SOME ASPECTS OF CNSL VARNISH

by

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Indian Patent No. 60166 describes the preparation of a stoving varnish based on Cashew Nut Shell Liquid (CNSL). Essentially the process consists decarboxylating the commercial CNSL at 160°—170°C and then heat polymerising the material at 315°C. 0·75% W/W litharge is then incorporated at 315°C, 1% manganese resinate at 260°C and lead linoleate dissolved in the minimum quantity of turpentine at 160°C. The varnish base thus obtained is then thinned with an equal weight of turpentine.

Results of examination of the CNSL used for making a batch of the varnish as per specn. I. S. 840-1956, the varnish base and the varnish as per Specification ISI 197-1952 and 344-1952 are given in Tables 1 and 2. The present report contains the results of some physical and chemical examinations of the varnish base.

The viscosity of the varnish base at 30°C at different shear rates ranging from 0·1 sec^{-1} to 10 sec^{-1} was determined by a Brookfield Synchrolectric Viscometer. No evidence of thixotropy or any other anomalous behaviour was noted and an average viscosity of $13·9 \pm 0·2$ poises was obtained.

The behaviour of the varnish base when heated at 145°C (The stoving temperature) under anaerobic conditions was then noted by determining its viscosity at the above temperature in a protected Ostwald Viscometer No. 4 under an atmosphere of nitrogen. The results are given in Table 3 and Fig. 1.

It will be seen from the above results that at 145°C the viscosity remains unchanged for about 10 mins. It was therefore, considered that it would be possible to determine the variation of viscosity of the varnish base with temperature provided the determination is carried out quickly enough after the specific temperature has been attained, of course a fresh sample of the base has to be used every time. The results of such determination are given in Table 4. All the viscosities except those at 30°C and 50°C were determined with a protected No. 4 Ostwald Viscometer and the last two with a Brookfield Synchrolectric viscometer. Fig. 2 gives a plot of $l_n\ \eta$ against $\frac{1}{T}$. It will be seen that the viscosity-temperature relationship within the region studied obeys the Andrade type Equation (1)

$$\eta = \exp\left(\frac{6260}{RT} - 7·26\right)$$

where η=Viscosity in poises

R=Gas constant

T=Absolute temperature

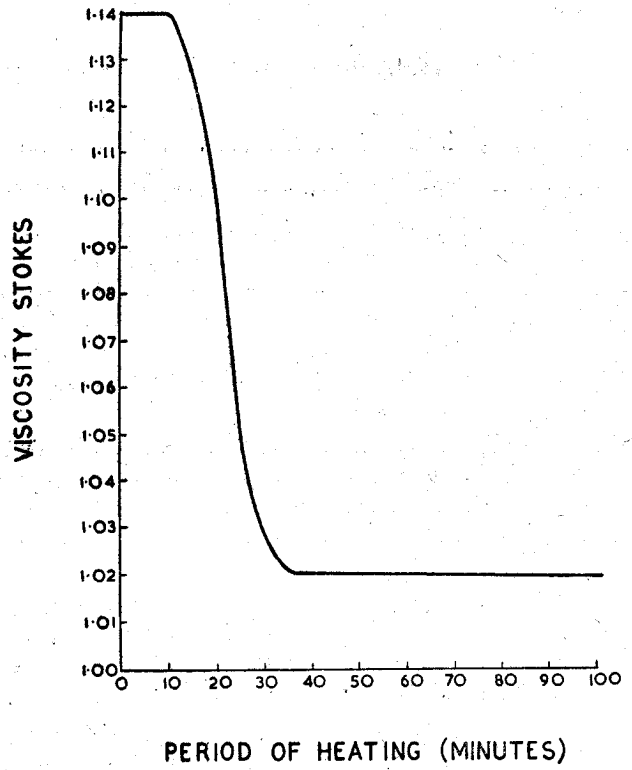

FIG. 1. Change in Viscosity of Varnish at 145°C under anaerobic heating

The changes occurring in the varnish base during stoving were then studied by spreading 0·50 gm of the varnish base on aluminium dishes 6·25 cm. dia. The loss in weight and change in iodine value during stoving were then determined after stoving the air-dried films at 145°C for different periods in a current of dry CO_2 free air. The results are given in table 5 and plotted graphically in Fig. 3. The iodine value of the film could not be determined after 35 minutes heating as the material became insoluble in carbon tetrachloride. H_2O and CO_2 were found to be liberated during stoving.

Discussion

Very little information is available in literature on drying of CNSL varnish of the type under consideration. From the slight change in hyroxyl value of the varnish base from that of the original CNSL (Table 2) it is suspected that the hydroxyl group plays no major part during condensation.

From Fig. 1, it will be seen that when the varnish base is heated at 145°C. (The baking temperature) under anaerobic conditions, the viscosity starts to fall after about 10 mins. After it has fallen by about 10% in 25 mins there is neither any further fall in viscosity nor any sign of gelation or thickening. This indicated oxygen is essential for hardening of the film.

