Investigating Shellac:

Documenting the Process,
Defining the Product.

A study on the processing methods of Shellac,
and the analysis of selected physical and chemical characteristics.

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Project-Based Masters Thesis

The Institute of Archeology,
Conservation and History

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I want to thank my loving Jody, for patience and support during these years of shared travels and adventures. Also, thanks to my mother and sister, for believing in me even when they thought I was a little too adventurous.

Abstract

This thesis examines shellac, a natural animal-produced resin and wax mixture, in relation to the conservation of furniture and objects of cultural heritage. As demands for shellac have changed with time, so have its processing methods. The thesis aims to determine whether these differences result in physical or chemical variations, and uses FTIR to investigate whether they can be identified using analytical analysis. Utilized methods include literature searches, fieldwork in India, a survey, FTIR and GC-MS analysis, as well as specifically devised experiments.

Part 1 of the thesis presents the history and entomology of the crop, and documents the traditional and modern processing techniques of the product. Part 2 offers a review of FTIR as a method of analysis, identifying GC-MS as a secondary method. FTIR is used to investigate whether or not different processing methods are detectable by examining the resulting spectra. The chemistry of Lac is explored, and 10 shellac samples are analyzed with FTIR, identifying the process of polymerization by esterification, and monitoring it during various stages of ageing and curing. Additionally, experiments are conducted to test the gloss, color and adhesion of shellac during various stages of polymerization, and whether there are any patterns due to processing techniques.

The results show that although certain relations can be identified, FTIR is not capable of differentiating between shellac processed by varying methods. The esterification of shellac is identified and monitored. The findings are related to the practical implications and uses for conservators. Further, the thesis divulges the failure of GC-MS testing, and concludes that further research is necessary to quantify the components of shellac processed by traditional and modern methods.

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During the course of the past two years, it has been my privilege to be graciously hosted and encouraged by institutions, organizations, and therein by individuals deeply committed to conducting and sharing their work and knowledge. The following are brief acknowledgements.

The Indian Institute on Natural Resins and Gums (IINRG).

While conducting visits to India, I was welcomed by the Director of the IINRG, Dr. R. Ramani. In addition to graciously hosting me and arranging field visits, I was given full access to the library, shown around the experimental orchards, as well as allowed to tour the processing demonstration plant on campus.[1]

Professional Assistance for Development Action (PRADAN).

In Jharkhand, I was welcomed and guided by Binju Abraham, a PRADAN employee. Mr. Abraham took the time to introduce me to numerous contacts within the shellac harvesting and processing community, enabling most wonderful intercultural experiences.[2] One week spent at Tajna Industries, in the home and business of Mr. Roshanlal Sharma and his family was one such experience.

The Smithsonian Museum Conservation Institute (MCI).

During the fall of 2011, I was very fortunate to be granted an internship at MCI, under the direction and supervision of a mentor and friend, Senior Furniture Conservator Donald Williams. My time at MCI gave me access to literature, knowledge and expertise, allowing me to perform technical analyses of shellac with dedicated conservation

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[1] The IINRG had its beginnings as the Indian Lac Association for Research in 1921. Today, the IINRG is an authority on the research, development and production of shellac and other agricultural products gleaned from the forests of India; providing training, consultancy, quality evaluations, as well as contributing research and scientific publications. (Indian Lac Research Institute, *Lac a Monograph*. B. Mukhopadhyay, M.S. Muthana. Howrah, India: Glasgow Printing Co. Private Ltd., 1962, ch.1).

[2] PRADAN is a Non Governmental Organization (NGO) working for the marginalized people of India's poorest areas, organizing self-help groups (SHG) working towards the vision of giving poor women, and their families, access to sustainable income earning opportunities.

scientists. Mr. Williams' knowledge, support and guidance are continuously a great source of inspiration to me.[1]

T*he National Institute of Wood Finishing, at DCTC.*

Mitch Kohanek has been a teacher, a friend and a sea of support for many years. My gratitude towards him will never end.[2] Thanks to Groop, for support and enthusiasm.

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[1] http://www.si.edu/mci/english/about_mci/staff/WilliamsDC.html

[2] http://www.dctc.edu/academics/instructor-bios/mitch-kohanek/

Preface

Origins of Interest

My first introduction to shellac was at Dakota County Technical College, and though that first encounter with brushing shellac was a challenge, I soon grew to enjoy the depth, glow, feel and smell of shellac as a coating and finishing tool. After many years of working with the product, I continue to be inspired by the beauty and warmth this widely applicable natural resin awakens in wood. I know I am not alone. Everywhere I go, artisans, restorers and conservators alike have expressed their enthusiasm and their interest in greater access to information about shellac. Through the Project Based Masters Program at the University of Oslo, I have had the opportunity to visit India and experience the wonder of a rich and colorful culture, while seeking out places and people whose lives depend on this nature's gift of Lac.

Cultivators

Most shellac exported from India comes from the areas of Jharkhand, Chattisgarh, Madhya Pradesh, Bihar, West Bengal, Orissa, and Maharashtra, areas mostly dominated by tribal populations with great economic constraints.[5] The forest villages are the main source for *sticklac*, which becomes shellac and its by-products. The propagation, care, and harvest of the raw Lac product depends largely on these tribal people scattered throughout the forested areas. As these remote villagers survive mainly on subsistence farming, the Lac cultivation and harvest can generate a substantial source of monetary income for the people in the area.[6]

Political developments over many decades have resulted in difficult conditions for the tribal people of the region.[7] Some find themselves displaced from their land, due to

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[5] Bangali Baboo, D. N. Goswami. *Processing, Chemistry and Application of Lac,* Indian Council of Agricultural Research, New Delhi, India: Chandu Press, 2010, p. 3.

[6] Baboo & Goswami, 2010, p. 3. & B. Abraham, personal communication, Ranchi, India. March 14, 2010.

[7] Professional Assistance for Development Action (PRADAN). 2005-2010. http://www.pradan.net/ (accessed March, 2010).

mining and natural resource exploration, as well as general poverty and poor living conditions, leading to forced migration into city centers.[8]

NGOs such as PRADAN organize self-help groups and teach enhanced skills for forest-based livelihoods to the cultivators in the region. As the tribal people face economic and physical hardships, many generations' worth of knowledge and tradition are threatened, as is the propagation, harvest and the end product that is shellac. In addition to being a cultural loss, this would have far-reaching implications for industries all over the world.

Half of all shellac consumed is bleached Lac, which is applied as an enteric coating for pharmaceuticals and an edible coating in the food industry. As Part 1 of the thesis will explain, these products demand modern methods of processing, with mechanized production units, and chemical knowledge and recovery capabilities.[9] As industrialization pressures the age-old processing techniques of Lac in rural India, traditional methods of rendering shellac and its by-products are threatened by demands of modernization and efficiency. These techniques are themselves a valuable part of intangible cultural heritage.[10] The cultivation and processing methods merit the status of cultural heritage, as Lac holds an esteemed position within Indian history and culture. As these traditional processing techniques may be at risk, the documentation of these processes is an important element of this thesis.

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[8] Ibid.

[9] Baboo & Goswami, 2010, p. 19.

[10] For more on safeguarding intangible cultural heritage, refer to UNESCO's 2003 convention: http://portal.unesco.org/en/ev.php-URL_ID=17716&URL_DO=DO_TOPIC&URL_SECTION=201.html

Glossary

Aghani-	Oct./Nov. Lac harvest of Kusmi strain beetle.
Ari-	Sticklac which has been removed from its host tree before the completion of the lac insect’s life.
Basakhi-	The June/July Lac harvest of the Rangeeni strain of Lac beetle.
Battha-	A furnace/oven made from clay, heated with coal. This oven is used as a heat source to melt seedlac during the filtration stage of traditional processing methods.
Belwaya-	Skilled laborer who stretches molten Lac resin into sheets of shellac, using his hands, feet, and teeth to do so.
Broodlac-	Section of stick from a tree, containing mature Laccifer Lacca eggs. The stick is tied to a desired host, in order to control inoculation.
Buttonlac-	Round discs of Lac resin, which resemble buttons.
Erythrolaccin-	Alcohol soluble, yellow coloring matter in Lac, removed by activated charcoal filtration while in solution, or by bleaching method.
French Polish-	Using shellac prepared as a spirit varnish, applying it with a specially formed pad/rubber/tampon, using oil as a lubricant for application, then ethanol to clear the surface of oil. Numerous coats are applied in succession by rubbing, padding, and sometimes pounding the pad, to create a gloss finish. The technique should result in a pore-filled surface.
Hand-Made (HM)	Shellac stretched by hand, by a traditionally skilled laborer.
Jethwi-	June/July Lac harvest of Kusmi strain beetle.
Karrigar-	The worker in charge of the hot filtration method of traditional processing methods, using a battha oven.
Katki-	Oct./Nov. Lac harvest of Rangeeni strain beetle.
Lac-	A term for products of the resinous secretions from the Laccifer Lacca beetle, both before and during the various stages of refinement.
Lac dye/ -	Dyestuff from the body of the Lac beetle, soluble in alkaline solution,

Laccaic Acid	mostly washed out of the Lac during the sticklac to seedlac process, when soda ash, or sodium carbonate (Na_2CO_3 – pH 11.4) is added to the washing water, turning it a reddish violet color.
Laccifer - Lacca	A beetle in the Hemiptera order, also known as the Lac beetle, which latches onto the branches of selected host trees, sucking sap and secreting a resinous material. There are two strains of beetle used for Lac production in India; the Kusmi and the Rangeeni.
Machine-Made (MM)	Shellac rolled into sheets of varying thickness, usually by steam-heated rollers.
Nand-	Stone or cement vats, which are filled with water, and traditionally used for washing seedlac.
Nera-	A palm leaf used by the Belwaya to manipulate the molten Lac resin across the surface of the hot pipa.
Pheraya-	The laborer who turns the wooden wheel (the charki) to uniformly heat and melt seedlac during the hot filtration of traditional processing methods.
Phunki-	Sticklac which is removed from its host tree after the completion of the lac insect’s life.
Pipa-	A tubular ceramic vessel filled with hot water and used by the Belwaya to keep the molten Lac in a (thermo) plastic state.
Seedlac-	Ground particles of Lac, washed free from larger stick particles and beetle remains, as well as most of the Lac dye.
Shellac-	The product of the resinous material exuded from the *Laccifer Lacca* insect, which has undergone one of many methods of refinement, including melting by a heat source, filtration, dissolving in solvents (spirit based, or alkaline), removing wax and/or bleaching color.
Spirit varnish-	A finish that hardens by the evaporation of the carrying solvent, often spirits of alcohol / Ethanol / CH_3CH_2OH.
Sticklac-	The harvested Lac encrustations, scraped or broken off the branches of the host tree.

Key to acronyms

AMDIS	Automated mass spectral deconvolution and identification software
FTIR	Fourier Transform Infrared Spectrometry
GC-MS	Gas Chromatography – Mass Spectrometry
IINRG	Indian Institute on Natural Resins and Gums
ILCC	Indian Lac Cess Committee
ILRI	Indian Lac Research Institute
IR	Infrared (radiation)
MCI	Museum Conservation Institute (of the Smithsonian Institute)
PRADAN	Professional Assistance for Development Action

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Introduction

Shellac, or Lac, is a natural animal-produced resin and wax mixture, which is utilized in a broad spectrum of applications, and within a variety of fields. When applied as a finish to wood, shellac imparts a depth, glow and beauty hard to match with any other product. In the 17th and 18th centuries, artisan furniture makers applied shellac to finish only their most exclusive creations, before it became commonplace on European furniture from the early 1800s and on.[1] Within restoration and conservation work, shellac is often used as a high gloss finish, applied as a varnish, or padded on with a French polishing technique. Shellac is also used as an adhesive, or as a film-forming finish for wooden objects, metals and frames, as well as floors and walls, as the versatility of the resin has proven invaluable for a variety of applications.[2]

In India, this resinous exudate material from the *Laccifer Lacca* beetle is often referred to as *Lac,* a general term for the product.[3] As the collective term of *Lac* is commonly used both in literature and in the vernacular, the term will be used throughout this dissertation and it should be understood as a general term for products of the shellac resin, both before and during the various stages of refinement.

Lac is available in a wide array of specifications, as powder, flake or button form, and with a variety of color and wax contents. The most highly refined grade of shellac is both bleached and de-waxed during processing, which is able to create a clear, edible, high gloss film. Dark Bysakhi buttons, on the other hand, contain all of their original wax content as well as a full bodied, deep amber color. In the traditional method of processing, *seedlac* is melted over a coal fire. The molten resin is pressed through a tubular cotton cloth bag, thin sheets are prepared from the mass, and these are later broken into flakes and packaged as a finished shellac product. Shellac buttons can also be

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[1] Rivers, Shayne, and Nick Umney. *Conservation of Furniture*. Oxford: Butterworth-Heinemann, 2003, p. 148.

[2] Mills, John Stuart, and Raymond White. *The Organic Chemistry of Museum Objects.* Oxford: Butterworth-Heinemann, 1994, p. 101.

[3] Objects and items associated with Lac will often have names including the term. An example of this is that the *Laccifer Lacca* beetle is often called the *Lac beetle*.

made using this traditional heating method, by allowing the molten material to drop onto a metal sheet and cool, solidifying into round disks.

Although the industry offers a plethora of product choice, shellac is often referred to as a generic product in conservation literature and little attention is afforded to defining which type of shellac is being used for treatment regimens, beyond choosing a product based on the color it imparts. Conservation science often focuses on the goal of the identification of shellac as a coating on objects of cultural heritage, or whether it is present as a component in a varnish mixture. While analytical markers are often identified in order to positively confirm whether or not shellac is in a sample, little attention is afforded to the differences between the various types of shellac available, or whether or not these varieties have distinct and recognizable characteristic qualities. In studies where varieties are mentioned, samples are referred to using arbitrary commercial names, telling nothing of the characteristics, or by which processing method the product was manufactured.[4] This generic presentation of shellac in academic literature obscures any type-specific qualities that may be present in products available on the market.

As industrialization pressures the age-old processing techniques of Lac in rural India, traditional methods of rendering shellac and its by-products are changing, as the market demands modernization and efficiency. With more mechanized production units, color and wax content can be controlled, and shellac can be bleached with sodium hypochlorite (NaClO) to give a colorless, wax-less finish. Applied as an enteric coating for pharmaceuticals and as an edible coating in the food industry, 50% of all shellac consumed is bleached Lac, demanding modern methods of processing, including mechanized production units, chemical knowledge, and recovery capabilities.[5] Facing the challenges of a world economy and pressures of modernization, it is likely that traditional processing techniques will be phased out, as more efficient methods of processing are favored and sought after.

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[4] See literature review in part 2 for more information on these topics.

[5] Bangali Baboo, D. N. Goswami. *Processing, Chemistry and Application of Lac,* Indian Council of Agricultural Research, New Delhi, India: Chandu Press, 2010, p. 19.

Detailing the variety of processing methods of shellac can reveal how the modern processing techniques of today differ from those of the past, and thus shed some light on how the end product may differ accordingly. As the various types of shellac are processed by either traditional or modern methods, how might the end products differ, and how may they behave differently when applied as a coating? As the physical and chemical characteristics of shellac may vary, it is the aim of this dissertation to investigate whether different types of shellac vary in performance characteristics, and whether these characteristics are detectable through analytical techniques.

As conservators are charged with the responsibility of choosing which type of shellac to apply to objects of cultural heritage, it is the goal of this research to contribute recommendations for applications and use of shellac for practicing conservators, through documentation, experimental testing and scientific analysis.[6] In order to attain these goals, a few main questions will have to be answered: Firstly, are there distinctions between various types of shellac, and can detailing the processing techniques shed light on potential qualities and characteristics within each product? Further, are the various types of shellac, and their processing methods identifiable, and does one method of production yield products that are preferable for use within furniture and objects conservation?

