Combinations of Lac and CNCL—Part II
Coating and Moulding Compositions

S. S. CHOPRA & Y. SANKARANARAYANAN
Indian Lac Research Institute, Namkum, Ranchi, Bihar

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S. S. CHOPRA & Y. SANKARANARAYANAN,

Indian Lac Research Institute,

Namkum, Ranchi, Bihar.

In the first paper of this series[1], a general review was presented of published literature on lac-CNSL compositions bringing out the versatile nature of these products and their possible uses in surface coatings, mouldings and laminations. It is proposed to present, in this paper, a connected account with brief experimental details of the study carried out at this Institute during recent years.

The work carried out here can be broadly classified into two categories in terms of the intended end uses, namely (i) for formulating insulating varnishes and (ii) for use as moulding material. However, some work has been carried out for formulating surface coatings also.

Insulating varnishes

As both lac and CNSL are noted for their electrical insulating properties, considerable attention was bestowed towards investigating the possibility of formulating insulating varnishes particularly analogous to the widely used oil-based baking type. Improvements were observed[2] in the electrical insulating properties and water resistance of the films from lac and CNSL varnishes, during preliminary investigation. The following procedure was evolved[3] for condensation of shellac with cashew shell oil and copolymerisation of the same with formaldehyde and urea in the presence of various acid and alkali catalysts.

Equal proportions of lac and CNSL were heated at 140-150°C for 2-3 hours and dissolved in a solvent, preferably n-butyl alcohol. To the solution, were then added 6-8% urea and 25-30% formalin (40%) on the weight of lac and the mixture heated under reflux on a water bath for 4-5 hours. The solution was then distilled in vacuum to remove the solvent, excess formaldehyde and water of reaction. The residual thick syrupy resin was finally dissolved in a solvent mixture containing equal parts of methylated spirit and toluene (or xylene).

Films of such varnishes, after baking at 120-130°C for one hour or at 100°C for three hours, were found to be glossy, hard and tough. They were unaffected by contact with water, 5% caustic soda, 5% sodium carbonate and 5% sulphuric acid solution for several days. It was also observed that by initially adjusting the proportions of lac and CNSL, varnishes could be formulated giving films with a wide range of hardness and flexibility — from highly flexible to very hard and brittle. However, their ageing properties were not satisfactory although their electrical properties were good. Therefore, the effect of adding small quantities of drying and non-drying oils was studied[4]. It was found that by heating lac, CNSL and linseed oil (or castor oil) in the ratio of 2:2:1 at 230-260°C for about 30 minutes, a homogeneous melt was obtained, which was soluble in an equal quantity of solvent naphtha or toluene. This solution, on further treatment with formalin and urea, gave a varnish, films of which were quite water-resistant after baking for 2-3 hours at 90-93°C. However, the varnish still did not pass the accelerated ageing test (IS 350: 1952). Attempts were then made to improve the flexibility still further either by reducing the amount of urea, or by incorporating plasticizers like castor oil, fatty acids, hydrolysed lac and fusel oil esters of lac, but without success.

It was then observed[5] that by initially combining CNSL with 30 per cent of its weight of mono- and di-glycerides of linseed oil and then treating the resultant product with lac at 190-200°C for 20 minutes and further condensing with the requisite proportions of formalin and urea, varnishes could be obtained which passed the ageing test (100 hours at 100°C) although the films turned dark brown during the test.

The investigations were then continued using, linseed oil itself in the medium instead of butyl alcohol, fusel oil etc[6]. CNSL (100 gms) was first heated at 130-140°C for 15-20 minutes to remove moisture. Then dewaxed lac (30 gms) was gradually added under efficient mechanical stirring. When the addition was complete, the temperature was quickly raised to 250-260°C and maintained for 30 minutes. Immediately thereafter, double boiled linseed oil, separately heated to 250°C, was added and the heating continued for a further 10-15 minutes. The product was finally cooled to 100-120°C and thinned with 300 cc of solvent naphtha and 2 g. of cobalt naphthenate was incorporated as drier. A control varnish was also made using CNSL and linseed oil only for comparing the film properties. It was found (vide table 1) that incorporation of lac reduces the drying time and improves the hardness although not to a substantial extent. The use of larger proportions of shellac was therefore indicated.

