

Quality of Oleoresinous Wood Varnish Prepared using Resin Synthesized from Tannin Extracted from Stem Bark of *Khaya senegalensis*

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ABSTRACT---- *Phenol is used as a starting material in the preparation of wood varnish. In this work efforts were made to substitute phenol from tannins extracted from the stem bark of Khaya senegalensis to produce wood varnish and assessed its quality. An extract with a Stiasny Number of 87.88 % and extractable phenols of 2.82 mg/kg was used to synthesize a phenol-formaldehyde called tannin-formaldehyde. Properties of this resin were compared with that of phenol-formaldehyde resin synthesized using a commercially available phenol following the same procedure. A yield of 89.82% for phenol-formaldehyde resins showed a good and efficient method of synthesizing the resins. The study indicated that tannin-formaldehyde resins had better solubility in linseed oil than phenol-formaldehyde resin. A dark-brown viscous resole-type phenolic resin was produced from tannin extract as against a yellow viscous resin for commercial phenol. the colour of the Subsequently, unfortified oleoresinous wood varnish (solutions of one or more natural or synthetic resins in a during oil and volatile solvent) of high gloss, good chemical resistance and good drying time paralleling each other were readily prepared from both resins. Varnish made from phenol-formaldehyde and tannin-formaldehyde resins had acid numbers of 9.9 mg KOH/g and 8.6 mg KOH/g varnish respectively: both falling within the 0.2-10.5 range for most satisfactorily commercial varnishes, this implies that tannin-formaldehyde resin is advantageous over phenol-formaldehyde resin since the source of tannins is cheaper and renewable as well as contributes to reduction in land pollution hence its production should be considered.*

Keywords--- *Khaya senegalensis*, Oleoresinous varnish, Phenol-formaldehyde resin, Tannin extract

1. INTRODUCTION

Many economies depend mostly on the petrochemical industry for the production of energy and raw materials for industry. Nevertheless, strong efforts are being made to replace fossil resources because of their limited satisfaction and the disadvantages of the fossil fuel derived products like their volatile prices and their harmful effect on the environment and humans [1]. Among the alternative solutions, biomass seems to be the most promising candidate; it offers both energy and a vast variety of chemical suitable for the synthesis of many materials and products. [1].

Logs in many cases have been underused (for furniture) mainly in the furniture industry. Little or no attention is given to the bark and is mostly burned in the open air resulting in air pollution. Furniture makers therefore resort to other products mainly from petrochemicals for polishing their product. Development and technology has informed the possibility of using the bark in making resins which in turn can be used to make varnishes which are relatively cheaper and simpler to polish furniture which are made from wood [2]. As a result, the interest in plants extracts is quickly growing. African mahogany (*Khaya senegalensis*) has been harvested from the Guinean rain forest of Ghana and other West African countries for over a century [3]. Mahogany is a major source of timber-derived revenue for Ghana and neighboring countries such as La Cote d'Ivoire [3, 4, 5].

Increasing demand for mahogany has led to severe reduction in natural stands in West African forest [3, 6, 7] This suggests that logs of mahogany tree are immensely used and the residual bark which is considered waste can be used to make industrial chemicals such as varnish to polish furniture made out of the logs. This in a way finds alternative

uses for the waste of the logs and thereby adding value to the wood. This will not only boost the economy by making an invaluable asset out of waste which hitherto was difficult to dispose, but also help in minimizing pollution.

Bark is the residue of wood processes with no suitable application previously. However, it has been found that stem bark of some tree species are rich in tannins which can be extracted and used as the raw materials in the manufacturing of phenolic adhesive and coatings. Papadopoulou and Chrissafis [1] compared a conventional phenol-formaldehyde resin, synthesized totally from petrochemical raw materials with an experimental phenol-formaldehyde resin with 20% phenol replacement from cashew nut shell liquid (CNSL) for their adhesion strength in plywood production. Wang et al [8] synthesized phenol-formaldehyde resole using organosolv pine lignins. Kumar and Setheraman [9] studied oleoresinous varnish and their natural precursors. Fechtal and Riedl [2] used spruce bark tannin and eucalyptus and *Acacia mollissima* bark extracts respectively to prepare synthetic resin in the manufacturing of particleboard and fiberboard.

