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Decorative Wood Varnishes from Limed-Cashew Nut Shell Liquid Product

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Abstract

Cashew nut shell liquid (CNSL) was recovered from cashew nut shells obtained from Ihube–Okigwe, Abia State by solvent extraction. The CNSL was treated with calcium hydroxide at ambient and elevated temperatures to produce limed-CNSL products. The products were characterized and used to formulate oleoresinous varnishes using blown linseed oil, soybean and soybean-linseed alkyds as the oil bases.

Results showed that the drying performances of the varnishes were moderate and they showed high gloss. The resistance of the varnishes prepared with different alkyd resins to water and acid media was very good, fair for base medium, and generally comparable to that of commercial products. The drying property of both the product with and without driers is discussed.

1. Introduction

Varnishes are unpigmented colloidal dispersion or solution of synthetic and/or natural resins in oils and/or thinners used as a protective and/or decorative coating for various surfaces such as wood and which dry by evaporation, oxidation and polymerisation of portions of its constituents[1]. They are less resistant to damage by light (since they are unpigmented) than are paints, enamels and lacquers; however, they furnish a transparent film, which accentuates the texture of the surface coated. Liquid from the shells of the cashew nut, once an undesirable by-product of the cashew kernel industry, has become a valuable raw material in the manufacture of numerous industrial products. The oil cells of the cashew nut shell are honeycombed and prevent ready removal of a kernel. Polymerization products of this oil, alone and in combination with other materials, have found their way into such diverse uses as insulating varnishes, typewriter rolls, oil- and acid proof cold-setting cements, industrial floor tiles, and automobile brake linings[2]. Processability characteristics and physico-mechanical properties of natural rubber modified with cashew nut shell liquid formaldehyde resins was reported by Menon et al.[3]. Also, products ranging from coir dust extract-CNSL modified wood finishes[4], CNSL modified peanut skin tannin wood adhesives[5] and red onion skin extract-CNSL plywood adhesives[6] have been reported.

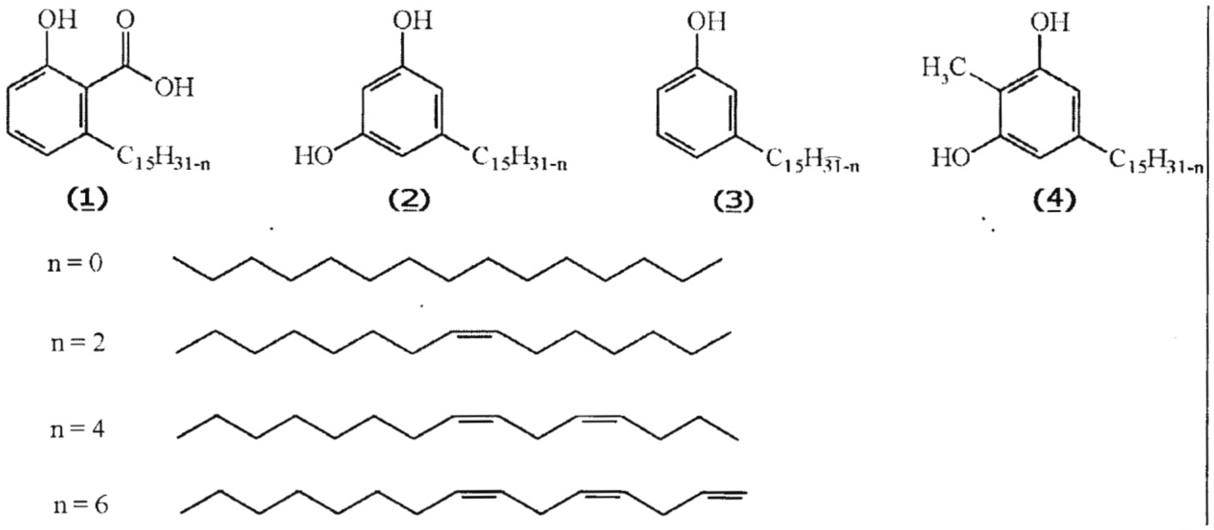
Varnishes formulated from cashew nut shell liquid based resins are resistant to acids and alkalis and possess unusual resistance to the softening action of mineral oils and find its uses in the coating of wood, paper for bottle cap liners and for many other water-proofing and insulating purposes[7]. A thermal polymerization car coating[8] as well as polyCNSL high hardness and glossy film[9] and thermosetting resin[10] products from CNSL have also been reported.