In order to facilitate this study, different mixtures of lac and CNSL could be heated together at the usual cooking temperature, viz. 250-260°C without gelation, was determined. In the light of the data obtained (table II), the above procedure was modified[7]. 50 g. of lac were added to 100 g. of CNSL at 180-200°C, and to the product 100 g. of linseed were added (preheated to 200°C). When the temperature reached 220-230°C, the lac polymerized and separated as a lump. This mass, however, gradually went into solution when the temperature was raised to 270-280°C, and maintained for 15 minutes. After cooling down to 140-150°C, it could be thinned with white spirit and necessary drier (2 g. cobalt naphthenate) incorporated. Films of this varnish were perfectly water-resistant and possessed good elasticity and adhesion to copper, tin and other metal surfaces. Other properties, however, had not been studied.

TABLE II.

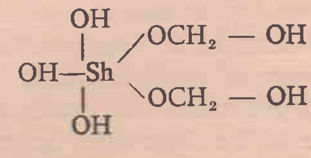
Polymerisation time, at 250-260°C, of mixtures of Kusmi, shellac and CNSL.

Sl. No.	Parts of Kusmi shellac per 100 parts CNSL	Time of polymerisation — Minutes
1.	30	75
2.	40	50
3.	50	30-35
4.	60	30-32
5.	70	25-28

The work was taken up (by the authors) to evolve a suitable formulation. Preliminary experiments indicated that raw CNSL or "pre-treated oil" did not give clear varnishes; so, for the present study, only fully treated CNSL, free from sulphur and other metallic impurities, obtained from a supplier of repute, was used. A series of varnishes were prepared using different proportions of dewaxed shellac, fully treated CNSL and raw and boiled linseed oil and linseed stand oil. It was seen (vide table III) that although these varnishes conformed to all the requirements for clear baking oil insulating varnishes, their electrical strength was just about the minimum, indicating the need for further modification.

Modification with aldehydes:

Shellac forms a formal by interaction with formaldehyde, and the formal has the property of being more plastic than shellac and a slower polymerisation rate under heat[8]. This material having the reported structure of



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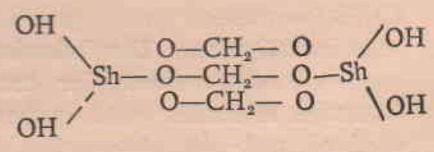

has made it possible to bring about condensation of shellac with phenols, the resulting resins having certain good characteristics, both for varnishes and plastic moulding compositions. Modification of shellac — CNSL — linseed oil varnishes were therefore tried by condensation with formaldehyde and paraformaldehyde under different conditions as follows:

(1) 150 g. of shellac was reacted with 45, 30, 22 and 15 g. of paraformaldehyde at 125°C for 3 hrs. 75 g. portions of the products were added to 100 g. of CNSL at 120°C. The mass became gell-like which became somewhat clear on adding 60 g. linseed oil. But adequate

TABLE I.

Effect of using lac in CNSL — linseed oil varnishes.

Sl. No.	Composition		Drying time Hours	Nature of the film	Effect of water (7 days immersion.)	Scratch hardness after one week air drying - g.
1.	CNSL dewaxed lac linseed oil	100 30 100	18	Smooth, glossy and non-tacky.	No effect	600
2.	CNSL dewaxed lac linseed oil	100 40 100	18	-do-	-do-	700
3.	Control CNSL linseed oil	 100 100	24	Smooth, less glossy and slightly tacky.	-do-	500

TABLE III

Properties of lac — CNSL — drying oil insulating varnishes (with 0.05% cobalt naphthenate as drier)

S. no.	Composition				Properties of the varnish			Properties of the films			
			Drying oil								
	Lac	CNSL	Oil	Quantity	Appearance	Viscosity at 25°C — Stokes	Drying time at 100°C — hours	Ageing test*	Acidity or alkability pH of film*	Resistance to oil*	Breakdown voltage at 90°C* volts/mil.
1.	10	100	Linseed oil	100.0	Bright & clean	1.4	3-4	Passes	5.0	good	865-980
2.	50	100	D. B. oil linseed	100.0	Clear	1.2	2-3	Passes	4.6	good	875-960
3.	50	100	Linseed stand	100.0	Clear	2.0	2	Fails	4.7	fair	900-990
4.	50	100	D.B. oil stand oil	50 50	Clear	1.5	1-2	Fails	4.7	good	905-950
5.	50	100	D.B. oil	50	Clear	2.5	2	Passes marginally	5.0	good	980-950
6.	75	100	Linseed oil	75.0	Clear	2.1	2	Passes	4.8	good	1120
7.	75	100	DCO	75.0	The mass gelled			—	—	—	—
8.	75	100	DCO linseed oil	37.5 37.5	Not clear	6.2	6	—	5.0	—	—
9.	100	150	Linseed oil	200.0	Not clear	3.5	5-6	Passes	4.9	poor	1039
10.	40	100		100.0	Clear	1.3	3-4	Passes	4.7	good	870