Structure

In order to address the various segments of these questions, the dissertation is divided into two main parts: the first focusing on the historical and procedural documentation of Lac; while the second part focuses on attempting to map out physical and chemical characteristics of the product, including chemical analyses performed to identify and monitor selected characteristics of shellac. Chapter 1 details and justifies the methods used throughout the dissertation, while chapter 2 affords a brief historical account on the longevity and prevalence of Lac, introducing the resin as a product, describing its natural origin, and following the chain of trade from the cultivation stage to the finished product,

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[6] These goals were partly inspired by Salvador Muñoz-Viñas, and his theories of conservation. Muñoz-Viñas, S. Contemporary Theory of Conservation. Burlington: Elsevier Butterworth-Heinemann, 2005. p. 78.

ready for export. The lifecycle of the Lac beetle is described, as well as the three most common host trees in India. Chapter 3 focuses on the processing techniques of shellac. The techniques of hand stretching, machine rolling, as well as accounts of more modern techniques involving mechanization and solvents are explained.

Part two of the dissertation explores the analysis of shellac, and includes a review of Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography-Mass Spectrometry (GC-MS) as analytical techniques used in studies of shellac. Chapter 5 introduces the uses of shellac within furniture restoration-conservation, and maps out the various physical characteristics recognized within the literature and by frequent users of the product. These characteristics are then tied to the chemistry of Lac. Chapter 6 details the research and experiments conducted on shellac samples, by various analytical methods and testing. Chapter 7 of the study presents and discusses the results of the tests and whether the processing methods have an effect on the composition, the characteristics, the qualities of the end product, and whether or not these differences are detectable with methods of analysis. Finally, there is a discussion of whether or not a particular method of processing is preferable for a shellac to be used within furniture and objects conservation.

Part 1

The Documentation of Lac

Methods, History and Processing

Chapter 1

Methods

Goals and Justification

It is the goal of this study to investigate a range of shellac preparations processed by both hand and mechanical techniques, to identify their character variations, and to determine whether these characteristics can be specifically identified using modern analytical methods. The detailing and documentation of the origin and processing methods of shellac is of great interest to the entire community of conservation professionals, and preserving this knowledge is part of the intangible cultural heritage for the field of objects and furniture conservation. In addition, conservators charged with creating treatment protocols for objects of cultural heritage will benefit from understanding the processing methods of shellac, and the effects these variations may have on the performance of shellac film coatings applied to objects in their care.

Initial Literature Searches

To lay the groundwork for detailing shellac as a product, it is important to understand the significance of the resin, and the prevalence of its use on the wide range of objects of cultural heritage that conservators encounter in their work. To better understand shellac in relation to conservation issues, its historical use on furniture and objects is established in Chapter 2, placing the use of shellac and shellac by-products in a historical context. This was accomplished by means of a thorough search of historic and modern literature. As shellac is a product used in many different industries, this study has drawn from historical information from several sources, including conservation literature and historical accounts, as well as pharmaceutical, industrial coatings and manufacturing research.

To investigate the distinctions between types of shellac, which is an agricultural product, a broad base of background information is introduced in order to detail the origin of shellac in India, including entomological information, as well as cultivation methods and information on host plants. A literature search was conducted at the IINRG library, which has produced a vast body of literature, much of which is industrial chemistry research and industry standards for the production and export of shellac as a product.[7] Biological research on the host trees of Lac, as well as entomological research on the Lac beetle itself and its predators was reviewed and is presented, as Chapter 2 continues. Industry information developed by companies dealing with coatings technology, including pharmaceutical research, is often considered proprietary, and access to results was therefore somewhat limited.

Field Work and Interviews

To gain more knowledge on shellac as a crop, a journey has been made to the main Lac producing regions of India, to remote rural areas, as well as the experimental orchards of the IINGR. Information was gathered by semi-structured interviews with development workers from NGOs and scientists from the IINGR, as well as observations in the field and photographic documentation.

Observing the cultivation and harvesting practices of shellac gave rise to questions about the processing of the raw material, and what it must go through to become a finished product. Although the main host trees and the cultivation practices were introduced, there are many more different types of finished shellac available on the market than there are variations within common hosts, leading the author to ponder whether the processing techniques create significant differences between shellac types, and what this might mean for the many uses of shellac within the conservation field.

To gain more information on the processing techniques of shellac, a semi-structured interview was conducted with Mr. Singhania, a third generation processor and major exporter of shellac, based in Kolkata, India.[8] This interview led to curiosity about the diversity of processing techniques, and a desire to further document both historical and modern processing methods of shellac. Fieldwork was carried out in Lac producing regions of India to witness the production first hand. Information was gathered by

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[7] Much of the literature found at the IINGR is unavailable outside the library itself, as it is not digitized or widely reprinted in many European sources.

[8] Renshel exports, Kolkata, India. http://www.renshel.com/about_us

personal observation, photographic documentation, and semi-structured interviews with scientists, economists, development-workers, producers, exporters, and farmers who deal with various aspects of shellac as their livelihood. Additional documentation was gathered by a guided tour through a demonstrative processing unit at the IINRG, visiting 7 smaller partially mechanized processing units, as well as 2 larger mechanized units, one of which had capabilities for recovering Lac dye, as well as bleaching shellac. The solvent method for processing shellac was not observed firsthand in India, but is described by reviewing available literature.

Questions Resulting from Field Work

Upon learning about the variation of processing techniques, it was theorized that several points within theses processes may have a significant impact on the final product, and the following questions were noted:

1. How does the length of washing time from sticklac to seedlac, and the amount of soda ash used, influence the color of the final shellac product? Further, what is actually removed during this washing process and what is the effect of adding oxalic acid (dicarboxylic acid, $H_2C_2O_4$) to brighten seedlac? What effect could this have on the final product, as the additive is not washed out during processing?

2. Does the use of either coal or steam heat during the melting process influence the finished shellac product? As the heat sources vary, so do the temperatures and exposure to steam. Does this affect the product, and is it detectable?

3. What does activated charcoal remove from shellac to yield a lighter colored product?

4. The bleaching of shellac is known to yield a product with a short shelf life. Why is this, and are there other issues with this type of shellac?

5. Do the variations within processing methods make for different characteristics in the film-forming qualities of the finished product?

To investigate these questions, searches were conducted in conservation literature, both historical and current industrial information from import and manufacturing companies, chemistry / spectroscopy / chromatography sources, the coatings technology industry, and in the edible coatings and pharmaceutical industry, supported by both physical observations and experimental chemical analyses.

Analytical Methods Used

The experiments devised and performed are intended to investigate whether the variations of shellac are identifiable by FTIR and GC-MS, and tests are conducted to observe and document selected physical and chemical characteristics of shellac.

Survey

To identify the physical characteristics of shellac as a finish, restoration-conservation literature was consulted, as well as surveying experts and professionals who frequently use the product. Characteristics of shellac were also discussed and identified through conversations with Mitch Kohanek, Director of the National Institute of Wood Finishing, in Rosemount, Minnesota USA.[9] A survey (Appendix 1) was conducted and distributed among members of a professional finisher's organization to evaluate which physical characteristics of shellac were considered most important by frequent users.[10]

FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) has been employed in a series of experiments, to determine whether or not the certified variety of shellac types give unique IR spectra. A mid-range IR with an ATR sampling accessory was utilized, as all the samples are solids, the accessory affords ease of use, and the samples can be retained and

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[9] For more information about Mitch Kohanek and the National Institute of Wood Finishing, see http://www.woodfinishing.org/

[10] For more information about the PRG, see http://www.professionalrefinisher.com/

reused for further study.[11] While gathering the data, transmission mode was not used in favor of the absorption mode as it allows for qualitative study as well as an indication of the actual quantity of functional chemical groups present. By employing the Beer-Lambert Law, which states that each spectral band is directly proportional to the concentration of the absorbing species, a linear relationship between bond intensity and concentration can be implied.[12] A review of FTIR theory and analysis is covered in Chapter 4 of the thesis.

Sample Description

During the past two years, 38 samples of shellac and shellac by-products have been collected by the author. The complete list of samples is in Appendix 2.

The following list of 10 samples were chosen for testing as they represent an array of different types of shellac and their varied processing methods. Specifically, these samples were chosen because they are examples of both similar and contrasting processing, in the hope that chemical analysis might show evidence of these disparities and likenesses.

Table 1: Selected samples for testing Lac

1	De-waxed/bleached Jethua, from Tajna Industries.
2	Full wax/bleached, made from Thai seedlac, by Tajna Industries.
7	De-waxed/carbon color removal (solvent/evaporated) Superfine, Ernst P.
14	Full wax/color content-hand stretched Lemon (coal heat) Renshel Exports.
18	Full wax/color content-machine rolled Lemon (steam heat) Ernst P.
19	De-waxed/full color content (solvent/evaporated) Recto, Ernst P.
24	Kusmi Sticklac- not treated.
36	Full wax content-buttons (coal heat) washed for1hr- Aloak Kusmi
37	Full wax content-buttons (coal heat) washed for 2hr- Aloak Special Kusmi
38	Full wax content-buttons (coal heat) washed for 3hr- Aloak Super Kusmi

(Sample numbers were kept from the original list of total samples, Appendix 2. Image [8] presents these samples in solution.)

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[11] Rizzo, Adriana. "Progress in the Application of ATR-FTIR Microscopy to the Study of Multi-Layered Cross-Sections From Works of Art." *Analytical and Bioanalytical Chemistry* 392, no. 1-2 (2008) p. 47.

[12] Derrick, M., Stulik, D., Landry, J. M., *Infrared Spectroscopy in Conservation Science. Scientific Tools for Conservation*. Tevvy Ball, Sylvia Tidwell. Los Angeles: J. Paul Getty Trust, 1999, p. 82-83.

IR spectra were collected from bulk product (sampled directly from the manufacturer's packaging) as well as from product cast as thin films. The thin film castings were used, as they were easier to handle, and they were a more homogeneous mixture. Comparing and contrasting the FTIR spectra of these samples in Experiment 2 will be used to determine whether evidence of differences due to wax content, color removal, variances within heat exposure, stretching/rolling mechanisms, and washing times can be identified by this analytical method.

Experiments for Testing Adhesion, Color, and Changes in Surface Gloss

To simulate the effect of ageing and exposure to UV light on shellac on common substrates, wooden slats were used to test selected physical characteristics of shellac in Experiment 3. Shellac preparation and application procedure is described in Chapter 6. Shellac samples applied to wooden substrates were exposed in a Weather-Ometer (an artificial ageing machine) exposing various types of shellac to light and heat degradation. The wooden slats were cut from one single piece of flat-sawn Maple, to ensure the same density and movement and/or shrinkage. Maple was chosen as it is a pale wood, allowing the hues of the shellac, and any change, to be visible. The density of maple also allows for more movement upon exposure to heat, straining the adhesion and flexibility qualities of shellac as a film forming finish. Surface gloss changes were measured by a gloss meter, before and after exposure. A standard tape "pull off" test was conducted to assess changes in adhesive qualities before and after curing treatments. Additional samples were cast on glass slides to measure any changes in color. These measurements were conducted with a spectrophotometer. The samples for measuring change in color were cast on glass to avoid measuring changes due to the wood substrate and were exposed in an identical manner to the wooden samples.

Tracking Polymerization

As shellac ages, it polymerizes, becoming increasingly impervious to alcohol. This process defines the shelf life of shellac, as it no longer dissolves in solvent, nor does it dry to a hard film if applied to a surface, once it has polymerized. The shellac manufacturing industry recognizes blocking (clumping) and polymerization as a problem, and it is not uncommon to experience shellac blocking and failure to dissolve in alcohol. It has been suggested that the polymerization of shellac occurs as an esterification process, yielding an increase in the formation of esters, while expelling water (H_2O). The polymerization reaction also occurs when shellac is subjected to heat, at levels above the melting point. The following test was devised and performed to identify and monitor the progression of esterification over time, and to compare the process of esterification between various types of shellac.

Test to Identify and Monitor Polymerization in Shellac

Experiment 4 included sample sets of shellac cast as films on glass slides, aged and cured by various methods, and scanned by FTIR to identify and monitor the polymerization process taking place.[13] One set was aged six months, to artificially speed the polymerization process, another set of samples was exposed to heat, rendering it fully cured/polymerized. In addition to dry heat curing, samples were also exposed to steam, and analyzed by FTIR to identify deviations in the esterification process caused by exposure to additional moisture during heat treatment. An alcohol solubility test was performed, ensuring that the samples were in fact cured (Appendix 9). FTIR was used to identify chemical changes and to monitor the process in the samples as they were exposed to the various stages of ageing and curing. All of the FTIR measurements tracking the chemical changes in aged shellac were conducted on sample material cast on glass slides, in order to avoid spectral interference from a wooden substrate. Sample preparation is described in detail in the experimental section of the study.

Technical Failure

The initially planned experiment, undertaken at the Museum Conservation Institute (MCI), at the Smithsonian Institution (SI) included exposing sets of 10 shellac samples to artificial ageing in a Weather-Ometer at increments of 6 months, 12 months, 36 months and 60 months. It was hypothesized that these amounts of exposure would show the progression of polymerization over time. The samples were loaded into the machine and

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[13] Sample preparation is described in the experimental section of part 2.

exposed to the equivalent of 3 months worth of ageing, before it started malfunctioning by turning itself off and cooling incorrectly, resulting in below average room temperature conditions. After several trials and errors, it was deduced that the machine's computer was disturbed by an earthquake, measuring 5.8 on the Richter scale, which shook the Washington D.C. area, on August 23rd, 2011. The sample exposure was therefore limited to naturally aged samples exposed to 6 months of ageing, as well as the heat and steam cured samples. While the resulting experiment does not detail the full number of progressions planned, the samples still show indications of the same trajectory.

A Secondary Method of Analysis and its Limitations

As FTIR only detects components comprising 1% or more within a sample mixture, a secondary method of analysis, Gas Chromatography coupled with Mass Spectrometry was used in Experiment 5, in an attempt to quantify the ingredients in shellac more accurately. The derivatization technique used to prepare the shellac samples for this study was prepared and carried out in cooperation with Jennifer Giaccai (Conservation Scientist at MCI), and are described in the Experimental section.[14] Although GC-MS tests were performed, the Automated Mass Spectral Deconvolution Identification System (AMDIS) library was unable to identify the shellac samples' individual components.[15]

Reviewing the Results

The results of the physical tests were compiled into tables and reviewed by comparative analysis. The results from the FTIR analysis were compiled with Spekwin32, and reviewed by visual comparison and literature searches within conservation and chemistry literature.

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[14] The derivatization solvent used contained Meth-Prep II (m-trifluoromethylphenyl trimethylammonium hydroxide (TMTFTH)), methanol and toluene. See experimentation section for full sample pre-treatment.

[15] The Automated Mass Spectral Deconvolution and Identification System (AMDIS) is a computer program that extracts spectra for individual components in a GC/MS data file and identifies target compounds by matching these spectra against a reference library. It was developed at NIST with support from the United States Department of Defense and is freely available. http://chemdata.nist.gov/mass-spc/amdis/, accessed 6-5-2012.

Chapter 2

History and Entomology

A Brief Historical Account of Lac

Lac has been an integral part of Indian history and culture for thousands of years, beautifying wood as a coating, used as a thermoplastic molding material, as well as having medicinal and cosmetic qualities within ayurvedic medicine.[16] The 3000 year-old Hindu scripture, the *Mahabharata*, portrays an entire palace formed out of Lac, used to entrap and destroy an enemy.[17] This common reference shows a familiarity with the resin and its uses within the ancient world. Lac was also known to the Romans, and described by the Roman natural philosopher, Pliny the Elder, who wrote his encyclopedia, *Naturalis Historia*, in 77 A.D.[18] During colonial times, in 1563 Goa Garcia de Orte, a physician to the Portuguese governor of India, published descriptions of both Lac resin and Lac dye.[19] The earliest European literary references to Lac, however, are from 1596, recorded by Jan Huyglen van Linschoten, who was sent on a scientific mission to India by the King of Portugal.[20] According to Noël Heaton, Lac was introduced to Europe at the end of the 16th century, although it had been used in eastern Asia for centuries.[21] Although the resin may have been available in Europe, Lac dye was the main Lac related import to Europe during the 17th century, as it was a cheaper alternative to cochineal.[22] According to Shayne Rivers and Nick Umney, button Lac was originally manufactured

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[16] Baboo & Goswami, 2010, p. 1. Suktha number five of the fifth boo of the Atharva Veda bears the title "Laksha" and gives a brief account of Lac, the Lac insect, the medicinal use of Lac and a prayer charm addressed to the fully developed adult female Lac insect personified as a beautiful young maiden. Bloomfield, Maurice. Sacred Texts, "Hymns of the Atharva-Veda." http://www.sacred-texts.com/hin/av.htm (accessed June 6, 2012).