CNSL is extracted from the spongy mesocarp of the nut shell and principally contains 90% anacardic acid and about 10% cardol with each containing four constituents with unsaturation at the 8'(mono-ene), 8',11'(di-ene) and 8',11' and 14' (tri-ene) positions[11-15]. The structures of the various components are shown in Scheme 1. The various components of Cashew Nut Shell Liquid have been assayed[16-19] and 2-methylcardol has also been isolated[20]. These constituents are given in Table 1. Anacardic acid is easily decarboxylated to cardanol or anacardol, a monovalent phenol during extraction involving the roasting process.

Table: Composition of Olefinic Constituents of Component Phenols in natural CNSL by Mass Spectrometry*

Phenol	Saturated	Monoene	Diene	Triene
Methyl anacardate	11.04±1.15	51.54±1.65	14.23±0.18	23.70±0.62
Cardol	1.41±0.11	9.95±0.56	23.93±0.11	64.74±0.51
Cardanol	7.79±0.6	46.03±1.25	20.19±0.41	25.99±0.41
2-Methylcardol	4.36±0.57	18.54±0.88	21.21±1.17	55.91±1.17

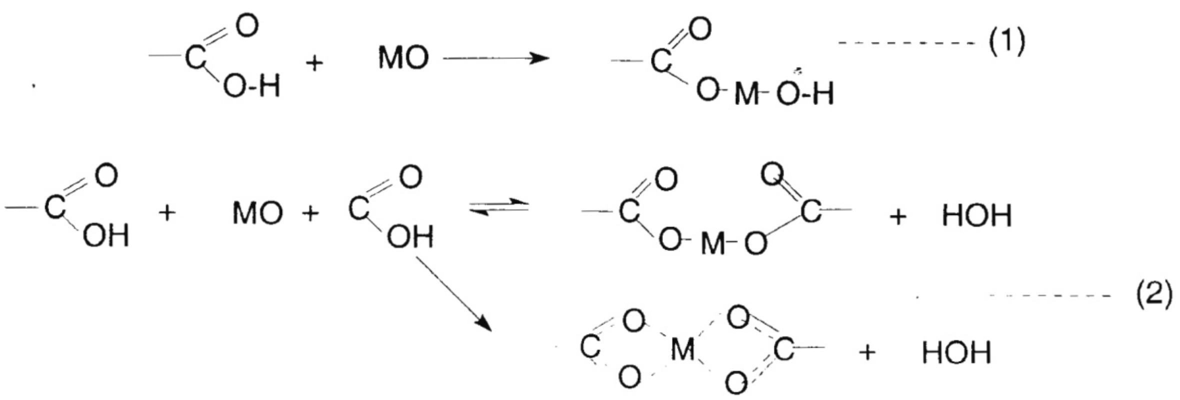
*% composition of natural product (uncorrected); Source: Ref. 14.



Scheme 1: Naturally occurring non-isoprenoid phenolic lipids from *Anacardium occidentale*. (1) = anacardic acid; (2) = cardols; (3) = cardanols; (4) = 2-methyl cardols.

CNSL undergoes the different reactions of phenol, carboxylic acid as well as unsaturated compounds. Unsaturated polyesters from diols and dicarboxylic acids containing free carboxyl groups form complex compounds (and are thus thickened) with some metal salts or ions acting as polychelating ligands. Also inorganic oxides and hydroxides belonging to the alkaline Group II of the Period Table[21] such as, magnesium oxide and hydroxide, calcium oxide and hydroxide and zinc oxide are used to thicken unsaturated polyesters.