* All these tests were carried out according to Indian Standard Specifications (IS:350-1952).

clarity could not be obtained despite further heating.

(2) CNSL, lac and formaldehyde were then simultaneously condensed in the presence of linseed oil. The varnish obtained was not clear and was full of specks.

(3) A condensate of CNSL and formaldehyde was prepared[9] by heating CNSL with 10% of its weight of formaldehyde and 2 per cent liquor ammonia in a round bottom flask at 80°C for 30 minutes, removing water under reduced pressure next morning and then incorporating shellac and linseed oil with this condensate. Even under these conditions, a clear varnish could not be obtained.

(4) Lac — CNSL — linseed oil varnish as mentioned earlier was first prepared and then treated with 10 per cent of its weight of formaldehyde and heated on a boiling water bath with stirring for 30 minutes, to remove water. A clear varnish was obtained with improved water-resistance.

Based on these findings, the following procedure was standardised.

Shellac (72 gms), CNSL (200 gms) and formaldehyde (40% 40 gms) were reacted over a water bath at 90°C for one hour. Glycerine (40 gms) was added at this stage, followed by (200 gms of) previously heated double boiled linseed oil. Reaction was completed by maintaining at 280°C for 30 minutes. After addition of driers and white spirit at 150°C, the varnish was filtered.

The properties of this varnish together with, for comparison, those of other compositions studied earlier by previous investigators[12], are indicated in table IV. It will be seen that this varnish is superior to all shellac — CNSL insulating varnishes prepared earlier in all respects including the ageing test (100 hours at 100°C) and also conforms to the Indian Standard Specifications for clear baking oil insulating varnishes (IS:350/1952).

Mouldings

The second end use for which shellac — CNSL combinations have been investigated is in mouldings. During these studies it was noted[2, 3] that CNSL improves the flow of the moulding powders and water resistance of the moulded articles. Conditions for combining lac and CNSL and further modification with formaldehyde and urea were studied. Partially polymerised CNSL, (made by heating the oil at 300°C for 15-20 minutes), could be combined in quantities upto 25-30% (on the weight of lac) during the preparation to lac-formaldehyde urea moulding powder (by boiling the ingredients under reflux for 2-3 hours) to produce moulded articles of superior finish. It was found that addition of CNSL also allowed more time

TABLE IV

Electrical properties of lac — CNSL — insulating varnishes.

Sl. No.	Proportion of constitutents: Dewaxed Shellac g.	CNSL g	Formaldehyde cc	Para-formal-dehyde g.	Urea g.	Others: Material	Others: Quantity g.	Thinner: Material	Thinner: Quantity	Electric strength. Break down voltage — volts/mil, at 90°C	At room temperature after conditioning in an atmosphere of saturated humidity for 24 hours
1.	50	50	—	6	4	—	—	n-butyl alcohol	100	1290 — 1480*	670-810
2.	50	50	—	5	2	—	—	-do-	50	460 — 530*	440-530
3.	150	100	40	—	12	—	—	-do-	100	920 — 1160*	633-666
4.	70	100	40	—	4	Asphalt	30	Fusel oil fraction	300	610 — 750*	420-490
5.	50	50	20	—	6	—	—	n-butyl alcohol	50	700 — 750*	500-690
6.	50	100	—	—	—	Linseed	100	White spirit		865 — 980 (for 7 mil film)	535-656
7.	72	200	40	—	—	D.B. linseed oil Gycerine	200 40	White spirit	360	1140 — 1280 (for 6.8-7.0 mil film)	600-660

* Film thickness not specified

for mixing the ingredients on the rollers wherever necessary. When lac and CNSL were reacted for the above at 120-130°C instead of 170-180°C, the resulting compositions were softer. It was shown[4] that a workable moulding powder could be prepared under the following conditions.