[17] Russell, M. *Shellac*. Calcutta, India: Angelo Brothers Limited, 1965, p.7., Lichtenberg, Hans Henrik. "HolyBooks.com." Last modified July 28, 2011. Accessed April 11, 2012. http://www.holybooks.com/mahabharata-all-volumes-in-12-pdf-files/.

[18] Gardner, William Howlett. *Shellac and Other Lacs, in Protective and Decorative Coatings: Paints, Varnishes, Lacquers, and Inks*, Vol. 1, ed. Joseph J. Mattielo. New York: John Wiley & Sons, 1941, p. 265., and Jona, Lendering. Livius, "Articles on Ancient History." Accessed April 11, 2012. http://www.livius.org/pi-pm/pliny/pliny_e.html.

[19] Gardner, 1941, p. 265.

[20] Gardner, 1941, p. 264.

[21] Heaton, Noël. *Outlines of Paint Technology*. University of Michigan: C. Griffin & Company limited, 1947, p. 301.

[22] Gardner, 1941, p. 265.

and used for the direct application of shellac to turned objects by simple friction, before the use of spirit solvents were common.[23] This practice was also described by Jan Huyglen van Linschoten, as a technique he observed during his travels in India.[24] When applied in this manner, the heat of friction fuses Lac onto the piece being turned on a lathe, giving a glass-like surface.[25] In the 1800s, manufacturers of buttons may have added cheap rosin to bulk out this type of shellac product, as well as adding orpiment (a yellow mineral pigment) to the Lac, in order to make the color lighter[26]. This practice would however, have made both the flakes and the varnish slightly opaque, and as a result craftsmen of the time who were using Lac as a spirit varnish preferred to purchase seedlac, thereby insuring that nothing was added during processing.[27] As alcohol became more commonplace in the early 1800s, so did the technique of French polishing and using shellac as a spirit varnish.[28] After the discovery of aniline dyes started displacing the use of Lac dye in the 1880s, the interest in the resin component of Lac and its uses greatly expanded, as did the export of the product.[29] According to Rivers and Umney, spirit varnish was one of the main classes of varnish applied to wood in 18th century, along with oil-resin varnishes, and the less common essential oil varnish.[30] By the late 1800s, it had become so common for artisans, cabinet makers and restorers to apply shellac and wax as a coating regimen on furniture, so that antique objects hailing from different places and times were often presented with the same treatment schedule, to the point of sometimes obscuring an object’s provenance.[31]

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[23] Rivers, Shayne, and Nick Umney. *Conservation of Furniture*. Oxford: Butterworth-Heinemann, 2003, p. 175. Purified alcohol would have been available as a shellac solvent in Europe after the 12th century, but with rather prohibitive costs, the spirit varnish solution was used mainly on small decorative objects, p. 148.

[24] Gardner, 1941, p. 264.

[25] Gardner, 1941, p. 264.

[26] Rivers & Umney, 2003, p 175.

[27] Rivers & Umney, 2003, p 175.

[28] Rivers & Umney, 2003, p. 148. & Edinger, Vibe; Holstein, Bodil; and Larsen, Birgitte, "Transparent surface coatings of Danish furniture between 1550 and 1828." *Meddelelser om konservering* 2 (1997) p. 30.

[29] Russell, 1965, p. 11.

[30] Rivers & Umney, 2003, p. 631.

[31] Rivers & Umney, 2003, p. 632.

Shellac

Throughout this paper, the term s*hellac* should be understood as the resinous material exuded from the *Laccifer Lacca* insect, which has undergone one of many methods of refinement.[32] Though there are many varieties, shellac is usually flaked, and apart from differences on account of host trees and harvesting times, it is the processing; the removal or modification of its ingredients, which yields the variety of shellac types available on the market.[33] Flakes are often characterized as *Machine-Made* (MM), or *Hand-Made* (HM). Although buttons may contain the same product as flaked shellac, they are typically referred to as *buttonlac*.

Lac is composed of the Lac resin, wax, dye, volatiles, as well as insect and wood impurities. Below is a simplified overview of the physical component ingredients in Lac during various stages of refinement. The remaining percentages are gums and other impurities, while the volatiles are moisture.

Table 2: The physical components of Lac

	Sticklac	Seedlac	Shellac
Resin	68%	88.5%	90.5%
Dyestuff	10%	2.5%	0.5%
Wax	6%	4.5%	4.0%
Volatiles	4%	2.5%	1.8%

(Indian Lac Research Institute, *Lac a Monograph*. B. Mukhopadhyay, M.S. Muthana. Howrah, India: Glasgow Printing Co. Private Ltd., 1962, p. 197.)

The resin component of Lac can be divided into two parts: 25% soft (ether-soluble) resin, and 75% hard (ether-insoluble) resin.[34] Further, the dyestuffs present are divided into Lac dye, or Laccaic acid (soluble in alkali solution) and erythrolaccin (soluble in alcohol).[35] These ingredients will be discussed further in chapter 5 of the dissertation.

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[32] Rivers & Umney, 2003, p. 175.

[33] Bleached shellac often comes in powder form, as it is precipitated out of solution.

[34] Baboo & Goswami, 2010, p. 29.

[35] Baboo & Goswami, 2010, p. 48.

When applied as a coating, shellac can be a component in a mixture, composing a varnish, or it can be dissolved in alcohol (Ethanol / CH_3CH_2OH), to form a spirit-varnish. A spirit-varnish is a finish that hardens by the evaporation of the carrying solvent.[36] Shellac also dissolves in alkali solutions such as hydrogen borate ($B(OH)_3$/boric acid), or hydrogen nitride (NH_3/ammonia), thus becoming a waterborne finish.[37]

Lac Producing Countries

India and Thailand are the two main exporters of Lac, while China produces enough to supply their domestic market.[38] Minor producers are Indonesia, Bangladesh, Myanmar, Vietnam and Sri Lanka.[39] According the to the Indian Institute on Natural Resins and Gums (IINRG), India produced 16,495 metric tons of Shellac in 2009-10, which is less than previous years, as the amount is generally 20,000 metric tons, about 70% of the total global production.[40]

Other Uses of Lac and Lac By-products

In addition to being used as a coating, shellac and its by-products have a multitude of applications. In its raw form, Lac contains laccaic acid, or *Lac dye*, a dye that is water-soluble in alkali solution, and used as a red colorant in food and for dying natural fibers, such as wool and silk.[41] Lac dyed wool was used in Persian carpets dated as early as 714 B.C.[42] Shellac wax is used in crayons and lipstick, as well as polishes and waxes for furniture.[43] Shellac can also be used as an electrical insulator, as well as a binder for man

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[36] Mussey, Robert. "Early Varnishes, The 18th century's search for the perfect film finish." *Fine Woodworking*. 35. (1982): 36-39, p.37.

[37] Minina, S. A., Efimova, L. S., Abramova, N. V., Raisyan, V. D., & Bril, A. S. "Development of an intestinally soluble coating based on an aqueous shellac solution." *Pharmaceutical Chemistry Journal* 12, no. 2 (1978): 254-258.

[38] Baboo & Goswami, 2010, p.5.

[39] Baboo & Goswami, 2010, p.5.

[40] Ramani, R., PhD. "Climate Change and Lac Crop." 09/14/2010.http://ilri.ernet.in/~iinrg/dirdesk.html (accessed 09/28/2010).

[41] Rossman, James M. "Commercial Manufacture of Edible Films." Edible Films and Coating for Food Applications, (NY: Springer Science & Business Media, LLC, 2009) 367-390.

[42] Baboo & Goswami, 2010, p. 139.

[43] Baboo & Goswami, 2010, p.59.

-made abrasive grinding wheels used in the crystal cutting and polishing industry.[44] Shellac was an ingredient in the making of gramophone records, until vinyl took its place.[45] As it is a natural, non-toxic resin, shellac can be used in the food industry as a coating for processed foods, fruits, candies, as well as for pharmaceuticals[46]. In the European system of food additives, shellac has been given the "E-number" of 904, and it is also FDA approved as a safe food additive in the United States.[47] One of the constituent acids of Shellac is aleuritic acid, from which many chemicals can be synthesized.[48] One of these chemicals is used in the perfume industry for its ability to microencapsulate, allowing a timed release of perfume in lotions and other beauty products.[49]

Lac Nomenclature

The word *Lac* is derived from the Sanskrit word, *laksha*, which means 100,000.[50] It is believed that the word refers to the large number of insects it takes to make a unit of finished shellac, and the word "lakh" is today used as a denomination for 100,000 units, frequently currency[51]. Indeed, it does take an estimated 50,000 beetles to produce about 1 Kg of finished shellac product.[52]

Laccifer Lacca

This productive insect was once known as *Tachardia Lacca*, named after Father Tachard, the Jesuit missionary who was the first to identify the beetle as the source of the resin, and record his scientific work on Lac and Lac products, in 1709.[53] Today, the Lac beetle

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[44] Baboo & Goswami, 2010, p.59.

[45] Mills, John Stuart, and Raymond White. *The organic chemistry of museum objects.* Oxford: Butterworth-Heinemann, 1994, p. 101.

[46] Greig, J. B., PhD. "WHO Food Additives Series 46: Cochineal Extract, Carmine, and Carminic Acid." May, 1998.http://www.inchem.org/documents/jecfa/jecmono/v46je03.htm (accessed 09/15/2010).

[47] Databasesør. Matvareguiden, "Oversikt Over E Nummere i Mat og Drikke." Last modified 2002-2012. Accessed May 6, 2012. http://www.matvareguiden.no/sider

[48] Greig, J. B., PhD. p. 141. & Rossman, 2009, p. 367.

[49] Rossman, 2009. & R. Singhania, personal communication, March 15, 2010.

[50] ILRI, *Lac a Monograph,* 1962, p. 1.

[51] Stappel, Matthias. "Schellack: Eigenschaften, Verwendung, Untersuchungsmethoden, Restauro." *Zeitschrift für Kunsttechniken, Restaurierung und Museumsfragen* 107, no. 8 (December 2001): 596-603.

[52] Baboo & Goswami, 2010, p. 4.

[53] Gardner, 1941, p. 265.

is classified as the *Laccifer Lacca*.[54] The Laccifer Lacca is in the Hemiptera order, known as a *true bug*, a soft scale insect in the Coccidae family.[55] The identifiable feature of the Hemipteran order of insects is their mouthparts, the *proboscis,* which can pierce plant tissue, and suck out the plant's sap.[56]

Location

By ways of nature, the Laccifer Lacca is a pestilent insect. While this insect can be found in many warmer climates, propagation and harvesting for economic gain occurs mainly in the forested areas of India, Thailand, and the People's Republic of China.[57] Since India currently supplies about 70% of shellac produced in the world, my investigatory travels and main focus will be limited to the areas of West Bengal, Bihar, and Madhya Pradesh, where a great part of India's harvest and processing takes place.[58] The *Laccifer Lacca* secretes the only animal-produced resin used commercially, and the tribal people living in the scattered rural villages in these areas have sought out trees infested by the Lac beetle, and gathered the resulting encrustations for generations. [59]

Life Cycle

The following section relies mainly on *Lac a Monograph*, pages 67-85, and is a brief description of the development and maturation of the *Laccifer Lacca.*

Starting out at the larval stage, the Lac beetle is also called a *nymph,* and is about 0.6mm long. There are both male and female insects, both of which hatch and crawl from the female beetle's Lac encrustation and immediately settle onto a fresh shoot of the host tree, using their proboscis to puncture the tender flesh of the young branch, in order to feed themselves. As the immature nymphs suck the tree's sap, they immediately exude a mixture of resin and wax through their bodies, forming a protective cell reminiscent of a

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[54] ILRI, *Lac a Monograph,* 1962, forword.

[55] Meyer, John R.. "Hemiptera." March, 2005. http://www.cals.ncsu.edu/course/ent425/compendium/homopt~1.html#life (accessed 09/15/2010).

[56] Meyer, 2005 (accessed 09/15/2010).

[57] Baboo & Goswami, 2010, p. 5.

[58] Baboo & Goswami, 2010, p. 6.

[59] Mantell, C. L. "The Natural Hard Resins-Their Botany, Sources and Utilization." *Economic Botany* 4, no. 3 (1950): 203-242.

cocoon. Male cells tend to form lengthwise on the branch, while female cells form across the length of the branch, and they can thus be identified. Within these cells, the insects moult several times before maturing, losing their legs, eyes and antennae along the way. While the male's eyes and legs grow back upon maturation, the female remains an amorphous shape, filling the entire space of her cell, only her back end being situated by an opening, available for copulation. Once mature, the males emerge from their cells; seek out and impregnate the females, shortly after which the male's mouthparts atrophy, and they die. After this stage of copulation, the female insects continue producing great amounts of Lac resin, and their cells become several times larger than those of the males. This production continues until the female's own eggs are mature, when she shrinks in size and lays her own larvae, which then hatch and escape, swarming new shoots to start the cycle anew. One female insect can produce between 300-1000 larvae. Because the insects settle so close together on the branch, the cells overlap each other, and there develops a continuous encrustation along the branches of the host tree.[60] [Image group 1]

Strains and Harvest Times

There are two main strains of Lac beetle used for the production of Lac in India, the Kusumi and the Rangeeni strains.[61] The Kusmi insect has the higher productivity of the two, its resin is the lightest in color, and considered the best quality in the world.[62] Not only are the two strains harvested at different times of year, but the maturation times of the beetles vary as well. Each strain has two harvest times a year, theoretically giving a total of 4 Lac harvests during a 12-month period. For the Kusmi strain, the *Jethwi* (June/July) harvest of crop started its life cycle in Jan./Feb., while the *Aghani* (Oct./Nov.) Lac harvest started its cycle in June/July.[63] For the Rangeeni strain, the *Katki* (Jan./Feb.) harvest started in June/July, while the *Baisakhi* (June/July) swarmed its host in Oct./Nov.[64] The names given to the harvest periods are the Hindi names for the

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[60] ILRI, *Lac a Monograph*, 1962, p. 67-85.
[61] Baboo & Goswami, 2010, p. 4.
[62] Baboo & Goswami, 2010, p. 4.
[63] ILRI, *Lac a Monograph*, 1962, p. 66.
[64] ILRI, *Lac a Monograph*, 1962, p. 66.

corresponding months, and some are echoed in the final names of the shellac produced, such as *Baisakhi* seedlac, sold by some manufacturers. By being familiar with the cycle of crops and harvest times, one can deduce that Baisakhi seedlac, for example, is of the Rangeeni strain of beetle, harvested in the month of June or July.

Although Kusmi Lac is considered to be of superior quality, Rangeeni Lac is produced 6 to-8 fold more than Kusmi, mainly due to the fewer numbers of Kusum trees.[65] An annual threat to the Baisakhi harvest of the Rangeeni strain of Lac on the other hand, is the heat of the summer months.[66] Lac beetles do not thrive in very hot and dry weather, and during prolonged periods of heat, large numbers of Lac insects may perish, affecting the Katki (Oct./Nov.) harvest of crop.[67] In fact, the beetles face several threats during the time of swarming, including frost, drought, winds, and rain.[68] With a traveling capacity of about 12 feet before being exhausted, if the nymphs do not find a lucrative spot on which to feed within the first day, they will become part of the 25% natural mortality rate of the brood.[69] In addition to meteorological concerns, parasites and predators also threaten the Laccifer Lacca. Parasites will insert a tubular egg-depositing appendage, called an ovipositor, into the Lac cells, and lay their eggs either in the cell cavity, or directly into the beetle's body, the larvae hatching and feeding on the surface of the Lac insect itself.[70] Predators of the Lac beetles are mainly moths, which in their larval or caterpillar state, eat both Lac and Lac beetles.[71] Additional threats to the Laccifer Lacca beetle today, are environmental issues such as the decrease in water table, higher levels of air pollution, abnormal changes in temperature due to climate changes, as well as deforestation.[72]

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[65] ILRI, *Lac a Monograph*, 1962, p. 67.

[66] ILRI, *Lac a Monograph*, 1962, p. 151.

[67] Ramani, R., PhD. "Climate Change and Lac Crop." 09/14/2010.http://ilri.ernet.in/~iinrg/dirdesk.html (accessed 09/28/2010).