Polyesters are known[20-21] to co-ordinate metal ions or metal compounds to their oxygen atoms through various kinds of bonds, some of which are shown in equations 1 and 2.



The purpose of this work is to ascertain whether CNSL can be thickened like the unsaturated polyesters of diols and dicarboxylic acids. It is also set to find out whether the introduction of the metallic radical, the type used in driers, into the CNSL moiety will confer drying property on the varnishes made from the metal complex and eliminate the use of driers like Lead and Cobalt naphthenates on the varnishes.

2. Experimental

Materials

Cashew nuts were procured from Ihube–Okigwe and were deshelled in our laboratory. Calcium hydroxide and zinc oxide are of technical grade. Modified alkyd resins were obtained from Nicil Resins, Enugu; Blown linseed oil was a product of Fullmount, England.

Methods

Extraction of CNSL

The cashew nut shells obtained after de-shelling were cut to smaller sizes (increased surface area) for ease of extraction. The extraction was done at two temperatures, 80±2°C and 120±2°C with a view to investigating the temperature effect on yield in extractions from shells using petroleum spirit as solvent in an apparatus adapted to serve as a Soxhlet extractor. A dark brown liquid was obtained after the removal of the solvent using rotary evaporator (BÜCHI, Switzerland).

Preparation of the Metal-CNSL Materials

2g of calcium hydroxide were mixed with 4ml of warm (50-55°C) water to give a white paste. 10g of CNSL was added into the beaker containing the white paste, mixed thoroughly and allowed to stand for 24h. The product was a brittle dark-brown solid which was pulverized and washed with acetone and petroleum spirit (to remove any excess CNSL) consecutively, and then filtered off.

In another set of experiment, 10g of CNSL was added into the beakers containing the white pastes, mixed thoroughly and the temperature of the system raised to 100 – 110°C as well as to 200 –210°C and the results recorded.

Solubility Test on the Limed- CNSL Product

Solubility in Solvents

About 0.6g of the brittle product was sequentially added to 5.0ml of the following solvents–toluene, xylene, acetone, dichloromethane, isobutyl acetate, n-hexane, ethanol and petroleum spirit - and the solubility determined[23-24] after shaking and placing the test tube (lightly covered) in a water bath at 70°C.

Solubility in Oils and Alkyd Resins

To 3g each of hot refined soybean, linseed and blown linseed oils as well as the soybean and soybean-linseed alkyd resins were added 1g of the metal complex in turn and stirred for 3 min. Two drops of the solutions were placed on a watch glass and the homogeneity of the solutions determined by the clear pill test.

Preparation of Varnishes

80ml of blown-linseed oil, soybean and soybean–linseed oil (1:1) alkyds were each measured into a 500ml beaker and in turn heated to 260°C. 1.8g of the limed CNSL was added in small increments at that temperature over a period of 60 minutes with continuous stirring. The beaker was each time cooled to about 60°C and 40ml of toluene added to thin it down to a brushable consistency. The varnishes prepared were filtered to remove undissolved resins and solid impurities and were labeled varnishes 1-3, respectively for blown linseed oil, soybean and soybean- linseed alkyds.

Characterization of the Varnishes

Drying Time

Various stages of drying were determined on the samples using standard methods[24] and these include dust dry, touch dry and hard dry times. The drying process is accelerated very considerably by the introduction of certain metals in the form of oil-soluble compounds or soaps. The catalytic activity of these metals is associated with their ability to exert more than one valency. Lead and cobalt naphthenates were used in this work.

Dust-Dry Time: This is the first stage of autoxidation. Several individual adsorbent cotton fibers were dropped on coated wood panel measuring 4cm x 8cm placed on a table, horizontally. The film was adjudged dust-dry when air gently blown across the fibers removed it from the coated panel.

Touch-Dry Time: The coated panel was touched with a fingertip and the time recorded when the film felt tack-free.