Commercial CNSL was heat polymerised at 300°C for 10-15 minutes. 3 lbs. of (kiri) lac were mixed on hot rollers for about half an hour with 25-30 per cent of this CNSL in the presence of 2 per cent hexamine as catalyst. A resinous composition was obtained which was mixed with half its weight of alcohol along with the requisite proportions of formalin, urea, fillers, lubricants, pigments, etc. The mixture was then transferred, to a steam heated kneader provided with refluxing arrangement and heated for 3-4 hours. The composition was then hot rolled till uniform sheets were obtained. The sheets were cooled, powdered to 60 mesh and dried for 1-2 hours before moulding. A typical moulding composition made as above using **haldu** saw dust as filler had the following properties.

Impact strength — 4.6-5 cm. kg/cm².

Heat resistance — 70-75°C (Martens).

Water absorption — 0.8-1 per cent.

These compositions had satis factory flow and finish but th curing time (2.5-3.5 minutes) wa however, somewhat high and th articles at the time of ejectio were softer compared with bake lite. To get improved strengt **haldu** saw dust could be replace upto 25% by paper pulp, cotto linters or jute waste.

Lac — CNSL — sulphur combinations

Incorporation of sulphur into these compositions was also found to be of advantage[6]. When CNSL was heated with 10-20% of sulphur at 200°-205°C, a thick viscous resin was obtained with evolution of hydrogen sulphide. When this viscous resin was further combined with an equal proportion of lac, a soft rubbery material was obtained which, when mixed on hot rollers with fillers like asbestos and suitable proportions of zinc oxide, hexamine, stearic acid, etc., gave a plastic composition which could be moulded hot or cold depending upon the proportions of the different ingredients used, temperature and duration of the reaction. In a typical experiment, using fine asbestos as filler, the composition could be moulded at 140°-145°C and removed at the same temperature with good gloss and finish. The water obsorption of the finished articles (on 24 hours immersion) was found to be as low as 0.38%; the impact strength was, however, low being of the order of 2.3-2.66 cm. kg/cm².

Moulding compositions containing lac, CNSL and casein

A typical composition[4] was prepared under the following conditions. CNSL (450 gms) and shellac (1,500 gms) were dissolved in water (3,000 c.c) containing ammonia (sp. gr. 0.9, 210 c.c.) by heating on a water-bath. Into the resulting solution was well stirred 450 c.c. furfural and 45 gms. aluminium stearate. Casein (180 gms) was soaked in water (500 cc) and then warmed to 60°C and finally dissolved by adding ammonia (30 c.c). The two solutions were then mixed and stirred well. Lime (15 gms) dispersed in water was then mixed to the above mixture and well stirred. The resulting product was then mixed with **haldu** saw-dust (1,500 gms) and pigment (100 gms) and kneaded well in a kneader. After leaving overnight at 40-50°C, it was hot rolled, powdered to 60-mesh and dried for 2 hours at 90-95°C.

The product could be moulded at 130-140°C under 1-1.5 tons per sq. in. pressure. The moulded articles possessed good gloss and strength; water resistance was improved after curing the samples at 100-105°C for 24 hours.

The above lac — CNSL — casein composition was also found to be suitable for impregnating jute felt, hessian, cloth and other fabrics which afterwards could be moulded into bowls, dishes, trays, etc. of great strength.

SURFACE COATINGS

(i) Lac — CNSL — furfural combinations.

Interesting results have been obtained[3] by combining lac with furfural in the presence of acid catalysts. Equal proportions of lac and furfural form a homogeneous solution on heating for 2 hours on a water bath. If this is dissolved in alcohol containing hydrochloric acid (1-2 per cent), a thick black resinous solution is formed which quickly polymerises to a soft non-tacky insoluble product. If, on the other hand, the solution is immediately thinned with butyl alcohol and spread over glass, a black glossy hard film is obtained, which, however, is not water-resistant. If the same reaction is carried out with lac-CNSL combination, a black varnish is obtained which when applied to metal sheets gives a glossy film with improved water-resistance, adhesion and elasticity.

(ii) Hot-dip coatings for hessian.