[68] Parry, Ernest J. *Shellac, Its Production, Manufacture, Chemistry, Analysis, Commerce and Uses*. London: Sir Isaac Pitman & Sons, Ltd., 1935, p. 17.

[69] Parry, 1935, p. 17.

[70] Parry, 1935, p. 48.

[71] Parry, 1935, p. 51.

[72] Baboo & Goswami, 2010, p. 10.

Host Trees

In total, 113 trees are identified Lac hosts, and while 14 species are listed as 'common' hosts, only three are recognized as the principal hosts for Lac cultivation and as important in the commercial harvesting of Lac in India.[73] The main Lac hosts in India are; *Kusum* (Schleichera Oleosa) [Image group 2], *Ber* (Ziziphus Mauritania) [Image group 1], and *Palash/Dhak* (Butea Monosperma) [Image group 3].[74] This is also the case in the areas of West Bengal, Bihar, and Jharkhand. Host trees do have an impact on the quality and quantity of the resin produced. In determining what conditions make for a good Lac host, qualities such as *sap-reactions* (amount of sap secreted by the host when pierced by beetle), or *sap-density* are mentioned, as well as having a sap Ph range between 5.8-6.2.[75]

Kusum

As previously mentioned, the Kusmi strain of Lac beetle settles on the *Kusum* tree. The *Kusum* is a deciduous tree with red leaves, a hardy tree found in well-drained soil.[76] Because it yields greater amounts of Lac, as well as seedlac with the lightest natural color, the *Kusum* is considered to yield the best quality shellac.[77] [Image group 2]

Ber

The *Ber* tree hosts the *Rangeenie* strain of the Lac beetle. It thrives in poor and dry soil, making it an important species for an ecosystem facing prolonged drought and heat periods.[78] In addition to being a Lac host, the *Ber* also produces a small, wild plum. [Image group 1]

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[73] ILRI, *Lac a Monograph,* 1962, p. 19.
[74] Baboo & Goswami, 2010, p. 4.
[75] ILRI, *Lac a Monograph,* 1962, p. 53. & Baboo & Goswami, 2010, p. 4.
[76] ILRI, *Lac a Monograph,* 1962, p. 29.
[77] ILRI, *Lac a Monograph,* 1962, p. 67.
[78] ILRI, *Lac a Monograph,* 1962, p. 30.

Palash

The third and most important host, also of the *Rangeenie* Lac strain, is the *Palash* tree.[79] [Image group 3] This tree was recognized as a host for the Lac beetle by the aboriginal tribes in India, with literary references in early Sanskrit.[80] Although the resin produced is of lower quality than both the *Kusum* and *Ber*, the *Palash* tree accounts for the bulk of India's Lac production.[81] Recognizable by its large orange flowers, the *Palash* is also known as the *Flame of the Forest*.[82] The *Palash* tree manages in a variety of soil qualities, making it very versatile.[83] In addition to hosting Lac beetles, the *Palash* is regarded as a sacred tree, its flowers harvested and used for medicinal purposes, as well as during religious rituals and ceremonies.[84]

Cultivation and Harvest

When a farmer wants to start the cycle of Lac cultivation, he or she obtains *broodlac* for the specific host tree and strain that is desired. *Broodlac* is a section of stick from a host tree, encrusted with Laccifer Lacca eggs that are mature and ready to crawl. The *broodlac* is tied to an appropriate tree, and the Lac beetle swarms its host, the tree selected by the cultivator. [Image group 4]

If needed, the Lac crop can be prematurely harvested, while the beetles have not reached maturation, and the encrustations have not yet reached maximum size. This product is termed *Ari.* The farmer may do this because there is an immediate need for income. Premature harvesting results in a smaller crop, overall. This practice also leads to a more pressing need for *broodlac* at a later stage.[85] *Broodlac* can be purchased at the market or saved by the cultivators themselves, although storage can be difficult. Some larger shellac processors, such as *Tajna Industries*, have developed their own orchards with infested

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[79] ILRI, *Lac a Monograph,* 1962, p. 25.
[80] Gardner, 1941, p. 264.
[81] ILRI, *Lac a Monograph,* 1962, p. 25.
[82] Russell, 1965, p. 6.
[83] ILRI, *Lac a Monograph,* 1962, p. 25.
[84] Himalaya Herbal Healthcare, "Herbal Monograph." Last modified 2002. Accessed April 5, 2012. http://www.himalayahealthcare.com/herbfinder/h_butea.htm.
[85] Haat at Bandagar, with Dr. Govind Pal (IINRG), November 24th, 2010.

hosts, in order to provide *broodlac* to local villagers.[86] As a measure in fostering a more predictable harvest, and thus providing a more predictable supply of raw material for the processors themselves, this system provides brood for farmers to infest the appropriate host trees in a more managed cycle of production.[87] By taking advantage of this reciprocal relationship, villagers can more easily concentrate on groves of trees in close proximity, and tend to the trees, providing preventative pesticides, pruning and resting periods between harvests, so not to wear the trees down. The beetles' life cycles theoretically yield two harvests of sticklac a year. For the health of the host, however, a resting period of about six-months is encouraged. As the beetles settle on the young shoots of a tree, these will be pruned off at harvesting time. A resting period allows new shoots to spring forth without straining the host unduly. [Image group 2]

Lac as a Cash Crop

Lac is a very important cash crop for the rural and tribal people in the forested areas of India. There are few options for farmers to earn money while remaining in these areas. Some cultivate vegetables, some make handicrafts or other saleable items, while others yet are forced to move into the cities and take labor jobs. Of all these options, Lac gives the best return as a cash crop option for the farmer. See Appendix 3 for a current price spread, provided by PRADAN. Men and women can equally cultivate the crop, and both receive the same price when selling at the market.[88] Organizations such as PRADAN, as well as the IINRG, and the IFP (Institute of Forest Productivity) educate cultivators and small-scale processors on responsible practices regarding production, and processing, while protecting the fragile ecosystems in which they live and on which they depend.[89]

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[86] Tajna Industries is located in Khunti, by the Tajna river, outside of Ranchi, in the state of Jharkhand. Started as an export house in 1984, it has grown during the course of the past 28 years, to employ over 200 tribal workers. The processing facility has the capacity of producing many types of shellac, but focuses on a high quality of bleached shellac, for which it has an exclusive contract with Kane International Corporation, who distributes shellac mainly for food coatings. (http://kaneinternational.com/shellac/)

[87] Roshanlal, Tajna Industries, personal communications, Khunti, India. November, 2010.

[88] Dr. Govind Pal (IINRG), Haat at Bandagar, November 24th, 2010. & PRADAN, informational brochure.

[89] Baboo & Goswami, 2010, p. 9.

Chain of trade

To sell their Lac crops, cultivators and farmers bring their product to a roadside market. [Image group 5] They sell their product to market agents, called *Paikars*, bringing between 2-10Kg to market, depending on their need for cash. The *Paikar* sits at the weekly markets, gathering sticklac from the farmers in the area. He then bags it, and brings it on to either a block agent/large trader, or directly to a processing unit. [Image group 6]

According to PRADAN, there are 250 small markets and 25 large markets nationwide, in which shellac is sold. The chain of trade can be broken down the following way:

<u>Cultivators/Lac Farmers</u>- Lac farmers are often tribal men and women who live in remote forested areas, and rely on forest-based livelihoods. They have few transportation possibilities of their own, giving them little or no bargaining power. Different tribes will sometimes specialize in a certain type of Lac, depending on available hosts, and the cycle of life in that specific area.[90]

<u>Haat (small market) Paikar</u> **-** The Haat Paikar has contact with cultivators/farmers and gathers product either from small local markets (haats), or by going village-to-village, acquiring product directly from the harvesters. Some malpractices by the paikar, such as incorrect weighing and adulteration of the product, have been reported.[91] The Haat Paikar functions as a collector and as a middleman, between the farmer and the *Block Paikar***.**
[Image group 6]

<u>Block Paikar/Agent</u> **-** Usually a somewhat wealthy intermediary between transporter and processor. This person has information about both supply and demand, giving him the possibility to manipulate the market. The Block Paikar provides transportation, sending agents to the large market with the raw material, which he has gathered from the Haat Paikars. Sudden swings in the market can occur because the Block Paikar is using his

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[90] Jose, J.K. *A Study on a Sub-sector Value Chain Analysis of Lac*, under PRADAN Jharkhand. Xavier Institute of social service, Faculty of Rural Development. Ranchi, Jharkhand: 2010, Ch. 5.

[91] Jose, 2010, Ch. 5**.**

information to manipulate supplies or demands in the market.[92]

Processors - Shellac processors vary in size and capacity. Larger units export their product directly to the international market, while others sell their product to exporters at the large markets. Processors run their own factories, either by traditional or modern methods, and do not usually speculate in prices, as they benefit from both a stable supply and demand of product.

Exporters –Are almost always also larger processors, and have a good overview of what is happening on the international market. Lac exporters procure processed Lac from regional markets and factories, and export them via the Kolkata port, to the main destinations of Western Europe, North America, and Southeast Asia.[93] There are a total of 11 large exporters of Lac in India, but a tradition of mistrust and a tendency to undercut fellow exporters, has kept this group from forming a cartel.[94]

Demand

The marketing and export council *SHEFEXIL* (Shellac and Forest Products Export Promotion Council) promotes shellac and Lac based products throughout the world, and also functions as an umbrella organization for issues concerning Lac export and sales from India.[95] Internationally, there is a 40,000mt (metric tonnes) annual demand for shellac: the worldwide production of Lac is at 30,000mt, while India generally supplies about 20mt of this amount.[96] There are often fluctuations within the supply and demand of Lac, because speculators make money by artificially manipulating the market.[97] The Lac farmers have experienced a wide variance in price over the last years, ranging from 50 INR to 300 INR per Kg of raw product. These fluctuations are demoralizing for the

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[92] Jose, 2010, Ch. 5.

[93] Jose, 2010, p. 52.

[94] Jose, 2010, p. 53.

[95] Baboo & Goswami, 2010, p. 9. Also, Shellac Export Promotion Council, "The Export Facilitator." Last modified 2003. Accessed April 1, 2012. http://www.shellacepc.com/.

[96] Govind Pal, Dr., Jaiswal, A.K, Dr., Battacharya, A., Dr. *Lac Statistics at a glance, 2009*. Indian Institute of natural Resins and Gums, Namkun, Ranchi, India: 2009.

[97] B. Abraham, Informational presentation, PRADAN, Ranchi, India. November 19, 2010.

farmer, and create instability around Lac production in general.[98]

Determining market value

To determine the quality and prices for Lac, the large markets have a regulatory board, which oversees transactions. An agent transports the raw material to the market, and the Lac is separated by type, such as *Rangheenie*, and *Kusmi*. The strains are harvested at different times of the year, and they are easily distinguishable to the trained eye. To determine the price for the raw product from the market, 6 random samples are taken from a truckload, mixed and then arranged in a circle (ca. 30cm diameter). This circle is divided into two halves. The one half of this circle is tested, while the other is kept in a locker with the agent's information. The sample is weighed. The testing consists of processing the raw material into seed Lac, and then being weighed again. The loss differential between products is calculated, and the percentage of seed Lac gleaned from the crude product is considered to be the resin content, or *Chowri*, of the raw, usable material. This resin content is then reported and a price is given according to that content. If the agent believes this report to be inaccurate or false, he can turn to the regulatory board of the market. The other part of the sample is then tested, and compared to the first results.[99]

Yield

As mentioned earlier, the yield of product is different, depending on Lac strain, harvest time, and host tree. Using information from the Indian Lac Research Institute, the yield from sticklac to seedlac is presented in the following table.

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[98] Abraham, 2010.

[99] Abraham, 2010.

Table 3: Yield of seedlac

Crop	Yield of seedlac as % of stick Lac
Baisakhi	63.4
Jethwi	70.1
Kusmi	68.7
Katki	59.7
Average yield:	63.1

(ILRI, *Lac a Monograph,* 1962, p. 280.)

Information relayed from visiting several small processing units in the area reported that from 40 Kg Kusmi seed Lac, the yield is 38 Kg finished buttons. For Rangeeni, it is slightly less; 40 Kg seed Lac yields 35 Kg finished buttons. However, there is very little loss between the seedlac stage, and the finished product with yield rates near 90%.[100]

Jharkhand State Co-operative Lac Marketing and Procurement Federation Ltd. helps cultivators receive fair pricing for their product, and the *Tribal Co-operative Marketing Development Federation of India Ltd.* focuses on sustainable produce possibilities for tribal communities, assuring fair market pricing.[101]

Observations in the field

During fieldwork at the IINRG, several markets as well as processing plants were visited in West Bengal, with Dr. Govind Pal. As an economic scientist at the IINRG, Dr. Govind Pal's main task is to gather statistics regarding the trade, cultivation, import, export and production rates of Lac. This information is then published yearly, under the direction of the agricultural department. Dr. Govind Pal visits local *Haats,* or markets, where he speaks with paikars (traders) and farmers, gathering information by survey, on the quantities produced, as well as the fluctuating rates of Lac. The Bandagar area is known for having fair market prices, the Paikar adding 3-5 INR/Kg mark up when reselling the product. In addition to interviewing the Haats, Dr. Govind Pal also visits shellac-processing plants. There are a total of 180 processing units in India, and he visits about

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[100] Dr. Govind Pal (IINRG), Field trip to visit processing units, West Bengal. November 25th, 2010.

[101] Baboo & Goswami, 2010, p. 9. See www.jascolampf.com, and www.trifed.co.in for more information.

40 plants regularly.[102]

Insect Mortality

During the harvest season in 2010, the Rangheenie crop yielded very poorly in the Jharkhand area. This was due to a prolonged heat wave, lasting 4 weeks, as opposed to the customary 2 weeks. This dry heat made conditions intolerable for the Lac insect during a crucial period of development, resulting in high insect mortality.[103] As a result, the price of sticklac increased 5 fold. This fluctuation leads to the perception that Lac is an unstable crop, making farmers less enthusiastic about cultivating it.[104]

Since the Rangheenie strain in the Jharkhand area largely failed during the 2010 *Baisakhi* season, the majority of Stick Lac at market was Kusmi; meaning the Kusmi strain of beetle, on the Kusum tree. The strains have characteristics that make them easily distinguishable, visually. Kusmi sticklac has larger, golden encrustations covering the stick it was made on, with intermittent cavities of crimson. The color is lighter, often with a white fuzzy layer on the exterior, which is a remnant of the waxy filaments excreted by the female beetle while still on the branch of the host tree.[105] The kusmi nuggets of sticklac are larger, without clumping together. Rangeenie sticklac is darker in color, and often clumps together, resembling lumps of dirt, or mulch. There is not the same amount of visible white waxy filament on the exterior.[106] [Image group 7]

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[102] Dr. Govind Pal (IINRG), Haat at Bandagar, November 24th, 2010. & Dr. Govind Pal (IINRG), Field trip to visit processing units, West Bengal. November 25th, 2010.

[103] Ramani, R., PhD. "Climate Change and Lac Crop." 09/14/2010.http://ilri.ernet.in/~iinrg/dirdesk.html (accessed 09/28/2010).

[104] Dr. Govind Pal (IINRG), Haat at Bandagar, November 24th, 2010, B. Abraham, Informational presentation, PRADAN, Ranchi, India. November 19, 2010.

[105] Russell, 1965, p. 7.

[106] Dr. Govind Pal (IINRG), Haat at Bandagar, November 24th, 2010.

Chapter 3

Processing Techniques

Introduction

Shellac products vary in color and wax content. Processors can have a range of products varying in color from the darkest *garnet*, to the clearest bleached *platina*. In addition, the wax content varies from the naturally waxy lemon grade, to the de-waxed super blonde. [Image 8]

Accompanied by Dr. Govind Pal, I visited several shellac processors in Balrampur. The Balrampur area has 142 small processing units or *arhatiyas*, producing button Lac, or hand stretched shellac. These manufacturers use the *bhatta,* a coal fired clay oven, as a melting source. There are 15 larger processors in the area, which have steam-heated melting machines, incorporating a heated roller to make machine made shellac flakes.[107]

When Lac is harvested, the encrusted branches of the host tree are removed, and the Lac is scraped or broken off the discarded branch, becoming s*ticklac*. [Image group 7]
This sticklac changes hands at the market, and is brought to a processor, where it is ground in a coarse grinder. These particles are washed and sorted, yielding *seedlac*. The wet seedlac is spread out in the sun to dry, and after this point, the process either follows traditional methods, or goes on to various modern treatment methods.