The success of these researches were due to the fact that tannins which are polyphenolic obtained mainly from wood bark extracts can be substituted for commercial phenols at about one-third the cost in waterproof adhesive and coatings production. Although these extracts sometimes require the addition of some resins to obtain the desired shear strength.

In this work, the problem of obtaining a very strong networked resin is being circumvented by allowing a smaller time of reaction to permit only a weakly networked resin to form. This obviates the need to prepare the varnish via heating at temperatures above 230 °C which is difficult to attain and unfavorable to work with in the laboratory. The objective of this work was to prepare oleoresinous varnish using tannin-formaldehyde resin synthesized from tannin extract from the bark of *Khaya senegalensis*.

2. METHODOLOGY

3.1 Extraction and Modification of Tannins

Tannins were extracted from dried mahogany stem bark powdered sample using methanol in soxhlet extraction apparatus. For each extraction, 140 g of stem bark powder was used and 400 ml of 80% methanol solution was the extraction solvent. Extraction was carried out at a temperature of 80 °C for 18 hours. Ascorbic acid was then added after extraction to prevent oxidation of phenolics in tannin [10]. The methanol extract was centrifuged for 15 minutes at a speed of 3500 rpm using a Sanyo MSE MISTRAL 3000E SG/10/256, UK centrifuge. The supernatant was placed on a Petri-dish and heated on a steam bath to evaporate the solvent to obtain a more concentrated extract. The process was repeated several times to obtain enough extracts for the actual work.

The tannin extracts were modified by heating with distilled water and 20 mL of 5% NaOH solution in soxhlet apparatus. The reaction mixture was then refluxed at 90 °C for 1 hour. The pH of the reaction mixture was adjusted to 8 by adding about 3 mL of 5% NaOH solution. Subsequently the mixture was dehydrated and dried in an oven at 104 °C.

Qualitative test for tannins was carried out using 0.1 M ferric chloride solution and the Lieberman test. Determination of condensed tannins (proanthocyanidins), a type of tannins present in the extract was performed by using the method of Porter et al., [11] Here a butanol-HCl reagent and 2 % ferric reagent in 2 N HCl solution were added to a small amount of tannin extract in a tube and placed in a water bath at 100 °C for 60 minutes.

Reactivity of polyphenolic content in tannin towards formaldehyde (stiasny precipitation number) was ascertained as follows: 20 g of unmodified dehydrated extract was weighed into a beaker containing 40 mL of water. This solution was then adjusted to a pH of 7 by adding sodium hydroxide pellets in pinches. One hundred (100 mL) of 37% formalin and 15 mL of concentrated HCl were added and the mixture heated at 90 °C for 85 minutes. The resulting solution was vacuum filtered and the solid residue was washed with hot water, dehydrated and dried at a temperature of 105 °C in an oven and weighed. The Stiasny number was determined as follows:

$$\text{Stiasny precipitation number} = \frac{\text{dry weight of solid residue,}}{\text{dry weight of extracts,}} \times 100$$

The total phenol present in the extract was quantitatively determined by colometric assay using the Prussian blue reagent.

3.2 Preparation of Resin

Here 20.93 g of extract was dispensed into a 600 mL beaker and 40 mL of distilled water added to dissolve it upon stirring. Again 100 mL of 37% formaldehyde was added and the mixture stirred continuously till all the extract dissolved. The pH was adjusted to 10 by adding few NaOH pellets a temperature of 90 °C. The reaction was allowed to continue at this temperature for 85 minutes on a heating plate. After the reaction, the flask and its content were cooled to a temperature of 25 °C. Acetic acid was added to adjust the pH to 7 to stop the reaction by preventing further condensation and cross-linking prior to acid number determination and varnish preparation. Three batches of resins were

synthesized. The same procedure was used to synthesize phenol-formaldehyde resole resin using a commercially available phenol. This served as the reference or control resin.