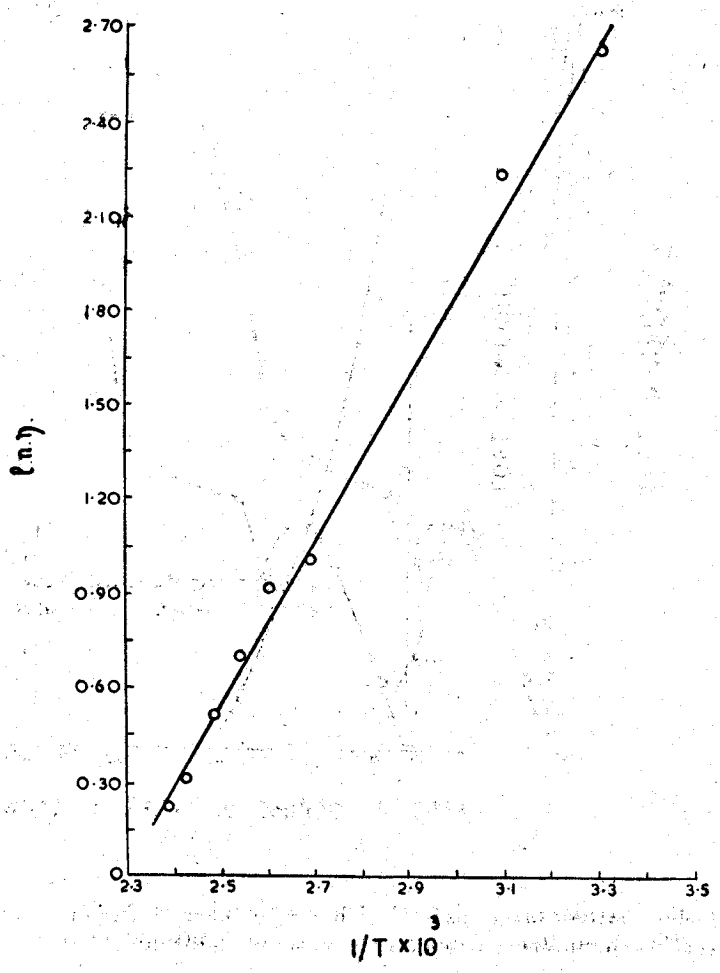

FIG 2. Variation of Viscosity with temperature

The fact, that the viscosity under anaerobic condition follows an Andrade type (1) Equation before any decomposition (as evidenced by fall in viscosity) commences, indicates that the molecules of the varnish base are not of the associated type. This is further corroborated by the work of cohesion, which calculated by the method of Grunberg and Nissan (2) comes to about 5,500 cals/mole. It will be seen that this is only 12% less than the viscosity energy of 6,260 cals/mole given by the Andrade equation. According to Grunberg and Nissan the difference should be more than 30%.

The changes under baking condition are very complex. From Table 5 and Fig. 3 it will be seen that the iodine value falls to about 26% of its original value within 35 mins of heating. The rate of fall in iodine value is of the unimolecular order with a rate constant of 0·0360 $_{m}\bar{n}^{1}$. As it is improbable that any condensation reaction will be of the unimolecular order, it is considered that the

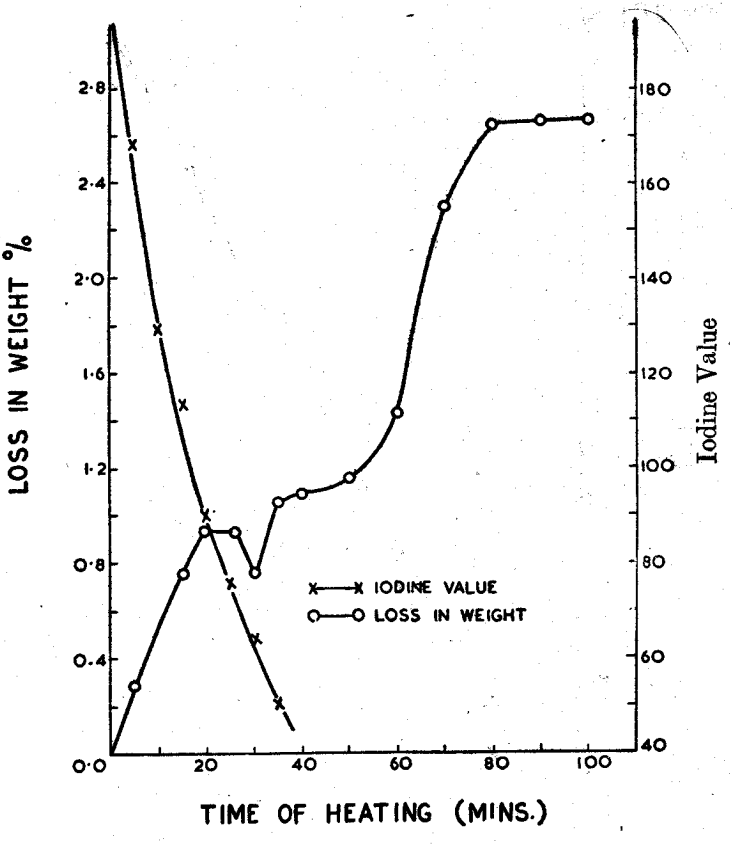

FIG. 3.

rate of fall in iodine value is controlled by the rate of diffusion of oxygen at the interfacial boundary between the film and atmosphere.