Hard-Dry Time: The thumb was pressed firmly on the film and rotated through an angle of at least 100degrees. The time was recorded when, for the first time, the film was not displaced or wrinkled.

Resistance to Water, Salt, Acid and Base

Tests for resistance of the varnishes in various media were carried out following the ASTM Method D-1647. The outer parts of test tubes measuring 15cm in length were coated with varnishes 1 to 3 by dipping and were inverted and supported on vertical pegs and allowed to dry at room temperature for 72h. The coated and dried test tubes were immersed and supported in beakers containing tap water, 5% sodium chloride solution, 0.1M HCl and 0.1M NaOH and were respectively allowed to stand for 20h. The whitening, blistering and removal of film effects of the different media on the three varnishes were recorded.

Gloss

This is the percent reflectance of a film at sixty degrees (60°). It was measured for the various varnishes coated on panels at an angle of 60° with a sheen gloss meter using an optical prism.

3. Results and Discussion

Extraction of CNSL

It was observed that at 80±2°C that the extraction took about 495min. (8.25h.), yielded about 23.2% CNSL and that at 120±2°C, the level of extraction, 25.6%, was achieved at 230min. (3.8h.). It is obvious then that percent yield increased with increase in extraction temperature. Too high a temperature, though will lead to complete decarboxylation of anacardic acid, the major component of CNSL, to cardanol making unavailable the carboxylic acid group in reactions designed to take place at the carboxylic moiety.

The direct relationship of yield with temperature is attributable to the increased ease of penetration of the shells by the energized solvent molecules as were reported for oil seed extraction[25-26]. This relationship, though, becomes less important at certain high temperatures[27].

Limed-CNSL Product Formation and Characterization

The product of the mixture involving $Ca(OH)_2$ and CNSL was a dark brown, brittle solid, an unpolymerized and unsaturated CNSL-metal complex. The attempt at making the metal complex at 100-110°C yielded a rubbery infusible and insoluble material while a charred product resulted at the higher temperature range of 200 - 210°C.

TABLE 2: Solubility of the Metal Complex in Different Media

Solvents	Codes	Oils/Alkyds	Codes
Acetone	IS	Refined Soyabean Oil	VS
Ethanol	IS	Refined Linseed Oil	VS
Isobutyl Acetate	SS	Blown Linseed Oil	VS
Petroleum Spirit	PS	Soybean Alkyd	VS
Toluene	PS	Soybean –Linseed Alkyd	VS
Xylene	PS		
n-Hexane	PS		
Dichloromethane	VS		

KEY: IS: Insoluble; SS: Sparingly soluble; PS: Partially soluble; VS: Very soluble

The solubility test on the limed-CNSL in various solvents is shown in Table 2. The fact that the product is soluble in hydrocarbon solvents mainly suggests that it is apolar in nature and as such is not soluble in polar solvents.

Characteristics of the Varnishes

Drying behavior

The drying times of the various varnishes in which one drop of drier mixture was added are shown in Table 3. Chemical process of drying involves the interaction of atmospheric oxygen with the resin molecules and is reduced to the minimum by the absence of catalysts (driers), and great cross-linking. Good drying times were reported by Anyaogu et al in the presence of 0.5% drier mix[28].

Table 3: Drying Property of the Varnishes

Property	Vanish 1	Varnish 2	Vanish 3
Dust Dry Time (min.)	127	141	165
Touch Dry Time (min.)	245	282	306
Hard Dry Time (min.)	1240	690	840

The dust and touch dry times increased from varnish 1 to 3. Soybean-linseed oil alkyd varnish with larger film thickness dried slower than soybean alkyd varnish. Thicker films dry more slowly, leading to a requirement of higher amount of cobalt driers; otherwise, a less densed crosslinked network will be formed[29].

