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STUDY ON THE BETTERMENT OF FAST DRYING QUALITY OF MYANMAR LACQUER THROUGH MODIFICATION METHOD

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ABSTRACT

Nowadays, only crude resins are used for lacquer wares. In Myanmar lacquer ware makers have not yet used modification methods for fast drying and brightness to improve the quality as in the Japanese lacquer wares. Thus it takes about three months to season the lacquer wares. The main factor which delays the seasoning is the slow process of drying of thitsi (Myanmar lacquer), which is extracted from naturally grown *Melanorrhoea usitata* Wall.

This paper is attempted to find ways for fast drying process. It was found that drying in oven at 100° C is the suitable treatment for commercial scale production.

1. INTRODUCTION

The thitsi tree (*Melanorrhoea usitata* Wall.) belongs to the family Anacardiaceae and is closely related to the well-known lacquer tree of Japan, *Rhus vernicifera* (Japanese urushi noki), which is a member of the same family. It is a large deciduous tree with a straight clean cylindrical bole and a spreading crown of dark green leaves. Thitsi grows mainly in Indaing Forest in association with In (*Dipterocarpus tuberculatus* Roxb.), Thitya (*Shorea obtusa* Wall.), Ingyin (*Pentacme saimensis* (Miq.) Kurz.), Mondaing (*Cycas rumphii* Miq.), Hmanni

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(*Gardenia erythroclada* Ham.), and Lunbo (*Buchanania lanzan* Spreng.). It abundantly grows in the forests of Southern Shan State and is also found in the forests of Upper Chindwin, Mu, Katha, Northern Taungoo and Pyinmana. In its natural habitat the absolute maximum shaded temperature varies from 37.8° C to 43.3° C and the annual rainfall from 889 to 2,540 mm. or more. It is distributed between 25° N and 11° S. It occurs below 1,158 m. above sea level. Soil type is characteristic of gravel and sand formation through poorer class of this type on laterite soils.

A natural varnish, known as Myanmar lacquer or thitsi, is obtained by tapping the thitsi tree through V-shape incisions at the bark. The collection of thitsi is made from June to January but the best season for tapping is July to October. Thitsi is widely used as a water-proof paint for boats, cloth and paper (umbrella), as glue for gilding, as a preservative paint for wood, metal and leather. In Myanmar, 71.6% of the total production of thitsi is used in the lacquer ware industry. Myanmar lacquer wares have not yet used modification methods for brightness and fast drying to improve quality as the Japanese lacquer wares. Thitsi in its pure natural state is very similar in appearance to pure Japanese lacquer. But in Japan, the lacquer is used after improvement of the quality.

The conditions required to dry Myanmar lacquer are identical with those of Urushic or Japanese lacquer. However, Myanmar lacquer takes longer time to dry than Japanese lacquer does. The quality of thitsi depends on its content of urushic acid (urushiol). Best quality lacquer contains the highest percentage of urushiol.

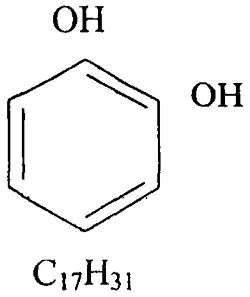
It takes about three months to season lacquer wares due to the slow drying nd hardening of thitsi coating. Research is underway for a better technique of salient properties. Modern methods of preservation of bamboo, which is imperative for the quality of lacquer wares, should also be explored.

LITERATURE REVIEW

In Myanmar thitsi can be divided into three classes by color: first class (black), second class (brown) and third class (red). In fact, the quality of thitsi varies with the concentration of urushic acid and impurities. The first class thitsi can be collected in summer times. The second and third classes can be obtained in rainy and winter seasons.

Pure thitsi is a greenish fluid of viscous consistency, which turns brown and then jet-black color on exposure to the air. It has a peculiar sweetish odor and it is slightly heavier than water. The specific gravity at 23° C of pure fresh Myanmar thitsi and Japanese lacquer is 1.0016 and 1.0020, respectively.

The molecular formula of thitsiol from thitsi is $C_{23}H_{36}O_2$. The structural formula of thitsiol is



Chemical composition of the three different classes of thitsi resin is shown in Table 1.

Table (1) Chemical composition of three different classes of thitsi resin

Composition	Black thitsi (%)	Brown thitsi (%)	Red thitsi (%)
Ash	0.033-0.045	0.108-0.125	0.087-0.089
Matter insoluble in benzene	2.58-2.65	2.77	2.75-2.76
Matter insoluble in water	7.83-8.00	16.47-17.00	29.27-30.04
Urushic acid	87.87-90.06	78.80-81.87	67.73-68.51

Source: Sein (1983)

The Myanmar varnish or thitsi consists of two kinds of particles, which can only be observed in microscopic view. Some particles are small globules in dark brown color and very numerous, whereas the others are light-colored globules scattered more sparsely than the former (Brewster, 1908).