The loss in weight is still more difficult to follow. Any change in the weight of the varnish film will be due to the following factors—

(*i*) Loss in weight due to loss of any volatile matter that might be present.

(*ii*) Loss in weight due to the escape of CO_2 and H_2O which have been found to be liberated during stoving.

(*iii*) Gain in weight due to the absorption of oxygen.

It will be seen from Fig. 3 that the rate of process (*iii*) has exceeded those of (*i*) and (*ii*) after 20 minutes heating and there is an actual gain in weight between 25 and 30 mins of heating. After that the loss in weight increases continuously till 80 mins after which no more loss occurs. It is noteworthy that though the baked film becomes insoluble in carbon tetra chloride after 35 mins heating, it does not become tackfree till after 80 mins heating *i.e.*, till the weight has become constant.

Acknowledgement

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References

(1) *Nature*, 125, 1930, p 580.

(2) *Nature*, 154, 1944, p 146.

TABLE 1

Results of examination of CNSL varnish made according to Indian Patent No. 60166 as per specifications IS 197-1952 and 344-1952

Test	Specn. Limits	Sample
1. Hard drying time	1 hr at 98°C 1/2 hr at 150°C	90 mins at 145°C
2. Finish	Smooth and glossy	Smooth and glossy
3. Scratch hardness	No such scratch as to show bare metal	No scratch
4. Flexibility and adhesion	No visible damage or detachment of film	No damage or detachment
5. Stripping test	Scratches free from jagged edges.	Passes specn.
6. Corrosion resistance at 42°C to 48°C and 100% R. H. with continuous condensation of moisture	..	No breakdown of film and no sign of corrosion for 500 hours exposure.
7. Flash point	35°C (min)	35°C
8. Viscosity at 30°C	..	75 cps.
9. Acid value	25 (max)	4-5
10. Keeping properties	Not less than 1 year	Not less than one year

TABLE 2

Results of Examination of CNSL and the Varnish Base as per I. S. Specification No. 840-1956

Test	Specn. limit	CNSL	Varnish base
1. Sp. Gr. 30°/30°C	0·940 0·960	0·957	0·985
2. Viscosity at 30°C cps	550 (Max.)	187	1300—1400
3. Surface tension at 30°C dynes/cm. ..	..	35·0	34·7
4. Matter insoluble in toluene% ..	1 (max)	0·03	0·017
*5. Volatile matter other than moisture % ..	1 (max)	0·84	..
6. Polymerisation—			
(*i*) Time in mins	19 (max)	2	..
(*ii*) Centipoises	30 (min)	180	..
7. Iodine value	220 (min)	256	190
8. Acid value	..	16·3	9·4
9. Hydroxyl%	..	6·19	5·74
10. Molecular weight (Freezing point in nitro benzene)	..	557	683

* The I.S.I. method which requires heating for 4 hours at 205±5°C gives a loss of more than 30% with all the samples of commercial CNSL examined. No CNSL could be obtained which passes the ISI requirement of a maximum loss of 1% under these conditions. The results reported were obtained by the method given in Irvington specification P 400-3.

TABLE 3

Variation of viscosity with period of heating at 145°C under anaerobic conditions

Time (mins)	Viscosity (stokes)
0	1·14
5	1·14
10	1·14
15	1·10
20	1·05
25	1·03
30	1·02
45	1·02
60	1·02
75	1·02
90	1·02
100	1·02

TABLE 4

Variation of viscosity and Density of Varnish base with Temperature under Anaerobic conditions

Temp O°C	Density gms/cc	Viscosity (Poises)
30	0·985	13·9
50	0·971	9·40
100	0·936	3·03
110	0·929	2·50
120	0·922	2·03
130	0·915	1·67
140	0·908	1·37
145	0·903	1·26

TABLE 5

Loss in weight and change in Iodine Value when a Film of the Varnish Base was heated at 145°C in a Current of Air

Time (mins)	Loss in weight %	Iodine value
0	..	190
5	0·31	166
10	0·66	129
15	0·76	113
20	0·95	90
25	0·94	76
30	0·76	64
35	1 06	50
40	1·09	
50	1·16	
60	1·43	Further iodine value not recorded as the material becomes insoluble in CCl_4.
70	2·31	
80	2·65	
90	2·67	
100	2·67	