The apparent long drying times of all the varnishes are not industrially very encouraging. Ikhuoria and Aigbodion reported set to touch time of 20-65s for refined rubber seed oil (RSO) phthalkyd and 40-65s for rubber seed oil methyl ester alkyd. They showed that blending of the RSO alkyds with phenol formaldehyde and nitrocellulose resins improved the drying behavior among other factors[30]. Singh[31] got the surface dry time of alkyd resins from deodourizer distillate as 90, 120 and 180 min., respectively for short, medium and long oil length alkyds and touch dry time of 720 min. for short oil alkyd and >1440 min. for hard dry time. Also, Nair et al described as satisfactory performance a report of surface dry after 24h., followed by a tack-free dry after 48h[32].

Experiment in the course of our work showed that the addition of 0.5% drier mix (lead and cobalt naphthenates) to the varnishes based on the weight of the varnishes reduced the drying times significantly as shown in Table 3. The drying rate of alkyd resins has been shown[33] to increase directly with the amount of drier employed. Since the action of drier metals does not cease when the film is dry but continues throughout the life of the film and so contributes to the ultimate embrittlement and breakdown[34], amounts in large excess of 0.5% are not encouraged. Again, due to environmental considerations, Pb catalysts are no longer used on an industrial scale[35].

Table 4: Drying (in 0.5% Drier Mix.) and Gloss Properties of the Varnishes*

Property	Vanish 1	Varnish 2	Vanish 3
Dust Dry Time (mins.)	27	43	61
Touch Dry Time (mins.)	35	49	71
Hard Dry Time (mins.)	242	206	305
Gloss* (%)	87	91	65

* The gloss for the commercial product was 72%.

Chemical Resistance

The three varnishes showed a high resistance to both pipe borne water (corroborating the work of Akaranta[3]) and sodium chloride solution, though a slight reduction in gloss was noticed for the latter as shown in Table 5. The resistance of the varnishes to 0.1M HCl followed the order Varnish 3 > Varnish 2 > Varnish 1, with respect to gloss reduction. None was washed off the test tube after the test. The same order was observed for alkali resistance.

Table 5: Chemical Resistance of Varnishes Prepared to Various Solvent Media*

Aqueous Media	Varnish 1	Varnish 2	Varnish 3	Commercial Varnish
Pipe-born water	5	5	5	5
5% NaCl	4	4	5	3
0.1M HCl	2	3	4	3
0.1M NaOH	1	2	2	1

* 5= not Affected; 4= reduction in gloss; 3= film shrinkage; 2=film blistering; film detachment

The varnishes generally showed a poor resistance to the alkali. This is not completely surprising, as poor alkali resistance[36] is characteristic of oils and oleoresinous materials[31,37,38]. This shortcoming of oleoresinous materials is being addressed by styrenation of oils[39] which can be done before varnish preparation.

Comparatively, a commercial wood varnish (Zeta Brand) obtained from a furniture maker was tested for its water, sodium chloride solution, alkali and acid resistance as well as gloss. It was observed that while it showed good resistance to water, its resistance to sodium chloride solution was inferior to that of the varnishes prepared in this work as shown in Table 5. It was also seen that the film detached completely from the test tube after 9h. during the alkali resistance test.

The gloss measurement conducted gave the gloss values shown in Table 3. This shows that the varnishes have good gloss. Even the least value of 65 for varnish 3 is adjudged good as commercial varnishes gives values between

50 and 72% [37], though Radicevic and Budinski-Simendic indicated a minimal acceptable level to be 80% [39]. The very high value observed for soybean oil alkyd relative to the soybean-linseed oil (1:1) alkyd may be due to higher degree of cross-linking in the former. High degree of cross-linking has been reported to eliminate surface irregularities and impart high gloss [4]

4. Conclusion

From this work it can be suggested that CNSL can be thickened like the unsaturated polyesters of diols and dicarboxylic acids. However, the introduction of the metal (calcium) into the CNSL moiety via complexation failed to confer drying properties to varnishes made from them. The varnishes prepared showed good promise for the furniture industry and could be another possible outlet for the cashew nut shell liquid from cashew tree, which we have in abundance in Nigeria and other countries.

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