Traditional Methods

Sticklac to Seedlac

Sticklac is obtained either from a *paikar*, or a *block paikar*, and brought to the processing unit. Here the sticklac is sifted, and put through a crusher, to obtain the optimum seedlac size. The crusher is either powered by a hand crank, or connected to a motorized power source. If a crusher is not available, this stage is done with a millstone, or by pounding the sticklac between two stones, by hand.[108] The particles of Lac are then cleaned with a soda ash solution (Na_2CO_3) to wash out insect and wood remnants as well as the water

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[107] Dr. Govind Pal (IINRG), Haat at Bandagar, November 24th, 2010.
[108] ILRI, *Lac a Monograph*, 1962, p. 157.

based dye materials in the Lac. Some units may still use traditional washing methods, where stone or cement vats, or *nands*, are filled with Lac and water. A worker called a *ghasandar*, or *rangkaria*, steps into the *nand*, and uses his feet to rub the Lac against the sides, scrubbing and cleaning the Lac. [Image group 9] After 10 or 15 minutes, the Lac grains sink to the bottom of the vat, while wood particles and other impurities float to the top, and are scooped out with a sieve.[109] At a more modernized plant, the Lac will be fed into an industrial sized mechanical washing machine after crushing. [Image group 10] Soda ash will be added in order to soften and separate wood pieces, and remove Lac dye and insect remnants from the resin-wax mixture. Differing amounts of water, time, and soda ash are used to obtain various end results of color, since more or less of the Lac dye is washed out of the seedlac at this stage. One lot (washing barrel full) of sticklac is about 480 Kg. This sticklac is flooded with 2000-2500 liters of water, and 1-2Kg of soda ash. The washing time varies from 2-4 hours, depending on the desired quality of the end product. A higher quality (more refined) product requires more water, more soda ash, and more washing time. [Image group 10] In the processing units I visited, three qualities where obtained by varying these elements;

-*Best quality*. Lightest in color, takes 4 hours washing time, sold for 750 INR/Kg at the time of my visit.

-*Medium best*. Medium color, takes 2.5-3 hours washing time, sold for 600 INR/Kg at the time of my visit.

-*Lower best*. Fuller color, takes 2 hours washing time, sold for 550 INR/Kg at the time of my visit.

All three of these qualities of product are used for making varnish for finishing purposes. According to the processors, the durability and performance properties are the same for all three grades of shellac, as it is only the Lac dye that is washed out in the cleaning process, changing the color of the finished product.

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[109] ILRI, *Lac a Monograph*, 1962, p. 157.

Seedlac

The material that emerges from this crushing and washing process resembles small seeds, and is called *seedlac*. The seedlac is then spread out on the cement floor to dry in the sun. [Image group 11] When dry, the seed Lac is sifted with woven basket-like tools, later sorted into piles according to size and grade. Seedlac is graded on the basis of color, and the amount of insoluble impurities when dissolved in hot alcohol.[110] According to information from the Indian Lac Research Institute, there are recognized standards of grading handmade (HM) shellac in the Kolkata market, presented in the following table.

Table 4: Recognized standards of grading HM shellac

Seedlac *becomes*	*Hand made shellac*
Nr. 1 Kusmi Seedlac	Superior Lemon/Lemon Superfine
Nr. 2 Kusmi Seedlac	Lemon nr. 1
Fine Baisakhi, Manbhum	Lemon nr. 2
Fine Katki, Manbhum	Standard 1
Seedlac under 5% (insoluble material)	TN*
Seedlac ordinary 5-7% (insoluble material)	4% ITN

**TN was the mark of an important trader, and is the oldest standard of shellac recognized in the world market, meaning that the product is handmade, of the Baisakhi crop.*
(ILRI, *Lac a Monograph*, 1962, p. 266.)

Polishing with Oxalic Acid

At the seven processing units visited during fieldwork, many of the various qualities of seedlac were "*polished*" with *oxalic acid*, in order to lighten the color, and make the product *shine* more brightly. This is done by dissolving 100gr Oxalic acid crystals in 2L of water, and mixing this solution into 40Kg seed Lac by hand, on the floor. The seed Lac with the oxalic acid is then again spread out on the cement floor, to dry in the sun. The oxalic acid is not removed or washed out of the product. The consequences of adding oxalic acid will be discussed in part 2 of the paper, where the chemistry of Lac will be explored.

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[110] ILRI, *Lac a Monograph*, 1962, p. 266.

Hot Filtration Method

When the seedlac is dry, it can be processed into shellac, either button or flake, by the *hot filtration method*. For the handmade process, the heat source is a furnace/oven built of local clay, and heated with coal, called a *battha*. The filter in this process is a densely woven cloth bag, filled with seedlac.

A daily production/lot for one *bhatta* is about 40-60 Kg of product. One lot takes about 25Kg of coal a day, and coal costs 11-12 INR/Kg. It takes three to four people to run a *bhatta*. The person turning the wooden wheel is called the *pheraya* (piraya), and makes about 2 USD a day. The person who sits by the fire and makes the buttons is called the *karrigar*, and he makes about 3 USD a day. If hand stretched shellac is on order, the stretcher is called the *belwaya* (bilwaia). The person in charge of filling and preparing the cloth bag/filter is called the *khalifa*.

The *bhatta* oven radiates all its heat outward, toward the cloth bag. The canvas bag, about 25cm in circumference and about 15-20 meters long, is filled with seedlac through a funnel, a *bharna*. This tube is then stretched across the length of the location, with the *bhatta* oven and the *karrigar* on one end, and on the other end, there is attached a wooden wheel, the *charki*. [Image group 12] The *pheraya* slowly turns this wheel, creating a torque. At the “hot end” of the tube, are the clay *bhatta* oven and the button maker, the *karrigar*, who is seated at the fireside. The seedlac inside the bag starts melting at around 75-80 degrees Celsius. The *karrigar* holds the end of the bag, regulating the pressure, as well as the exposure to the heat, splashing water onto the mass if it gets too hot. A wooden support, called a *khoonti*, holds the canvas bag above ground, and allows it to slowly rotate in front of the fire. As the seedlac heats and melts, it seeps through the bag, the canvas acting as a filter. The molten Lac comes through, while the impurities such as wood and insect remains, stay inside the tightly twisted bag. A stone slab in front of the fire is kept wet, so it can help cool the molten Lac, without the resin sticking to the surface.

Buttonlac

When the molten Lac starts coming through the cloth, the *karrigar* scrapes it off the outside of the bag with a u-shaped metal tool, the *kurni*, gathering it up and placing small dollops of melted resin on a metal sheet, to cool. Kusmi buttons are made slightly smaller in size than other types, but buttons are roughly 8cm in diameter. The *kalligar* has an assistant, who quickly brings him new metal sheets, called *khola*, after having stamped the buttons with the factory seal and grade, and let them cool before popping them off the metal sheets, and onto the cement floor. [Image group 12]

Hand-Stretched Shellac

If hand-stretched shellac is on order, the *kalligar* gathers the appropriate amount of molten Lac off the canvas tube, and hands it to the stretcher, the *belwaya*. The *belwaya* has a large ceramic tubular vessel, the *pipa,* which is filled with boiling water and corked. The molten mass is transferred onto this tube to keep warm, and manipulated and stretched with a *nera, a* long and broad palm leaf dipped in water, spreading the mass out over the tube. When the mass is the required size and thickness, the *belwaya* peels it off the tube and starts working with his hands and feet, sometimes using his teeth to pull and prod the sheet to the required thickness. When needed, the *belwaya* will heat the sheet of Lac by the fire, enabling it to stretch into the desired shape and thickness, until he has a sheet as large as his body stretched out in front of him. These sheets are left to cool and become brittle, after which they are broken into flakes, and later packaged as shellac. [Image group 13]

Secondary Products

Kiri

After a while, the flow of molten Lac coming through the canvas bag starts slowing due to the accumulation of wood debris and other impurities clogging the pores of the bag. The *karrigar* will then lengthwise split the bag open, and remove the remaining mass, making it into flat, round discs, called *kiri*. These discs are mostly exported, and contain between 50 and 60% Lac.[111] Garnet buttonlac is made from *kiri*, by the solvent method, and will be covered later in this section.

Passewa

When the canvas filtration bag is twisted tightly and cooled, it becomes stiff and looks like a stick, and it is called a *danri*. To recover the resin still in the *danri*, the bags are boiled in a kettle, with water and soda ash. [Image group 14] The melted Lac floats up and is removed from the kettle, being pressed into cakes between the palms, and called *passewa*. *Passewa* can be used to make inferior grades of shellac, by being ground up and added to seedlac in varying proportions.[112] The waste product that is washed out of the bags is recovered and used for making handicrafts or other domestic articles. [Image15] The tubes used as filters can be mended and reused 3-4 times.

Lac Dye

Laccaic acid, or Lac dye, is a natural alternative for coloring food and beverages today, and was once the main product gleaned for export from the cultivation of Lac, used for dying natural fibers of wool or silk. The dyestuff is present in the body fluid of the Lac beetle, and soluble in the alkali solution of the wash water with added soda ash (sodium carbonate, $Na_2CO_{3,}$ pH 11.4) used for the cleaning of *seedlac*.[113] Lac dye quickly deteriorates in alkali solution, but can be recovered from the wash water by acidifying the solution, and letting the precipitate settle, after which the sludge is thrice boiled and treated with calcium carbonate ($CaCO_3$).[114] The calcium salt of the dye is kept in water at room temperature for seven to ten days, when the dye crystallizes out, and it can be washed out and dried, yielding approximately 0.5% of the weight of the original sticklac.[115] [Image16] Many small processing units do not have the capabilities of recapturing laccaic acid from the wash water, and it is channeled into the fields to enrich

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[111] ILRI, *Lac a Monograph*, 1962, p. 164.

[112] ILRI, *Lac a Monograph*, 1962, p. 164.

[113] Baboo & Goswami, 2010, p. 44.

[114] Baboo & Goswami, 2010, p. 45-46.

[115] Baboo & Goswami, 2010, p. 46.

crops, having some value as a fertilizer.[116]

Modern Methods

Machine-Made Shellac

If the processing unit has more modern machinery, the sticklac will be washed, sifted and crushed by motorized machines to yield seedlac, then spread to dry in the sun. The melting process, however, happens by steam jacketed heating elements, and the molten mass is pressed through a cloth filter. The melting vessels are square, about 1meter by 1meter. Steam is applied at 150 degrees Celsius, and the molten Lac is pressed through a square piece of canvas cloth attached to the melting vessel's edge. [Image group 17] The molten mass of Lac is transferred to a heated vat, which siphons a determined amount, pressing it through to steam-heated rollers, which roll out a thin sheet of shellac. The system can be adjusted to make a specific thickness of flake. As the sheet of shellac comes off the roller, it is grabbed by a *runner*, and whisked across the room, where it is hung over a line to cool and become brittle. [Image group 18] These sheets are later broken into flakes and packaged as machine made shellac. At the time of my visit, the price for machine made orange flake was about 450 INR/Kg, while hand stretched costs 475 INR/Kg. This method of producing machine-made shellac was originally adapted by the Angelo Brothers, in 1898.[117]

Bleached Lac

Another method developed in the 1800s, was the bleaching process, yielding a product capable of producing an almost clear finish. In order to remove the color component in Lac that is not water-soluble, and thus not washed away during the sticklac to seedlac process, Lac may be bleached with sodium hypochlorite (NaClO).[118] Although the first

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[116] Parry, Ernest J. *Shellac, Its Production, Manufacture, Chemistry, Analysis, Commerce and Uses*. London: Sir Isaac Pitman & Sons, Ltd., 1935, p. 151.

[117] Russell, 1965, p. 47.

[118] Baboo & Goswami, 2010, p. 19.

reports of bleaching Lac are from the 1830s, the process is fairly technologically advanced, and requires a processing unit skilled in the chemistry involved.[119] The main uses of bleached shellac today is as an edible food coating, and for pharmaceutical purposes, as an enteric coating which delays the release of medication before the medicated pill reaches the relatively alkaline environment of the small intestine.[120] As mentioned above, the IINRG reports that nearly 50% of shellac consumed by the world market today, is bleached Lac.[121]

Bleaching Procedure

After dissolving seedlac in a hot solution of water with sodium carbonate at 85 to 90℃, the solution is filtered and bleached with a bleach liquor, added a small amount at a time.[122] Cooling the liquid to 20℃, the bleached Lac is precipitated by adding a thin stream of 5% sulfuric acid (H_2SO_4), after which it is washed repeatedly in cold water, and dried until it contains no more than 2% moisture.[123] The Lac precipitated in this manner is in the form of a white powder. During the bleaching process, the sodium hypochlorite causes changes in the molecular structure of the shellac, resulting in a shorter shelf life and lowered durability of the finished product.[124] This effect will be discussed further in part 2 of the paper.

If dewaxed bleached Lac is desired, the seedlac and soda solution can be boiled, in order to melt the wax, letting it float to the top to cool, and later breaking it up and ladling it off.[125] A less time consuming method is to treat the boiled solution of seedlac and soda with Stoddard solvent (mineral spirits).[126] The solvent dissolves the wax, and as the wax

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[119] Russell, 1965, p. 41.

[120] Minina, S.A, L.S Efimova, N.V Abramova, V.D Raisyan, and A.S Bril. "Development of an Intestinally Soluble Coating Based on an Aqueous Shellac Solution." Pharmaceutical Chemistry Journal. 12. no. 2 (1978): p. 256.

[121] Baboo & Goswami, 2010, p. 19.

[122] Baboo & Goswami, 2010, p. 19.

[123] Baboo & Goswami, 2010, p. 19.

[124] Mantrose-Haeuser Corp., *Shellac Technical Guide*, Zinsser Group, Westport, CT (no date), p.6.

[125] ILRI, *Lac a Monograph*, 1962, p. 192.

[126] ILRI, *Lac a Monograph*, 1962, p. 192.

and solvent layer separates out and rises to the top of the Lac resin and alcohol solution, it allows the lower layer to be siphoned off.[127]

Solvent Process

With the solvent method of refining Lac, dewaxed or decolorized shellac is produced without bleaching. This method requires the technological ability to reclaim the solvent after the process, as the Lac is dissolved in hot alcohol.[128] After the Lac is dissolved, the impurities are allowed to settle, and the resin and alcohol solution is transferred into a closed vat, where the alcohol is boiled out, and reclaimed for future use.[129] The resin is then passed through a series of evaporators, until no alcohol remains, and the molten Lac is stretched and rolled out into sheets, let to cool, and later broken into flakes or buttons.[130]

Determining Wax Content

An advantage to the solvent method is that a variety of wax contents can be achieved, merely by adjusting the strength of the alcohol used during processing.[131] Shellac wax is only partially soluble in alcohol, and most of it is merely suspended in solution when the resin is dissolved in spirits.[132] By using a weaker alcohol, at a lower temperature, less of the wax dissolves, and is left at the bottom of the dissolving vessel, along with other impurities.[133] The following table shows the relationship between the concentration of alcohol used and the final wax content.

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[127] ILRI, *Lac a Monograph*, 1962, p. 192.

[128] Sen, H.K., and M. Venugopalan. *Practical Applications of Recent Lac Research* (Revised and Enlarged). Calcutta: Orient Longmans Ltd., 1948, p. 3.

[129] Sen & Venugopalan, 1948, p. 5.

[130] ILRI, *Lac a Monograph*, 1962, p. 171. For more details on solvent processing, consult Farag, 2010, p.11.

[131] ILRI, *Lac a Monograph*, 1962, p. 173.

[132] Baboo & Goswami, 2010, p. 55.

[133] Sen & Venugopalan, 1948, p. 5.

Table 5: Alcohol concentration determining wax content

Alcohol strength (Over proof-UK)	Proof (USA)	Alcohol by volume	Final wax content
40	140	70%	1.8%
45	145	72.5%	2.3%
50	150	75%	3.1%
55	155	77.5%	3.8%
60	160	80%	3.8 to 4.5%

(ILRI, *Lac a Monograph*, 1962, p. 173.)