The Japanese lacquer under the microscope appears as a brown emulsion consisting of minute globules of two kinds. They are the sparsely scattered small globules in dark color and the large globules of lighter color. Therefore, it may be inferred that the Myanmar varnish or thitsi exhibits similar microscopic appearance to the Japanese lacquer (Yoshida, 1983).

Thitsi causes violent erysipelatous swelling when it comes in contact with the skin, followed by pain and fever. An oily non-volatile substance present in the lacquer was liable to cause dermatitis. The poisonous substance is not volatile and is also present in the petroleum ether or alcoholic extract. The substance may be precipitated by lead acetate The poisonous substance is identical with urushiol that is the main component in lacquer However, [illegible]

Sing (1908) carried out the experiments on the rate of drying of varnish with the original juice and also with various mixture of its several constituents under different conditions. For the purpose of shortening the drying period, he used a very thin layer of the experimental material coated on the glass plate, which was exposed to the action of air. He kept the glass plate which was coated with original thitsi. The results indicated the following:

~~(1) At 25º C under a bell jar along with a dish-full of water, it dried in 22 hours.~~

(2) In a wooden chest, at 22-25° C, with pieces of wet cloth hanging inside and also pinned onto the sides of the chest, which were soaked with cold water from time to time, it dried after 5½ hours.

(3) In a desiccator over sulfuric acid, it had not dried even after 2 days. Accordingly, he reported that keeping the atmosphere of the drying chamber as moist condition as possible hastened its drying process.

He also reported that the urushic acid, the main constituent of thitsi, could not dry by itself when exposed to the action of moist air. When he coated a glass plate with a mixture of gum, water and urushic acid to determine the rate of drying and allowed to stand for 48 hours exposed to moist air at the temperature of 22°-25° C, it was observed that the mixture did not dry and its consistency did not change. Thus he stated that the gum, though useful in increasing the adhering power of the varnish, took no direct part in the drying process. When the rate of drying was determined by using the mixture of urushic acid, water and nitrogenous constituents, he found that the mixture dried almost at the same time as the original thitsi. Thus he concluded that the presence of nitrogenous constituent is essential for the drying of the varnish

He [illegible] the composition [illegible] to any extent from that of the Japanese one. He stated that sesame oil, the common adulterant of thitsi, greatly impairs the drying power of the varnish. The Japanese make their varnish with linseed oil which, if not in excess, helps the drying power of varnish. Thus he stated that the presence of an oily substance in natural varnish inhibits to a more or less extent the catalytic action of the nitrogenous constituents in helping the drying process (Sing, 1908). Myanmar lacquering and drying process is done in cool, damp underground cellars because thitsi cannot be dried by heat, light and dry air (Rosenthal, 1962).

Hixson and Zee (1962) studied the drying of the sap of the lacquer tree (*Rhus vernicefera*) alone and also in mixture with China wood oil. They reported that the drying process differed from that of the usual drying of oils and also varied with drying conditions. In the presence of moisture drying is accomplished by initial volatilization, formation of intermediate transition compounds and final oxidation These steps are accelerated by the action of moisture and the oxidase enzyme laccase that is present in the lacquer. The temperature, as well as humidity, plays an important part in the drying process, 25° C being more favorable than 0° C or 40° C for the drying of the most lacquer oil varnishes. Lead, cobalt and manganese accelerate the drying about to the same extent, the manganese being slightly better The optimum amount of manganese needed is about 0.2%. The most favorable condition for drying lacquer is at 25° C with 80% relative humidity and the most satisfactory varnish is that containing 80% Chinese lacquer and 20% China wood oils (Hixson and Zee, 1962).

According to the report of Shreve (1906), the drying rate of paints is hastened by the addition of driers that are oxygen carriers usually soluble in oil. The driers are lead, manganese and cobalt resinate, linoleate, oleate, acetate, or oxide. These driers are required only in small amounts like one part of metal to a thousand parts of the paint.

Drying oils of vegetable or animal origin are extensively used in paint formulation and partially synthesized dry oils. They undergo oxidation and polymerization on exposure to air in thin films and form a continuous coating free from tackiness. Oils containing conjugated double bonds can dry more quickly than those which contain non-conjugated bonds and yield hard water resistance film. Drying oils may be subdivided into yellowing and non-yellowing oils according to the tint that they take on exposure to atmospheric or elevated temperature.

Important non-conjugated yellowing oils are linseed, perilla and fish oils. They are composed of mixed glycerides of linoleic and linolenic acid. Linseed oil is extensively used in the paint and varnish industry.

Non-yellowing natural oils include soybean, tobacco seed and sunflower oils. They are virtually free from linolenic acid but rich in linoleic acid. They are more slowly drying than linseed oil and are generally used in combination with tung, linseed or perilla oils.