When lac is added to an equal amount of CNSL previously heated to 120°C for one hour, and the heating continued for 2-3 hours at this temperature, a resinous product is obtained, which in molten condition can be applied on hessian. From the experiments carried out at the laboratories of Shellac Export Promotion Council, it was found[10] that the shellac/CNSL coated gunny bags were fairly resistant to moderate concentration of acids, alkalies and salts and suitable for the packing of commodities containing some free acid or alkali. Typical properties[11] of hessian coated with this material are summarised below :-

(1) Strength measurements : expressed as lb/inch. width, shellac coated 11 oz. sample of hessian).

Machine direction	84 lbs.	71 lbs
Cross direction	96 lbs.	88 lbs.

(2) Bleeding resistance : (T.A.P.-P.I. test). Slight bleeding at 40°C and progressive increase with temperature and becomes very severe at 80°C.

(3) Water proofness test (cone test and cobb test). Satisfactory — in regions free from pinholes.

(4) Coating or coverage weight value varies from 281 gms/sq. meter to 625 gms/sq. meter depending on the sample.

(5) The coating is impermeable to insects such as (i) Tribolium (ii) Calendra (iii) Rhizopartha.

(6) Under accelerated conditions of storage 100 degrees F and 92% R.H. the experimental bags showed no signs of deterioration of the product even at the end of 2 months.

In a solvent such as alcohol, this composition can be applied[11] by brush, roller or spray. Packing materials can be made waterproof, and resistant to chemicals, acid and even dust-proof.

The coated gunny bags, however, on trial, were found to have

TABLE V.

Summary of experiments on hot-dip coatings from lac, CNSL and drying oils

Sl. No.	Procedure followed	Observation	Performance on hessian
1.	Heated CNSL at 180°-5°C and added an equal weight of lac.	Gelled within 20 minutes, no change even on adding stand oil.	—
2.	Heated CNSL (200 gm) at 170°C, added (200 gms) lac, heated to 200°C and added 100 gms linseed stand oil.	The mass gelled, which did not become clear even on further heating at 280°C.	—
3.	Heated lac (200 gms), CNSL (200 gms) and linseed stand oil (50 gms), at 180°C for 25 mins.	The mass gelled.	—
4.	CNSL (200 gms) was polymerised at 280°C using cobalt acetate (4 gms) as catalyst. Incorporated lac (200 gms) at 180°C.	No gelling.	The composition dried hard in 15 minutes at 100°C, and air dried in 30-40 minutes, but the coating was brittle.
5.	Heated CNSL (200 gms) at 180°C, after adding lead naphthenate 4 gms., continued heating to 280-300°C, and maintained for 20 minutes, added lac (200 gms) at 180°C and maintained the temperature for 15 minutes.	-do-	The composition dried hard in 30 minutes, and was flexible, but failed in "bleeding test".
6.	The CNSL (200 gms) was partially polymerised by heating for 90 minutes at 280°C. Lac (200 gms) and linseed stand oil (50 gms) were added at 220°C, and kept for 30 minutes.	-do-	The composition gave a tacky film on hessian.
7.	CNSL (200 gms) and linseed stand oil (40 gms) were together at 280°C for one hour, lowered to 180°C and added 160 gms of shellac. After 15 minutes the product was cooled.	-do-	The coating on hessian was slightly tacky.
8.	CNSL (100 gms) and linseed stand oil (150 gms) were heated at 260-280°C for 6 hours. Lac (100 gms) was then added at 150°C to this viscous mass.	-do-	The baked coating (80°C/20 minutes) was hard and flexible and conformed to the requirements of specifications although the air-dried coating was not satisfactory.

the drawback of tackiness. Experiments were conducted to study the reaction of lac and CNSL at temperatures varying from 150-200°C, using "fully treated" CNSL and polymerised CNSL. It was possible to get hard films thereby, but mechanical strength of hessian suffered, as the coating did not have sufficient elasticity. To make the coating both hard and elastic, many experiments to incorporate linseed stand oil in the composition were made as shown in Table V. It was observed that CNSL partially polymerised, with stand oil gives with shellac a hard and plastic composition on hessian, which passes the above mentioned tests on water resistance and bleeding resistance etc. Strength measurements and packing trials could not be carried out for want of facilities.

Shellac and CNSL are thus complementary materials capable of producing a variety of products of considerable industrial importance, particularly in the fields of surface coatings and plastics.

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