The solubility of each of four resulted partially cured tannin-formaldehyde (TF) and phenol-formaldehyde (PF) resins (acid catalyzed resin each of TF and PF and basic catalyzed resin each of TF and PF) were separately checked in the following solvents; ethanol, benzene, ethanol-benzene (1:1) mixture and linseed oil at room temperature. The solubility of the acid catalyzed resins (obtained during the Stiasny number determination) in these solvents were also checked with the same solvents. The acid number was determined by dissolving 17.6 g of resin in 50 mL hot ethanol. The sample was titrated against 1.0 M KOH solution using phenolphthalein as indicator.

3.3 Preparation of Varnish

Fifteen (15) minutes into the synthesis of the resins, 50 mL of ethanol and 10 mL of blown linseed oil were added to the beaker containing the resin and stirred vigorously and carefully for 3 hours at a temperature of 90 °C. The resulting viscous solution was cooled to room temperature to obtain the wood varnish. This was stored in a tightly covered bottle as described by Gardner and Sward [12].

The drying time, chemical resistance and physical properties such as color, the gloss after 4 days of air drying and heat resistance of the prepared varnishes (both TF and PF) were tested for following the method described by Gardner and Sward [12] and their results compared.

3. RESULTS AND DISCUSSION

Stem bark of hardwoods are known to contain 20-30 % of tannins (depending on the specie) of which only a fraction is extractable. A tannin percentage yield of 24.16 % from the stem bark of *K. senegalensis* satisfactorily fell within the range above, which gives an indication of an effective solvent used for extracting the tannins. A blue-green solution obtained in both the ferric chloride and Lieberman tests is an indication of the presence of phenols in the extract

Stiasny numbers close to one hundred (100) have been determined for tannin containing extracts [10]. The higher the Stiasny number the higher the amount of reactive polyphenol in the tannin extract for polymerization. A high Stiasny number (87.88 % w/w) obtained from this extract is an indication of a good extract and hence its suitability for the resinification process.

The concentrations of polyphenolic expressed as tannic acid equivalent in the extracts were found to be higher than that of phenol. The pink color generated in the test for tannin types indicated the presence of flavan-3,4-ols in the tannin and hence the presence of condensed (proanthocyanidin) tannins since these are characterized as having polymerized flavonoid units. This was in accordance with Hernes et al., [13] and Hedges [14] who stated that condensed tannins are ubiquitous phenolic compounds, representing the second most abundant natural phenolics after lignin and the fourth most widespread components in vascular plant tissues.

When the reaction proceeded at a temperature of 80 °C for about 85 minutes, the reactant cured in the reactor and formed a sticky dark brown substance for tannin-formaldehyde (TF) with yields of 15.11, 15.10 and 15.11 g obtained for the three batches. On the contrary, phenol-formaldehyde (PF) resin was yellowish with yields 17.61, 17.6 and 17.60 g for the different batches.

For all the resin formulations, the viscosity of the reaction mixture increased slowly during the initial stage of co-polymerization and then increased more rapidly as the reaction aged but subsequently produced a less viscous product. The control resin prepared from commercial phenol had a higher viscosity than that synthesized from tannin extract even though the concentration of tannins was found to be higher than phenol.

The less viscous resin produced from the plant extract may be due to the fact that the tannin molecules are big and therefore cannot rotate freely about their backbone. Again the high reactivity of tannins caused premature cured. Consequently, the residual active centers become too far apart for the formaldehyde molecules to bridge. The resulting incomplete cross-linking enhances loss of structural integrity and hence less viscosity. There may be fewer numbers of active sites (ortho and para positions to hydroxyl groups) available for condensation than in phenol hence there is the formation of a three-dimensional networked structure in PF resin due to extensive cross-linking while the molecular nature of tannin could allow for if any at all only a few cross-linking hence a less viscous solution.