Castor oil, basically a non-drying oil, is used in the paints, varnish and lacquer industry after dehydration at 176.7°-204.4° C.

Drying oils are processed to enhance their drying rate, water resistance, color retentiveness, etc. Raw oils are refined after treatment with alkali or acid to prevent them from breaking up (depositing sediment) at high temperature and at the same time to improve color retentiveness property.

The bulk of drying oils are used in the form of 'bodies' (thickened by heat polymerization at 121.1°-162.8° C in an inert atmosphere with or without catalyst), or with little or no heating. They possess satisfactory drying, wetting and color retentiveness properties.

High polymer resins are used along with drying oils in the formulation of coating compositions. They react with drying oils when heated and form co-polymers which enhance the drying rate and improve hardness, gloss and durability of films.

Metallic soaps, the driers, are incorporated in composition to serve as oxidation and polymerization catalysts and speed up solidification and drying. The driers in common use are salts of lead, cobalt, manganese, zinc, calcium, and iron with polythenoid fatty acid, rosin acids, naphthenic acid, and octoic acid (Anon, 1965).

The usual driers are salts of metal with a valence of two or greater and unsaturated organic acids. The approximate order of effectiveness of the common metals is cobalt, manganese, lead, chromium, iron, nickel, uranium and zinc. They are usually prepared as the linoleates, naphthenates and resinates of the metals. Paste driers generally are such metal salts as acetate, borates or oxalate dispersed in dry oil (Hawely, 1981). Driers of naphthenates and octoates are more stable than linoleates, and resinates. Thinner is employed for adjusting the consistency of coating formulations. Turpentine was formerly used as thinner for resin and oil coatings.

Surface-active agents are used for improving the dispersion of pigments and for promoting emulsifying, leveling, and spreading properties of coating composition. Organic chemicals commonly employed for this purpose may be classified into cationic, non-ionic, and anionic agents. They improve moisture resistance, adhesion, and anti-corrosive properties of paints. The cationic agents containing 12-18 carbon atoms, such as lauric, oleic or steric acids. The anionic surface-active agents include metallic soaps (Anon, 1965).

3. MATERIALS AND METHODS

3.1. Materials

Thitsi samples were collected from Moenai (Shan State), Kawlin (Sagaing Division) and Pyinmana (Mandalay Division) during the period of April to June in the year 2000.

The following materials were used for testing.

1. Soxhlet apparatus
2. Bamboo sheets
3. IR spectrometer
4. Oven
5. Thitsi (resin from *Melanorrhoea usitata* Wall.)
6. Castor oil
7. Lead acetate
8. 70% linoleic acid
9. Naphthenic acid

3.2. Methods

The following methods were used for determination of purified Thitsi (Thitsiol).

3.2.1 Determination of purified thitsi (thitsiol)

Method I

The percentage of thitsiol in thitsi was determined by distillation method. About 10 gm of thitsi was accurately weighed in a porous thimble and placed in the soxhlet apparatus. The extraction was carried out with 100 cm^3 ethanol until the mixture was clear. After the extraction the alcoholic extract was distilled, dried at 105° C and weighed. Brownish paste-like thitsiol was obtained.

Method II

The percentage of thitsiol in thitsi was determined by distillation method. About 10 gm of thitsi was accurately weighed in a porous thimble and placed in the soxhlet apparatus. The extraction was carried out with 100 cm^3 pet ether until the mixture was clear. After the extraction the extract was distilled, dried at 105° C and weighed. Brownish paste-like thitsiol was obtained.

3.2.2. Infrared spectroscopy studies on thitsiol

For the infrared spectroscopy, the samples of thitsil obtained from thitsi (Moenai, Kawlin, Pyinmana) were sent to Myanmar Scientific and Technological Research Department, Yangon. The samples were determined by Fourier Transform Infrared Spectrometer in September of the year 2000.

3.2.3. Determination of drying time

After the purification, thitsiol and thitsi samples were mixed with drying agents such as dehydrated castor oil lead naphthenate and lead linoleate. The

Method I

About 0.5 gm of thitsiol (Moenai, Kawlin, Pyinmana) was mixed with 0.1 gm of dehydrated castor oil and one drop of terpentine. The mixture was heated at 100° C.

Method II

About 0.5 gm of thitsiol (Moenai, Kawlin, Pyinmana) was mixed with 0.1 gm of lead naphthenates and one drop of terpentine. The mixture was heated at 100° C.

Method III

About 0.5 gm of thitsiol (Moenai, Kawlin, Pyinmana) was mixed with 0.1 gm of lead linoleate and one drop of terpentine. The mixture was heated at 100° C.

Method IV

About 0.5 gm of thitsi (Moenai, Kawlin, Pyinmana) was mixed with 0.1 gm of dehydrated castor oil and one drop of terpentine. The mixture was heated at 100° C.