To make fully dewaxed shellac, however, one must physically separate out the remaining wax, by filtering the mixture through a fine cloth.[134] The solvent method is employed when making Garnet, which is refined from *Kiri*, a by-product reclaimed during the heat processing of Lac.[135] Garnet buttons are darker in color, due to the higher concentrations of dyestuffs that are trapped within the filtration tube used during the heat filtration process.

Decolorized Lac

When processing Lac by the solvent method, the coloring matter, erythrolaccin, can be removed by using activated carbon filters.[136] This process is more efficient when performed at high temperature, and with few alcohol-soluble impurities present, so not to unduly clog the surface of the carbon.[137] It therefore stands to reason that de-colorization by this method is carried out on dewaxed product only.

Grading Lac Products

The Name or grade of seedlac and shellac products depends on the color of the final product. The product's color is given a color number, obtained by determining its color by the *Iodine method.* Below is the method used to determine the color number, as described by the Indian Lac Research Institute:

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[134] Russell, 1965, p. 49.

[135] Russell, 1965, p. 49.

[136] ILRI, *Lac a Monograph*, 1962, p. 177.

[137] ILRI, *Lac a Monograph*, 1962, p. 177.

10gr of shellac (or 10.5gr of seedlac) is dissolved in a test tube with 100ml of alcohol (95%). Impurities are filtered out. An Iodine solution (0.005N solution of iodine in KI solution) in a similar test tube is compared to it, adding alcohol to the Lac solution until the color matches between the two. The added volume (in ml) of alcohol plus "5" is the color number.[138]

Without decolorizing, if one starts with Kiri, the final product will be a Garnet Lac, with a color number between 25-40.[139] However, if one decolorizes the product, one can arrive at the color of Dewaxed Orange, which has a color number of 15.[140] Dewaxed Orange shellac is usually produced from Bysaki seedlac with a natural color number around 15, while Dewaxed Lemon is from Kusmi seedlac with a color number of about 7.[141] Decolorized shellac will have a color number between 0.9-5.0, with the most decolorized product having been subjected to successive treatments of activated carbon.[142] Bleached shellac is considered colorless, or very pale yellow.

Table 6: Shellac specifications

	Traditional	Machine-made		Bleached	
Analysis	Hand made	Orange	Wax-free	Regular	Dewaxed
Moisture %	1-2.0	1-1.5	1-1.5	3.0-6.0	3.0-6.0
Wax%	4.0-5.0	4.0-4.5	0.1-0.2	4.0-5.5	0.1-0.2
Ash%	0.5-1.0	0.3-.05	0.1-0.4	0.5-0.7	0.3-0.5
Alc. Insol%	1.5-3.0	0.1-0.5	0.1-0.2	0.5-0.7	0.1-0.2
Arsenic, ppm	-	1.4	1.4	1.4	1.4
Chlorine%	-	-	-	1.5-2.7	1.0-2.7
Rosin	-	None	None	None	None

(Baboo & Goswami, 2010, p. 161, Martin, p. 465)

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[138] ILRI, *Lac a Monograph*, 1962, p. 340.

[139] ILRI, *Lac a Monograph*, 1962, p. 174.

[140] ILRI, *Lac a Monograph*, 1962, p. 174.

[141] ILRI, *Lac a Monograph*, 1962, p. 174.

[142] ILRI, *Lac a Monograph*, 1962, p. 174.

Through detailing the processing methods of shellac, we can see that there are substantial differences in how the product is refined. While some buttons go through a minimal coal-heat and melting procedure, other Lac products are exposed to solvents, bleaching and water-washing before being precipitated from solution as a powder. The traditional methods of hand processing yield buttons and hand-stretched varieties of shellac, all melted by coal-burning fire, and containing wax. The color grade of traditionally processed Lac is determined by type and quality of Lac crop, as well as some variances within washing time, or the addition of oxalic acid. From partially industrialized units, MM shellac is melted with the help of steam, and rolled into much thinner flakes than the hand stretched variety. An advantage of these thin flakes is that they dissolve more quickly into solution, and because the wax is more finely disbursed, machine-made shellac has a higher viscosity than traditionally processed shellac.[143] Industrialized units have the possibility of reclaiming solvents, giving the possibility of controlling wax content, either by filtration, or by manipulating the strength of alcohol used during processing. Lac Dye can also be reclaimed from the washing water. In addition, color can be removed by activated carbon filtration, or by bleaching with sodium hypochlorite. Part 2 will investigate how these varieties of shellac may behave differently, and whether differences are detectable by methods of analysis.

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[143] Martin, p. 463.

Images Documenting the Processing of Shellac.

Image group 1: Ber host tree.

Image group 2: Kusum host tree.

Image group 3: Palash host tree.

Image group 4: Broodlac on host.

Image group 5: Sticklac at market.

Image group 6: Market paikar.

Image group 7: Sticklac.

Image 8: 10 shellac samples showing a range of shellac products.

Image group 9: Traditional cleaning of sticklac.

Image group 10: Mechanized crushing and washing.

Image group 11: Drying, winnowing and grading seedlac.

Image group 12: Traditional buttons.

Image group 13: Hand stretching shellac.

Image group 14: Cleaning and reusing cloth tubes.

Image 15: Resin for handicrafts.

Image 16: Lac dye.

Image group 17: Filtering method for MM shellac.

Image group 18: MM shellac.

[1]

Image group 1: early stage inoculation of a Ber host tree. Notice the white wax filaments, as well as the small red plum fruit above the insert. Insert shows a more developed encrustation on the same tree.

[2]

Image group 2: The Kusum tree in the foreground has been pruned after harvest, while the dark red foliage is still present on the tree in the background. Insert shows a Lac nugget from the tree. Notice the deep purple Laccaic acid residue.

[3]

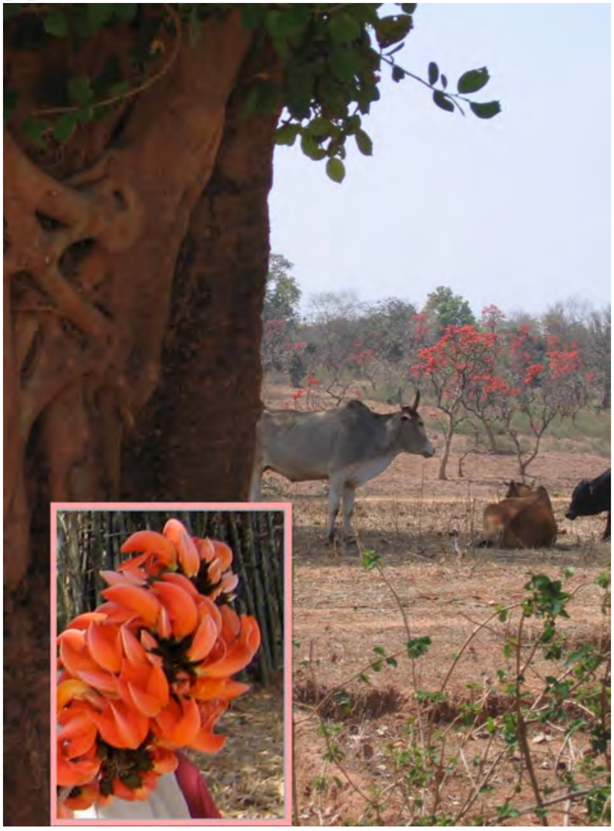


Image group 3: One can easily spot the Palash when its magnificent flowers are in bloom, also known as *flame of the forest.*

[4]

Image group 4: Broodlac is tied onto a branch, in order to innoculate the host tree. Here in the orchards at the IINRG.

[5]

Image group 5: Sticklac is brought to roadside markets by local cultivators in Balrampur, India.

[6]

Image group 6: The market Paikar purchases Sticklac.

Insert: the sticklac is bagged for transport to either a block Paikar, or a processing unit.

[7]

Image group 7: Rangeenie sticklac is darker and resembles mulch, while kusmi (insert) consists of more solid nuggets of Lac, taking the shape of the stick they were formed around.

[8]

Image 8: A range of shellac, including: waxed, dewaxed, bleached and decolored.

[9]

Image group 9: The traditional method of cleaning sticklac and separating the Lac resin from the stick -and beetle particles by foot, in the *nand*. Note the screen, used as a ladle to scoop out stick particles.

The insert on the left shows the washing water, tinted with the coloring matter laccaic acid, or Lac dye.

The insert on the right shows seedlac before winnowing.

[10]

Image group 10:

To the left: a mechanized washer tumbles the crushed sticklac with water and soda ash, resulting in seedlac (insert). Note the crimson laccaic acid residue on the metal bowl.

Above: a mechanical crusher breaks up the clumps of sticklac.

[11]

Image group 11: Seedlac is spread out to dry on the cement floor. Top insert: raking, sifting and winnowing equipment, along with baskets of sorted product. Bottom insert: Cloth makes a circular barrier as the winnowing includes tossing the seedlac into the air, and seperating the particles by size.

[12]

Image group 12:

Top left: The *pheraya* turns the *charki*, which rotates the cloth bag filled with seedlac. This turning provides uniform heating in front of the *bhatta* oven.

Top right: The karrigar scrapes the molten Lac from the bag and fashions round discs/buttons.

Bottom left: The remainder of the filtration bags, the *danri*, from three different types of shellac, and their corresponding buttons in the center. A boy stamps the buttons with a manufacturer, grade and quality stamp.

Bottom right: Mounds of finished buttons.

[13]

Image group 13: The *kalligar* gathers an appropriate mass of molton lac for the *belwaya*, who then uses the *nera* to spread the mass out on the warm *pipa*, before he peels it off and stretches the mass into a thin film. The insert to the right shows the end product, after it has cooled and been broken into flakes.

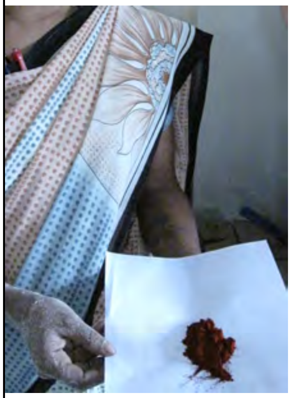
[14]

Image group 14: The cloth filtration-tubes are boiled with soda ash, dried and mended for further use.

[15]

Image 15:

Resin recovered from the danri. This material will be used for domestic handicrafts.



[16]

Image 16:

Reclaimed laccaic acid from the wash-water is manufactured into Lac dye. Here in powder form.

[17]

Image group 17: For MM shellac, the melting and filtration of the seed lac happens through a cloth in a steam heated press. Insert: The steam is generated by a coal burning furnace.

[18]

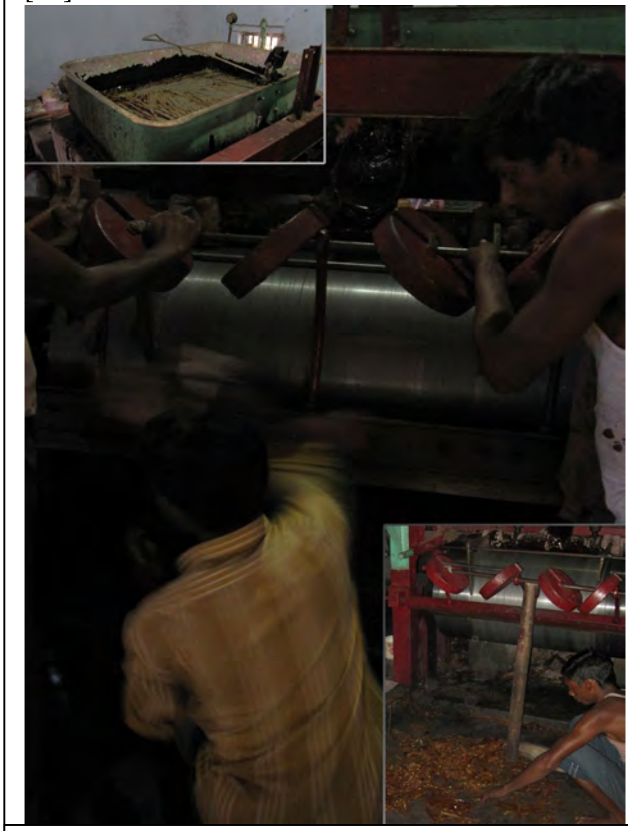


Image group 18: Top left insert shows the heated vat that siphons the molten Lac to the rollers, at center. Right insert shows remnants of shellac after sheets have been rolled out and removed from the machine.

Right: A runner with a sheet of shellac, still warm and soft. The sheets are hung to cool and harden, before they are broken into flakes.

Part 2

The Investigation of Lac

Physical and Chemical Characteristics

Introduction

Analyzing an object of cultural heritage necessitates the identification of existing elements, including the surface finishing, which may include previous treatments and repairs, as well as any original coating materials. For most wooden objects the quest to identify resinous finishes such as shellac, is of primary concern in the development of a treatment strategy. The identification of finishing material is carried out to guide conservators in their decisions to leave in place or selectively remove coatings as part of a comprehensive plan for the long-term stability and presentation of the object. In cases where recoating is recommended, the matrix of decision making may include concerns about compatibility with the existing finish, whether or not the new material is historically acceptable and whether the treatment can be repaired or fully reversed in the future.

These complex decisions and their respective consequences must be based on the best available scientific evidence coupled with detailed research into the historical context of the object, while considering ethical guidelines. By reviewing theory and case studies within the field, the groundwork is laid to explore all available methods and generally accepted “best practices” currently in use within the conservation community. Experimental studies within conservation science, such as this dissertation, have the goal of exploring conditions and products to inform and guide the approach of conservators when determining further treatment of the objects entrusted to their care. Part 2 of the thesis will review common analytical methods of shellac, explore elements of its physical and chemical characteristics, and relate findings to a conservator’s point of reference.

Chapter 4

Analytical Methods for Shellac in Conservation Science

A Review of FTIR and GC-MS

Introduction to Analytical Methods for Resins

The main part of this literature review will focus on theory and the applications of Fourier Transform Infrared spectrometry (FTIR) for the analysis and characterization of resinous coatings such as shellac. Though there are many analytical methods, IR spectroscopy is often used for analyzing and determining the subsequent conservation schedule for objects finished with organic, resinous varnishes. Spectroscopy is the study of the interaction between electromagnetic radiation and matter. FTIR is often used to identify finishes such as organic resins, which show strong and characteristic bands, or peaks in the IR region.

A review of various uses of FTIR spectroscopy is useful in determining techniques and methods for examining shellac varieties. Furthermore, since FTIR spectroscopic techniques do not give definitive quantitative results, a complimentary method is often employed. A section of the text will therefore also investigate Gas Chromatography-Mass Spectrometry (GC-MS). The possibilities and limitations of both analytical methods are mentioned, as are relevant reviews and case studies within the literature.

Sources for Theoretical Review

For a thorough understanding of the fundamentals of FTIR, Michele Derrick, Dusan Stulik and James Landry gave an in-depth introduction to both theory and the practical application of spectrometry in the conservation field.[1] Silvia Prati, Edith Joseph, Giorgia Sciutto and Rocco Mazzeo presented a good overview of the method in their article from 2000.[2] The article discusses the utilization of Infra-Red (IR) spectroscopy, as well as developments within sample preparation methods. For a chronological survey of applications of IR spectroscopy, turn to Francesca Casadio and Lucia Toniolo for their

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[1] Derrick, M., Stulik, D., Landry, J. M., *Infrared Spectroscopy in Conservation Science. Scientific Tools for Conservation*. Tevvy Ball, Sylvia Tidwell. Los Angeles: J. Paul Getty Trust, 1999.

[2] Prati, S., Joseph, E., Sciutto, G., Mazzeo, R., "New Advances in the Application of FTIR Microscopy and Spectroscopy for the Characterization of Artistic Materials." *Acc. Chem. Res* 43, no. 6 (2010): 792-801.