The viscosity of the copolymer resins was affected not only by the amount of phenolic group present but also and more importantly by the molecular structure (functionality) and the reactivity of the extracts. Because commercial phenol had higher functionality than tannin, it possibly caused the copolymer resins to have the higher viscosity via cross-linking. The tannin extract was not completely purified (thus it still contained impurities of unknown forms) and these impurities may affect the formation of the resins. Nevertheless, the reduced viscosity of the resins from the plant extract will allow for easy penetration and bodying with oil and solvent in the varnish prepared thereafter.

The yield for the PF resin was very high (89.82 %) which showed a very good and efficient method of synthesizing the resin. However because the molecular weight of the extract could not be determined, it was deduced that the percentage yield for TF resin is expected to be lower than that of PF since it is conceivable that the polyphenolic nature of the extract would confer a higher molecular weight on the extract hence a relatively lower moles of formaldehyde would be needed for use.

Table 1; Acid number and solubility of the acid catalyzed resins (PF resin-H and TF resin-H) and base catalyzed resins (PF resin-N and TF resin-N).

Resins	Acid number (mg/g)	solubility			
		linseed oil	ethanol	benzene	ethanol/benzene
PF resin-N	9.9	S	S	PS	S
TF resin-N	8.6	S	S	PS	S
PF resin-H		I	PS	PS	PS
TF resin-H		I	I	I	PS

* S = soluble; PS = partially soluble; I = insoluble

The acid numbers of PF and TF based varnish were 9.9 and 8.6 mg/g respectively indicating the amount of free acid present (Table 1). Higher acid number implies higher amount of undissolved fatty acid from the oil in the resin during the varnish preparation. This then means that the PF resin was well cured than TF resin under the same conditions of reaction. TF had a larger amount of methylol groups and hence could homogenize properly with the oil through ester linkages. The lower the acid number of varnish the lower the amount of free acids left undissolved and the more it spreads hence its suitability to be used as a surface coating. For a moderately satisfactory varnish, a range of (0.2-10.5) acid number is most desirable [15].

The desirable characteristics of the base catalyzed resins were capitalized for the varnish preparation resulting in slightly viscous substance which skinned out upon exposure to air. Varnish obtained from base catalyzed resins made from TF and PF were dark brown and yellowish in appearance as presented in Fig. 1. The appearance of varnish from the TF was improved when the extract was decolorized with activated charcoal. Here yellowish non-tinted color of the TF based varnish was obtained.



Fig 1: Varnish made from TF (left) and PF (right) resin

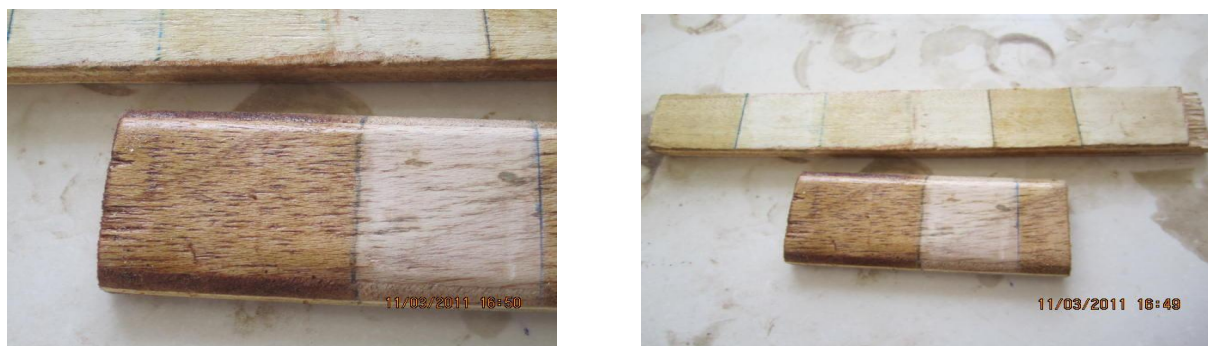


Fig.2: TF-varnish coated surface on left and PF-varnish coated surface on right.

