture of mono, di and tri glycerides and some of the free fatty acids react with the litharge and form lead soap.

When lac is incorporated in the mixture of glycerides the following possibilities of chemical reaction between lac and mixed glycerides (mainly mono-glycerides) exist.

i) The OH group of the mono glyceride may react with the —COOH group of lac. Diglycerides do not react with lac[4].

ii) The OH group of monoglyceride may react with the OH group of lac.

iii) The free COOH of fatty acids liberated during hydrolysis may react with the OH of lac.

iv) A double dicomposition type of reaction between the mettalic soap (lead soap) and the COOH of lac may take place resulting in the formation of metal soap of lac and the free fatty acids.

In view of the fact that the reaction of lac and mixed glycerides completes in 20 minutes only esterification type of reaction, as envisaged above is possible. The other reactions which involve etherification or ether-interchange type of reactions are not possible in such a short time of reaction. But Bhattacharya and Gidvani[2] were of the view that mainly etherification type of reaction take place between OH of lac and OH of mono glycerides.

Y. Sankaranarayanan[6,8] who had studied the preparation of lac-oil varnishes was, however, of the view that since the metal soap of fatty acids, especially lead soap, acts as solubilizing agent for lac[10] in oil probably the lac resin is being peptised in the oil by the lead soap present there. In the present study also it has been observed that the reaction between lac and double boiled linseed oil completes in 20 minutes and that during the course of reaction no appreciable changes in acid and hydroxyl values of the reaction product take place indicating that none of the chemical reactions as envisaged above take place during formation of lac double boiled linseed oil varnish. The above observations support the findings of Y. Sankaranarayanan and show that the lac resin is most probably peptised in the oil in the presence of lead soap and that no major chemical changes take place in the molecule of lac resin during formation of lac-oil varnish.

Modification of lac-oil varnish with melamine resin

With a view to further improve upon the water resistance and the hardness of the film lac linseed oil varnishes obtained by the improved process were modified with different proportions of butylated melamine resin. Invariably clear and homogeneous solutions were obtained which produced hard, smooth, uniform and glossy films on various substrates such as tin, wood etc. Performance of both air dried as well as baked films of lac-oil M/F varnishes was studied. It was observed that the air dried films did not show any appreciable improvement in the performance but the baked films containing 20% melamine resin gave much better performance in respect of search hardness and resistance to water, acids, and hydrocarbon solvents. Baked films did not show any blushing in water upto 24 hours and gave scratch hardness of 1100 g. The data are given in Table III.

Lac-oil paints

Lac-oil varnishes obtained by the improved process as well as by using double boiled linseed oil were thereafter pigmented with titanium dioxide and coloured pigments etc. to produce oil paints of applied both by brush and spray to produce smooth, uniform and glossy films.

Performance of both air dried and baked films of these paints was also studied. Air dried films of the paint composition containing double boiled linseed oil was found to give better performance. These films did not show any blushing in water up to 24 hours and gave a scratch hardness of 1000 g. They also showed improved resistance to acids and solvents. The data are summarised in Table IV.

CONCLUSIONS

Lac-double boiled linseed oil varnishes are soluble in the usual varnish solvents like white spirit. These varnishes possess very good drying characteristics and produce air dried films which are hard, smooth, glossy and flexible. These films can also be baked to hasten drying and obtain improved performance. The use of these varnishes is indicated as vehicle for rapid drying enamels and anticor-

TABLE — 3
FILM PERFORMANCE OF LAC DOUBLE BOILED LINSEED OIL VARNISHES MODIFIED WITH MELAMINE RESIN (20%)

Properties	**Air dried films (air dried for 7 days)**	**Baked films (baked at 150°C for 30 mts.)**
Appearance of the film	Smooth, uniform and glossy	Smooth, uniform and glossy
Drying time		
i) Tack free	3-3.5 hours	30 mts. at 150°C or 60 mts. at 100°C
ii) Hard dry	18 hours	—do—
Hardness Load in grams on 1 mm steel ball	900	1100
Flexibility (film bent round 1/8" mandredl)	Good	Good
Water resistance (film immersed in water)	Blushed in 10 hours	No blushing upto 48 hours
Resistance to hydrocorbon solvents (white spirit)	Good	Good
Resistance to dilute acids	Good	Good
Resistance to dilute alkalies	Poor	Good

TABLE — 4
FILM PROPERTIES OF LAC-LINSEED OIL PAINTS

Properties	Paints prepared by using shellac-alkali refined linseed oil vehicle		Paints prepared by using shellac-double boiled linseed oil	
	Air dried films	Baked films	Air dried films	Baked films
Appearance of the film	Smooth, uniform & glossy	Smooth, uniform & glossy	Smooth, uniform & glossy	Smooth, uniform & glossy
Drying time				
i) Tack free	3 hours	—	1.2-2 hours	—
ii) Hard dry	18 hours	1 hour at 100°C	16 hours	1 hour at 100°C
Hardness (Load in grams on 1 mm steel ball)	800	1100	1000	1300
Flexibility (film bent round 1/8" mandrel)	Good	Good	Good	Good
Resistance to water (film immersed in water)	Poor	Good	Good	Good
Resistance to white spirit	Poor	Good	Good	Good
Resistance to dilute acids	Good	Good	Good	Good

rosive primers and as clear baking oil insulating varnish.

SUMMARY

An improved lac-linseed oil varnish has been prepared by reacting shellac with double boiled linseed oil in the ratio 60:100 at 290°C for 20 minutes in the presence of litharge as catalyst and lime as accelerator. This varnish possesses very good drying characteristics and produces hard, smooth, glossy and flexible films which show good resistance to water and aromatic hydrocarbon solvents. Baked films of this varnish possess high breakdown strength of the order of 2KV/mil and many other desirable properties of a baking type insulating varnish. This varnish in conjunction with hiding and tinting pigments produce decorative paints which can be used as general purpose paints for painting wood and metal articles.

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