2001 article, which reviews how the method has been used from the 1960s-2000.[3] For a recent review of analytical methods for characterizing binding media and coatings in artworks, Maria Teresa Domenech-Carbo published such an article in *Analytica Chimica Acta* in 2008, containing sections covering spectroscopy as well as mass spectrometry and chromatographic techniques.[4] Barbara Stuart gives overviews of technical techniques for, among others, FTIR and GC-MS, in relation to the field of conservation.[5]

The IR Region of Electromagnetic Radiation

Light is expressed as a wavelength corresponding to a frequency along the electromagnetic spectrum, and spans from low wavelength (high frequency) radio and television rays (from thousands of meters to around 30 cm), to high wavelength (low frequency) gamma rays (less than 1 x 10^{-11}meter).[6] Infrared (IR) radiation is just below the frequency of visible light, in the middle regions of the electromagnetic spectrum, with wave numbers ranging between 14,000-20 cm^{-1}, which are further divided into three sub regions.[7] The span from 500-20 cm^{-1} is the Far-IR region (FIR), and is suited for the study of organometallic or inorganic compounds, and the identification of minerals and colorants.[8] The Mid range IR (or Mid-IR) region is where you see the fundamental vibrations for organic molecules, spanning from 4000-500 cm^{-1}. Mid-IR can be still further divided into the Group frequency region (4000-1300 cm^{-1}), and the Fingerprint region (1300-500 cm^{-1}).[9] The group frequency is used to determine the chemical class of a material, while the fingerprint region produces a characteristic pattern useful for material identification when compared to reference spectra.[10] The third region of IR is Near-IR (NIR) (14,000-4000 cm^{-1}) which consists of overtones and combinations of vibrations from the Mid-IR region. NIR is useful for in situ monitoring of reactions in

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[3] Casadio, F., Toniolo, L., "The analysis of polychrome works of art: 40 years of infrared spectroscopic investigations." *Journal of Cultural Heritage* 2, no. 1 (2001): 71-78.

[4] Domenech-Carbo, Maria Teresa. "Novel analytical methods for characterising binding media and protective coatings in artworks." *Analytica Chimica Acta* 621, no. 2 (2008): 109-139.

[5] Stuart, Barbara. *Analytical Techniques in Materials Conservation*. West Sussex: John Wiley & Sons, Ltd, 2007.

[6] Jang, Ph.D., Yun Hee. California Institute of Technology, "Infrared Spectroscopy." Last modified 29-Nov-2009. Accessed April 20, 2012. http://www.wag.caltech.edu/home/jang.

[7] Derrick, et al., 1999, p. 5.

[8] Derrick, et al., 1999, p. 204.

[9] Derrick, et al., 1999, p. 203.

[10] Derrick, et al., 1999, p. 14.

combination with Mid-IR.[11] The following table summarizes the IR regions and their uses.

Table 7: Regions of the electromagnetic spectrum

Region name	wave numbers	Useful when identifying
Far IR	500-20 cm^{-1}	Organo metallics, or inorganics
Mid IR	4000-500 cm^{-1}	Organic molecules
Group	4000-1300 cm^{-1}	Chemical class
Fingerprint	1300-500 cm^{-1}	Characteristic patterns
Near IR	14,000-4000 cm^{-1}	In situ monitoring

(Derrick et al., 1999)

Although each range of IR can be successfully applied to the analysis of resins, Mid IR has been used for this study.

Fourier Transform Infrared Spectroscopy (FTIR)

When matter is exposed to IR radiation, rays are absorbed at an atomic level, causing changes in the vibrational energy of the molecules, resulting in translational, rotational, and vibrational energy transitions.[12] Each exposed molecular structure results in a unique movement. [13] When detected by an interferometer, and processed by an attached computer with FTIR calculation capabilities, the detection of the specific molecular movements within a functional group result in a spectrum, where the energy lines of particular elements are reflected as specific absorption bands.[14] It is the detection and interpretation of these movements with high-resolution instruments that allows one to characterize compounds with infrared radiation. The spectral absorption is recorded and can be viewed as bands (in transmittance units) or peaks (in absorption units).[15] These absorption bands show the frequency, shape and intensity, which uniquely identify each individual molecule or material.[16] Spectra produced by different techniques will vary, and this must be taken into account when comparing reference spectra obtained by different

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[11] Derrick, et al., 1999, p. 13, 203.

[12] Stuart, 2007, p. 110.

[13] Stuart, 2007. The movements that occur can be a change in bond length (stretching) or bond angle (bending), some bonds stretch in-phase (symmetrical stretching) or out-of-phase (asymmetric stretching), scissoring and rocking (in-phase), as well as wagging and twisting (out-of-phase). For entertainment only, animated models of molecular vibrations can be viewed at: http://en.wikipedia.org/wiki/Molecular_vibration, accessed 5-31-2011.

[14] Derrick, et al., 1999, ch.2.

[15] Derrick, et al., 1999, p12.

[16] Derrick, et al., 1999, ch.2.

methods.[17] IR spectra can be plotted out in either transmittance or absorbance, depending on personal preference.[18]

Modes of FTIR

Transmission mode

The transmission mode of IR spectroscopy depends on the energy beam passing through the sample, with the unabsorbed portion of the beam continuing into the detector, thereby defining a sample's transmittance. This method is helpful in the analysis of gasses, liquids, and solids.[19] Until the 1960s, transmission measurements were the standard for IR analysis, and many reference spectra may still be in transmission mode.[20] When using transmission analysis, the sample can either be freestanding, fastened by, or contained in a supporting material, or formed out of various alkali salt compounds (also called salt pellets) which are transparent to IR radiation.[21]

The traditional method of analyzing solids in transmission mode, is by powdering the sample with a mortar and pestle, and mixing it with an IR transparent material; usually an alkali salt, such as Potassium Bromide (KBr).[22] The mixture is pressed into a pellet under pressure with a die casting tool, and can be stored for re-analysis, as pellets are introduced directly into the sample compartment of the IR spectrometer.[23] Samples can also be analyzed unsupported, or as thin films, but a disadvantage of analyzing unsupported samples is that it may be necessary to grind, dissolve, melt, or flatten the sample in order to obtain the appropriate thickness, which can alter the spectrum slightly.[24] Films, fibers and tapes can be mounted on disposable thin polymer film IR cards and placed directly in the path of the IR beam, but problems one can encounter when analyzing self-supporting materials include: the sample being too thick, absorbing

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[17] Derrick, et al., 1999, p. 43.

[18] Stuart, 2007, p. 112.

[19] Stuart, 2007, p. 112.

[20] Derrick, et al., 1999, p. 45.

[21] Derrick, et al., 1999, p. 45-48. Many salts are hygroscopic, and should be protected from moisture. A drawback when making pellets, is the potential for contamination. For a table on support materials and their properties, consult p. 48. For a detailed description of pellet preparation, consult p. 52.

[22] Derrick, et al., 1999, p. 52.

[23] Derrick, et al., 1999, p. 52.

[24] Derrick, et al., 1999, p. 52.

too much radiation for measurement, an uneven surface causing the beam to scatter, or internal reflections of the IR beam in free film samples, which should have a uniform thickness.[25]

Transmission mode measurements have not been used for this study, as there is an ample amount of sample material to make homogeneous thin films, and therefore no need to create pellets. Although thin films can be analyzed in transmission mode, the possible problems listed above outweigh the benefits, such as available reference spectra. For this study reference spectra are not needed. The goal is not to identify the samples, as they are all known samples of shellac, but rather to compare samples to each other, as well as to monitor the development during the process of polymerization.

ATR Absorption Mode

The absorption method is employed for solid, liquid or powdered samples, and measures how much of the IR beam is absorbed by the sample; the intensity of the peak is directly proportional to the concentration within the sample.[26] A commonly used method that measures the absorption of the sample is Attenuated Total Reflection (ATR): a technique where the IR beam slightly penetrates the sample, making it useful for surface analysis.[27] ATR systems depend on IR radiation to strike a medium with a high refractive index, an internal reflection element also known as the ATR crystal.[28] When a reading is made during a sample's contact with the crystal, a spectrum is made of the attenuated waves reflected off the absorbing medium of the sample. The sample absorbs energy at certain wavelengths, and reflects the beam's loss of energy, which is then measured and plotted as a spectrum in absorbance mode.[29] Samples are not destroyed during analysis, and can be retained for further study.[30] Nevin et al. 2009 conducted Mid-IR-ATR-FTIR analyses

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[25] Derrick, et al., 1999, p. 56-58.

[26] Derrick, et al., 1999, p. 201.

[27] Rizzo, Adriana. "Progress in the application of ATR-FTIR microscopy to the study of multi-layered cross-sections from works of art." *Analytical and Bioanalytical Chemistry* 392, no. 1-2 (2008) p. 47.

[28] Stuart, 2007, p. 113-114.

[29] Stuart, 2007, p. 113-114.

[30] Rizzo, 2008, p. 47.

in their study of the triterpenoid resins Dammar and Mastic, successfully documenting oxidation as a function of ageing in their samples.[31]

Numerous positive aspects of using Mid-IR-ATR in absorption mode are noted as additional advantages for this study, including the need for minimal sample preparation, and the ease of introducing the sample into the machine.

Micro Spectrophotometer

The ATR technique can also be coupled with a microscope, making it capable of microspectroscopy, which is useful when studying micro samples from works of art, such as paint layers, binding media, varnishes, waxes, dyes, and other materials.[32] Microspectrophotometers have the imaging capabilities of an optical microscope and some provide photomicroscopy and videomicroscopy, both with moveable apertures that can reposition the sample, allowing for sample isolation and component identification.[33]

When adhering to the standard sampling preparation technique for IR analysis, which requires grinding and mixing with an alkali salt such as KBr, the stratigraphy of a sample's cross-section is destroyed.[34] In an article from 1992, authors Derrick, Stulik, Landry and Bouffard present microspectroscopy as a tool for identifying individual finish layers, by linear mapping of a sample. Using a motorized micro-positioning stage, and moving methodically across the cross-sectioned samples at 20 µm steps, the bands/peaks characteristic of shellac, copal, mastic, rosin, and sandarac were detected as layers with uneven boundaries. This method also allows the thickness of various layers to be calculated. The technique was praised as a valuable tool, but the authors emphasized the importance of analyzing several samples before making projections about the overall composition of a finish, as the layers can be incomplete or vary considerably in

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[31] Nevin, A., Comelli, D., Osticioli, I., Toniolo, L., Valentini, G., & Cubeddu, R. "Assessment of the Ageing of Triterpenoid Paint Varnishes Using Fluorescence, Raman, and FTIR Spectroscopy." *Analytical and Bionanalytical Chemistry*. 395. no. 7 (2009): 2139-49. http://www.ncbi.nlm.nih.gov/pubmed/19669734 (accessed April 13, 2012).

[32] Derrick, et al., 1999, p. 68.

[33] Rizzo, 2008, p. 47.

[34] Derrick, M., Stulik, D., Landry, J., Bouffard, S.P., "Finish Layer Identification by Infrared Linear Mapping Microspectroscopy." *Journal of the American Institute for Conservation* 31, no. 2 (1992) p. 226.

thickness.[35] Adriana Rizzo also presents several examples of ATR-FTIR microscopy, applying the technique in cases where original appearance and future presentation are in question.[36] Rizzo emphasizes the importance of ensuring full exposure of the sample layers, as well as surface flatness, keeping in mind that ATR-FTIR is a surface-sampling technique.[37]

For this study, there are no samples taken from actual objects. Homogeneous thin films were prepared for experimentation. Future studies, however, may include the characterization of various shellac types used by museums and restorers in the past. Analyses of multi-layered varnish samples conducted by microspectrophotometer would be greatly beneficial in uncovering the stratigraphy on such artifacts, without destroying the layers during sample preparation.

Mid-range IR with a Fiber Optic Extension (FORS)

When non-destructive methods of surface analysis are required, Mid-IR Fiber Optic Reflectance Spectroscopy (FORS) can be applied.[38] FORS measurements are taken in ATR mode, with a fiber optic extension, allowing in-situ measurements, and making sampling unnecessary. In a 2011 article, T. Poli and colleagues claim that hand held ATR devices and portable FTIR benches suffer from poor quality spectra and fluorescent interference. Although portable benches give better mid-IR readings than the hand held devices, their shape and size sometimes pose measuring problems, particularly in the case of larger objects. Specular and diffuse reflection of radiation can also produce complex interactions, leading to distortions in the shapes, frequencies and intensities of absorptions in resulting spectra.[39] However, this extension technique allows measurements to be done on objects where sampling is not an option.

Non-destructive techniques are not necessary for the purposes of this study, but taking in-situ measurements with FORS may be a valuable way of performing unlimited numbers

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[35] Derrick, Stulik, Landry, Bouffard, 1992, p. 225-236.

[36] Rizzo, 2008, p. 52.

[37] Rizzo, 2008, p. 52.

[38] Poli, T., Chiantore, O., Nervo, M., Piccirillo, A., "Mid-IR fiber-optic reflectance spectroscopy for identifying the finish on wooden furniture." *Anal Bioanal Chem* 400, no. 4 (2011): 1161-71.

[39] Poli, Chiantore, Nervo & Piccirillo, 2011, p1162.

of surface measurements on preserved objects with shellac finishes. Poli et al. do provide tables of IR absorptions and peak assignments for shellac in various IR modes, which are helpful for reviewing the results of this study, and making visual comparisons.[40]

Near-IR

In an article from 2009, M. Vagnini et al. suggest using Fourier Transform Near-Infrared (FT-NIR) spectroscopy for the identification of natural polymers and resins on cultural heritage objects.[41] A main drawback of the method in the past has been the difficult band assignment of broader and less resolved fundamental bands, but the authors claim that the specificity of the method has been increased.[42] Tables of band assignments and corresponding wave numbers in the NIR range are provided as a reference tool.[43]

When measuring samples on wooden substrates, one should be aware of the possibility that the radiation penetrates deep into the sample, and the measurements can be affected by substrate absorption; wooden substrates present absorption bands across the MIR-NIR spectral range, especially between 900-1200 cm^{-1}.[44] In the case of shellac however, band assignments in Near-IR show peaks between 4000 cm^{-1}, and 8200 cm^{-1}, well beyond any interference from the wooden substrate.[45] Taking this into account, Near-IR could be a beneficial tool when finish samples cannot be detached from their wooden substrates. For the purposes of this study, samples were cast onto glass plates covered in aluminum foil, in order to avoid any spectral interference from the substrate.

Recent Advancements with Far-IR

A recent article by Prati et al. evaluates the use of far-FTIR as an alternative technique to characterize and distinguish between similar natural resins.[46] The authors found that far-

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[40] Poli et al., 2011, p. 1167.

[41] Vagnini, M, Miliani, C., Cartechini, L., Rocchi, P., Brunetti, B. G., Sgamellotti, A., "FT-IR spectroscopy for non-invasive identification of natural polymers and resins in easel paintings." *Analysis & Bioanalytical Chemistry.* 395, no. 7 (2009): 2107-2118.

[42] Vagnini, Miliani, Cartechini, Rocchi, Brunetti & Sgamellotti, 2009, p. 2107.

[43] Vagnini et al., 2009, p. 2113.

[44] Poli, et al., 2011, p. 1163.

[45] Vagnini et al., 2009, p. 2113.

[46] Prati, S., Sciutto, G., Mazzeo, R., Torri, C., Fabbri, D., "Application of ATR-far-infrared spectroscopy to the analysis of natural resins." *Anal Bioanal Chem* 399, no. 9 (2011): 3081-3091.

IR allowed the identification of certain resinous sub-compounds within the resins analyzed, while mid-IR had trouble distinguishing between the resins overall.[47] The authors conclude that far-IR can be used as a complimentary technique to FTIR in the mid region, as well as a control of cleaning procedures during restorations, since inorganic pigments and corrosion products are IR active and detectable in the 200-50 cm^{-1} region.[48] A drawback of the method is that FIR produces less intense spectra, and does not perform well on a microscopic scale.[49]

For this study, the samples are all known samples of shellac, and there should be no other resins present. The results may be helpful as a control method to ensure that there are no adulterants present in future shellac products sampled, as some producers modify the content of their shellac by adding rosin or other bulking materials.

Synchrotron Radiation for future possibilities

Methods within Infrared spectroscopy are constantly developing and expanding the possibilities for analysis. Synchrotron radiation was observed in a laboratory as early as 1947, and by the 1980's it was used as a source of radiation for the analysis of cultural heritage objects.[50] In 2005 Nati Salvado et al. presented a study where a synchrotron radiation source was used for FTIR microspectroscopy (SR-FT-IR).[51] Synchrotron radiation occurs when charged particles are accelerated to high speeds in a curved path, and the acceleration of these particles is achieved by magnetic fields placed around the circumference of a circular facility.[52] The use of SR-FT-IR microspectroscopy has the

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[47] Prati, Sciutto, Mazzeo, Torri & Fabbri, 2011, p. 3086.