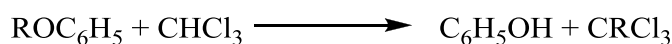
It was observed that both TF and PF varnishes have similar drying times (Fig.2). The varnishes gave hard dry films within 4 hours of air drying. An aged varnish of this type may become increasingly insoluble, producing very tough, quite hard-wearing films which may be difficult to remove. The varnish films possessed high gloss properties after

four days of air drying which indicate the homogeneity of the resin in the linseed oil and hence the smooth surface of the varnish coat on the substrate. The high gloss property of the varnish films could be attributed to the possibility of the cross-linking within the varnish during drying. The films were also found to be steam and heat (120 °C) resistive. It is conceivable that such a thermosetting resin when use will confer the resistance to heat on the varnish. It also suggests that the coatings are not porous hence they can prevent the ingress of water into the substrate.

Again, the water resistance of all the films was excellent. This may be ascribed greatly to the formation of ether linkages (methylene ether brigdes) in the structure of the resin used [16]. These ether bridges are unreactive towards water, acids and bases hence unaffected by them. Possibly, some of the free hydroxyl groups in the tannin molecules may react with the acid anhydride groups (produced in the blown oil) to form esters, which reduces the possible interactions between the tannin hydroxyl groups and water molecules.

The perfect resistivity of vanish to acid and water may be due to the conjugated nature of the linseed oil which was use as the vehicle during coating. The higher the conjugation the lesser the ability of the oil to form peroxy linkages [15] and the higher the resistance towards water and acid.

The low alkaline resistance could be ascribed to the susceptibility of the condensation product (ester linkages) between any remaining hydroxyl groups of the tannins or mainly the alkoxy groups of the ethanol (used in excess) and the carboxylic acid and anhydride of the oil. Again the fact that linseed oil is a saponifiable vegetable oil, makes it forms soaps or salts with basic substances even in the polymerized state. This could be the cause for the low level of alkali resistivity [9]. The varnish offered little resistance to chloroform mainly due to the decomposition of the strongest bonds-ether as shown below.



It had been reported that films based on TF resins exhibit poor alkali resistance [17]. It had also been reported that blending tannin-formaldehyde resins with bitumen improved the alkali resistance of the oleoresinous varnish films [17]. Formaldehyde and benzene were found to have no effect on the air dried varnishes.

Traditionally, varnish films have a high gloss, but by varying the varnish constituents and the method of application, it is possible to vary the degree of gloss as well as the hardness, toughness and flexibility of the film. Varnishes may be colorless or tinted by the addition of dyes or pigments. Varnishes prepared from oil and natural resins tend to be rather dark in color in bulk; the more they are heated, the darker they become, although their drying properties are improved [17]. The synthesized varnish from TF resin was no exception from this. This color problem was solved by decolorizing the tannin extract with activated charcoal. A transparent varnish was formed from a yellowish resin after the extract was decolorized with activated charcoal.

The viscosity of the varnishes was observed to be higher than that of the linseed oil, indicating the extent of the bodying of the resins with the oil. As a matter of fact, the oil bodying of these resins were high and hence the viscosities were high.

4. CONCLUSION

It can be concluded that vanish with considerable qualities such as high gloss properties, high chemical resistance and good drying time can be produced from the stem bark of *Khaya senegalensis*. About 87.88% polyphenolic content of its bark extract were reactive towards formaldehyde. This work has also demonstrated that using copolymer resins of tannin-formaldehyde (TF) as replacement for phenol-formaldehyde (PF) resins in the synthesis of oleoresinous varnishes leads products of parallel. This implies that TF resin is advantageous over PF resin since the source of tannin is cheaper and renewable as well as contributes to reducing pollution. the use of TF resins to produce vanish will add extra value to the log from *K. senegalensis*.

The quality of vanish produced from the TF resin can be improved if impurities such as low molecular mass polyflavonoids and aliphatic sugars could be removed from the tannin extract to increase aromatic structures. This work must be carried on other *khaya* species to ascertain if their concent can be used to produce vanish on a commercial scale.

5. REFERENCES

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