Method V

About 0.5 gm of thitsi (Moenai, Kawlin, Pyinmana) was mixed with 0.1 gm of lead naphthenates and one drop of terpentine. The mixture was heated at 100° C.

Method VI

About 0.5 gm [illegible]

[illegible]

Method VII

About 0.5 gm of thitsi (Moenai, Kawlin, Pyinmana) was mixed with only one drop of terpentine. The mixture was heated at 100° C.

3.3. The Lacquering Process

The above mixtures (from Method I, II, III, IV, V, VI and VII) were painted on clean bamboo sheet with a brush to form a thin layer of uniform coating, the weight of which must have 0.06 g/ in^2. The sheet was tested for different conditions: in underground cellar of 80% relative humidity and in oven at 100° C. The specimen was said to be dried if no tackiness was felt by a finger press on the lacquered surface.

4. RESULTS AND DISCUSSION

The percentage of thitsiol from different location is summarized in Table 2.

Table (2) Percentage of thitsiol in thitsi from different locales

Sr. No.	Provenance	Thitsiol %	
		Extract with ethanol	Extract with pet ether
1	Moenai	91.36	95.90
2	Kawlin	89.50	91.43
3	Pyinmana	69.14	72.03

It was found that the highest thitsiol content are from Moenai and the lowest from Pyinmana. Therefore, the first class thitsi are from Moenai, the second class thitsi are from Kawlin and the third class are from Pyinmana When the thitsiol was extracted in pet ether [illegible]

The result of drying time is shown in table 3 and 4.

Table (3) Drying time of thitsiol in different conditions

Sr. No.	**Method**	**Underground cellar (week)**			**Oven at 100° C (hour)**		
		Moenai	**Kawlin**	**Pyinmana**	**Moenai**	**Kawlin**	**Pyinmana**
1	I	*	*	*	8:20	8:20	
2	II	2	2	2	3:05	3:30	
3	III	2	2	2	3:00	3:05	

* not dried

Table (4) Drying time of natural thitsi in different conditions

Sr. No.	**Method**	**Underground cellar**			**Oven at 100° C (hour)**		
		Moenai	**Kawlin**	**Pyinmana**	**Moenai**	**Kawlin**	**Pyinmana**
1	IV	*	*	*	8:30	8:30	9:00
2	V	2 week	2 week	2 week	3:05	3:35	5:20
3	VI	2 week	2 week	2 week	3:05	3:05	5:20
4	VII	4 day	4 day	4 day	*	*	*

* not dried.

In table 3 and 4, drying time of thitsiol in 3 different conditions and drying time of natural thitsi in 4 different conditions are summarized. It shows that drying in oven at 100° C was better than drying in underground cellar.

The results of oven dry condition for thitsi and thitsiol are very similar in Table 3 and 4 All of the methods show that drying in underground cellar for both thitsiol [illegible]

The study of the infrared spectrums revealed as follows:

The band at 3500-3300 cm^{-1} corresponds the stretching frequency of the phenolic –OH group (υOH).

The band at 3100-3000 cm^{-1} represents the stretching frequency of the phenolic –CH group (υCH).

The bands at 1495 cm^{-1} and 1463 cm^{-1} are the typical stretching frequency of the C=C groups of the aromatic system and the side chain of thitsiol (υC=C).

~~The band at 1328 cm^{-1}, 1279 cm^{-1}, and 1188 cm^{-1} are the stretching frequency~~ of the C-OH groups (υC-O).

The band at 732 cm^{-1} and 698 cm^{-1} are the typical out-of-plain bending frequency of the CH groups of aromatic system and the unsaturated side chain of thitsiol (δCH).

5. CONCLUSION

The quality of the product largely depends upon the quality of raw materials used for its production. The black thitsi, the best quality thitsi of *Melanorrhoea usitata* from Moenai contains a high percentage of thitsiol which could be extracted with pet ether.

Thitsi serves as a natural form of lacquer because of its excellent spreadability in painting. Thitsi film, when coated on an article, has elegant charm and durability in indoor use. In addition, one of the salient features of thitsi is that it attains a maximum hardness in the presence of moisture once it is dried. The dried films of thitsi. despite the well-knit and highly cross linked structure, is both flexible and rigid having high frictional resistance

The comparison showed that the drying time in oven at 100° C for thitsiol and natural thitsi was almost the same. In underground cellar all the treatments could even prolong the drying period of both thitsiol and thitsi. There is no significant difference in drying period among the various provenances. Therefore, it is suggested that thitsi and thitsiol be dried in oven at 100° C for faster drying in commercial scale production. More, the overall result shows that the use of lead linoleate and a drop of terpentine at 100° C gives the shortest time of drying lacquer ware.

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