[48] Prati et al., p. 3083.

[49] Prati et al., p. 3091.

[50] Harbottle, G., Gordon, B.M., Jones, K.W., "Use of Synchrotron radiation in archeaometry." *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 14, no. 1 (1986): 116-122. Also, Robinson, Arthur, L. "History of Synchrotron Radiation." http://xdb.lbl.gov/Section2/Sec_2-2.html (accessed 6-1-2011).

[51] Salvado, N., Buti, S., Tobin, M. J., Pantos, E., Prag, A. J. N., W., Pradell, T., "Advantages of the Use of SR-FT-IR Microspectroscopy: Applications to Cultural Heritage." *Anal. Chem*. 77, no. 11 (2005): 3444-454.

[52] University of Manitoba, Hyper Physics. "Synchrotron Radiation." 2005.http://hyperphysics.phy-astr.gsu.edu/hbase/particles/synchrotron.html (accessed 6-4-2011). Also, The Journal of Synchrotron Radiation, http://journals.iucr.org/s/m, accessed 6-4-2011. The *Journal of Synchrotron Radiation* provides comprehensive coverage of the entire field of synchrotron radiation research including instrumentation, theory, computing and scientific applications in areas such as biology, nanoscience and materials science.

advantage of a higher signal to noise ratio, and examining samples as small as 5µm squared.[53] Readings can be done in both transmission and reflection mode, and using an extension attachment in reflection mode, one can study the surface of large objects, making the technique completely non-destructive.[54] The microscopic properties of this technique can pinpoint a single particle or compound, which can also be a drawback, since microscopic contamination particles can represent such a significant fraction of the material being analyzed.[55] Limitations of this radiation source and method also include limited access, as accelerator facilities are very large in size, as well as high in costs.[56] Although the SR-FT-IR method is not applicable to this study, it is important to be aware of the possibilities within the field, and perhaps applicable to future projects.

Interpretation of Spectra

Spectral Quality

When interpreting a spectrum, it is important to determine that it is of good quality, and conforms to known standard parameters. According to Gregory D. Smith, a quality spectrum should have a flat and level baseline, positioned near 0.0 absorbance.[57] A sloping baseline may indicate that the radiation has been diffracted or scattered, the sample's surface may not be flat, or it may have been poorly ground.[58] There should not be "noise" (similar to radio static) greater than 1% of the strongest band, as intense noise may mean that the sample is too small, or that there have been an insufficient number of scans.[59] The intensity of a band should not be stronger than 10% transmittance (1.0 absorbance), which would indicate that the sample may be too concentrated, or too thick.[60] The functional group bands for water vapor and carbon dioxide should be less than 2% transmittance (0.1 absorbance), as a higher reading would indicate that the background does not match the sample spectrum, or that the instrument was not purged

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[53] Salvado, Buti, Tobin, Pantos, Prag & Pradell, 2005, p. 344-345.

[54] Salvado et al., 2005, p344-345.

[55] Salvado et al., 2005, p. 3446.

[56] Smith, Gregory, D. "Infrared Microspectroscopy using a Synchrotron Source for Art-Science Research." *JAIC* 42, no. 3 (2003): 399-406.

[57] Smith, 2003, p. 88.

[58] Smith, 2003, table p. 88.

[59] Smith, 2003, p. 88-90.

[60] Smith, 2003, table p. 88.

properly, which must be done with carbon dioxide-free air.[61] Visual examination and comparison to reference spectra can provide definite identification of an unknown sample, and although digitized databases are available for referencing, human judgment should still be the last step when making a final comparison to reference spectra.[62]

Band frequency, band shape, and band intensity define each band in a spectrum, and although identical samples prepared under identical conditions should produce identical spectra, any difference may be due to sample composition, preparation, spectral plotting format, or instrument parameters.[63] Derrick et al. have found that it is important to document the conditions of analysis, as well as the instrumental parameters, when conducting FTIR analyses.[64] It is also important to keep the potential for differences in mind when viewing spectra collected and recorded in other studies.

Several of the articles mentioned thus far provide tables and discussions detailing band/peak assignments identifying shellac, and may be used as tools when reviewing the results of this study.[65] Even though the goal is not to identify the samples, the relevant peaks should be monitored during ageing, and changes should be noted, as they may help identify the polymerization process, taking place in the samples.

Quantitative Analysis in Absorption Mode

According to the Beer-Lambert Law, each band is directly proportional to the concentration of the absorbing species, implying a linear relationship between bond

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[61] Smith, 2003, p. 90.

[62] Smith, 2003, p. 91. Some digital reference sources available are: Wiley (http://www.wiley.com/legacy/products/subject/reference/index.htm), NIST (http://www.nist.gov/pml/data/asd.cfm), Sadtler & Aldrich (http://www3.bio-rad.com).

[63] Derrick, Stulik & Landry, 1999, p. 82-83.

[64] Derrick, et al, 1999. When attempting to characterize an unknown sample, one identifies the functional groups present in the spectrum, while also comparing to reference spectra. To characterize the sample, it is helpful to divide the spectrum into frequency regions: the OH-NH region (4000-2600 cm^{-1}), C-H stretching region (3200-2800 cm^{-1}), window region (2800-1800 cm^{-1}), Carbon double bond region (1800-1500 cm^{-1}), and the fingerprint region (1500-500 cm^{-1}). Identifying peaks of the functional groups contained in these sub-regions can lead to a positive identification of a material, but acknowledging the absence of a functional group can also help rule out the possible materials in a sample. Correlation charts and flow charts can be helpful classification tools, as they show lines for each functional group, indicating where to find the strongest, most characteristic bands/peaks in a sample. Organic materials used within the art conservation field are often grouped into: resins (tree), resins (insect, shellac), oils, gums, waxes, and proteins.

[65] Derrick et al., 1999, p. 107. ; Vagnini et al., 2009, p. 2113. ; Prati et al., 2010, p. 3083. ; Poli et al., 2011, p. 1166.

intensity, and concentration in absorbance mode: “There is a linear quantitative relationship between absorbance and concentration of absorbing molecules”.[66] The intensities of the absorption peaks can therefore be used as an indication of quantity for each functional group.[67] This function can also be helpful when monitoring chemical reactions, such as the polymerization process in ageing shellac. FTIR measurements are relatively easy and affordable to conduct, and the quantitative indications can track changes in samples as the process takes place, comparing and contrasting the rate of degradation between the various types and formulations of shellac.

Mathematical Manipulation of Spectra

It is possible to further refine the empirical data by using mathematical methods to achieve resolution enhancement. Methods such as self-deconvolution, or derivative spectroscopy, are optimization processes, which artificially narrow bandwidths, and help minimize overlap.[68] Spectral subtraction separates spectra of components in a mixture, by removing bands of impurities, or detecting small changes in a sample. When one non-target component is identified, its reference spectrum is then subtracted from the sample spectrum, making the resulting spectra useful for the evaluation of chemical reactions, or monitoring the ageing of a sample.[69] Deconvolution can improve the resolution of individual bands, correcting the broadening that occurs during the production of a spectrum, but even though resolution enhancement methods can be helpful in identifying a component, care must be taken to insure that a differentially processed spectrum does not give false results or characterizations.[70]

Complimentary Methods of Analysis

Infrared spectroscopic analysis has proven to be a very useful tool within art and objects conservation, and for this study. As a qualitative identifier, FTIR can recognize and match components of samples through the use of reference spectra. The technique is also useful in monitoring changes in samples. While relative quantities can be deduced with

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[66] Derrick et al., 1999, p. 122.

[67] This is not so in transmission mode, and those values must be recalculated with a logarithm for this to be case. Derrick et al., 1999, p. 123.

[68] Derrick et al., 1999, p. 124-128.

[69] Derrick et al., 1999, p. 125.

[70] Derrick, 1989, p. 43-44.

subtractive and comparative techniques, FTIR is still mainly a qualitative method. Thus, a complimentary method of analysis, such as Gas Chromatography (GC), coupled with a Mass Spectrometer (MS) is useful, as it has the possibility of quantifying components in a sample.

Chromatography

Chromatography was first described as a separation technique for plant pigments, by Russian botanist Mikhail Tswett at the turn of the 20th century.[71] Chromatographic techniques separate components of a mixture, analyzing the substances of what can sometimes be complex mixtures.[72] This separation ability makes some of the techniques very useful as a tool for identification and quantitative analysis of artworks within conservation science, but the process does unfortunately completely destroy the sample.[73] A successful chromatographic technique separates the compounds of a sample, plotting its distinct peaks far apart and narrow. The time it takes for each component of the sample from the injection point to the detector is referred to as its “retention time”, and extended retention times can result in wide and crowded peaks indicating a poor separation of the sample’s compounds.[74]

GC-MS was chosen as a secondary method for this study, as quantitative measurements of various shellac types were desired. As mentioned in chapter 1, AMDIS was unable to identify the individual compounds present within the various shellac samples. The outcomes of the GC-MS analyses are detailed further in the discussion section.

Chromatographic Techniques

There are many chromatographic techniques that have been applied to analyze various aspects of shellac. Paper chromatography (PC) is the simplest chromatographic method,

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[71] Farlex, Free Dictionary. "Tswett, Mikhail Semyonovich .", 2009. http://encyclopedia.farlex.com/Tswett,+Mikhail+Semyonovich (accessed 6-5-2011).

[72] Domenech-Carbo, Maria Teresa. "Novel analytical methods for characterising binding media and protective coatings in artworks." *Analytica Chimica Acta* 621, no. 2 (2008) p. 121.

[73] Stuart, 2007, ch. 8.

[74] Stuart, 2007, Chromatography, 2010,"Chromatography-basic operation." 1994.http://www.rpi.edu/dept/chem-eng/Biotech-Environ/CHROMO/chromoper.html (accessed 6-6-2011).

and uses paper as a separation medium. This method has been used as a technique for monitoring the separation of Lac acids. [75] Thin Layer Chromatography (TLC) applies a sample in solution on one end of a plate, and submerges it in solvent. Capillary action carries the components up the plate, and a visualization agent is sprayed on the plate to identify the components.[76] TLC has been applied to recognize natural resins. Using non-polar solvents and alcohols on a silica gel adsorbent, with vanadium pentoxide as a detection agent, one can recognize a resin in a varnish mixture. Identification is, however, hindered by oxidation products and polymerized materials.[77] As this study revolves around a resin that polymerizes, TLC does not seem a prudent choice. Precise quantitative analyses are also not possible with TLC. High-performance liquid chromatography (HPLC) is a technique that uses a pump to move the solvent and the sample components through the chromatographic machinery, and within conservation, HPLC is mainly used to identify proteinaceous media and drying oils. [78]

Gas chromatography (GC) can be used to analyze most organic materials, and it is the most widely applied chromatographic technique used to identify varnishes.[79] In GC a heated injector volatizes the components, then introduces them to an inert gas, such as helium, hydrogen, or nitrogen. For quantitative analyses in GC, measuring the area of a chromatographic peak is involved.[80]

Sample Pre-Treatment

One or more pre-treatment steps are necessary when using a chromatographic method, and generally the three steps are: hydrolysis, suppression of interferences, and derivatization.[81]

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[75] Khurana, R.G., A.N. Singh, A.B. Upadhye, V.V. Mhaskar, and S. Dev. "Chemistry of Lac Resin-III, Lac Acids: An Integrated Procedure for Their Isolation From hard Resin; Chromatography Characteristics and Quantitative Determination." *Tetrahedron*. 26. (1970): 4167-4175.

[76] Stuart, 2007.

[77] Domenech-Carbo, 2008.

[78] Domenech-Carbo, 2008.

[79] Domenech-Carbo, 2008.

[80] Stuart, 2007.

[81] Domenech-Carbo, 2008, p.121. Pyrolysis is a heating pre-treatment, commonly between 500-800℃, resulting in the decomposition of the molecules of the binding media, thus breaking them down into smaller, more volatile fragments. The decomposition products are used as a fingerprint for the sample

Hydrolysis

Hydrolysis, the breaking of chemical bonds by the introduction of water, is used to release the compounds found in natural polymeric materials, and Domenech-Carbo describes that there are three categories:

1. Acidic hydrolysis: Variables such as the choice of acidic reagents, temperature range, and reaction times are dependent on the composition of the binding medium or varnish, and for other proteinaceous media. Hydrolysis is performed under vacuum, or an inert atmosphere containing argon or nitrogen, with temperatures ranging from 105℃ to 110℃, for the duration of 24 hours.[82] To reduce the risks of oxidation or degradation, vapor-phase acidic hydrolysis has been performed in a microwave oven, with considerably shorter reaction times.[83]

2. Enzymatic Hydrolysis: This method breaks down the peptic bonds of proteinaceous materials by the use of enzymes, and the reaction time is 12 hours, at 37℃.[84]

3. Alkaline Saponification is utilized to break down lipid (fatty) binders. Potassium hydroxide (KOH) is dissolved in methanol for 24 hours at room temperature, or 1 hour in 70-80℃, in a sealed reaction phial.[85] Colombini et al. present a method giving an in-

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compound, and are displayed as peaks in a pyrogram (Stuart, 2007). Lili Wang et al. presented a method of PY-GC in the presence of an organic alkali, to identify mole distributions of the acidic components in shellac samples grown in India vs. Thailand, being able to distinguish between samples produced in the different countries (Wang et al., 1999).

Coupling pyrolysis with gas chromatography-mass spectrometry (PY-GC-MS) can be useful in identifying natural resins, since MS gives a more accurate identification of the components than conventional GC. An additional advantage includes easier sample preparation, since a sample can be analyzed in a solid or liquid state without hydrolysis or derivatization pre-treatment. The derivatization reagent is applied as an aqueous solution before pyrolysis (Domenech-Carbo, 2008). One can also obtain structural information from the fragmentation pattern produced by the process (Stuart, 2007, Domenech-Carbo, 2008, Wang et al., 1999). The pyrograms are, however, more complex than chromatograms obtained from conventional GC-MS, showing an increased number of peaks. Colombini et al. present a method of PY-GC-MS to rapidly identify Lac resin in their 2003 article (Colombini, Bonaduce, Gautier, 2003). PY-GC-MS was not available for this study.

[82] Domenech-Carbo, 2008, p. 121-122.

[83] Domenech-Carbo, 2008, p. 121-122.

[84] Domenech-Carbo, 2008, p. 121-122.

[85] Domenech-Carbo, 2008, p. 121-122.

depth understanding of Lac resin composition. The method is based on saponification of the sample, assisted by microwave, then GC-MS analysis.[86]

For terpenoid resins, such as shellac, hydrolysis is generally not required, and a simplified extraction is performed. For shellac, one hour in an ultra-sonic bath with methanol has been proposed by Domenech-Carbo.[87] A 2003 article by Colombini et al. proposes saponification with 10% potassium hydroxide (KOH) in ethanol for 60 minutes, at 80℃, then treated with trifluoroacidic acid (TFA) to dissolve aleuric salts.[88] Sutherland, 2010, suggests sample pre-treatment with Methprep II (m-trifluoromethylphenyl trimethylammonium hydroxide (TMTFTH)), methanol and toluene) for GC-MS of shellac.[89] The sample pre-treatment used for GC-MS in this study was prepared and carried out in cooperation with Jennifer Giaccai (Conservation Scientist at MCI), and is described in the Experimental section.

Suppression of Interferences

Accurate determinations for resin acids (among other things) from coating and binders on works of art can be hindered by interference of pigments (paint) and other inorganic (furniture polish) materials also present in the sample.[90] Suppression techniques to separate the organic compounds from inorganic include the extraction of proteinaceous matter with water, aqueous sodium hydroxide (NaOH), or ammonia (NH3).[91] Methods using an ion exchange resin, or a strong chelating agent are suggested for suppressing inorganic interferents.[92] Suppression of interferences is not something required for this study, as the samples in question are not mixtures, but pure shellac films.

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[86] Colombini, M.P., Bonaduce, I., Gautier, G., "Molecular Pattern Recognition of Fresh and Aged Shellac." *Chromatographia* 58 (2003): 357-364.

[87] Colombini, Bonaduce & Gautier, 2003.

[88] Colombini et al., 2003, p. 357-364.

[89] Sutherland, Ken. "Bleached shellac picture varnishes: characterization and case studies." *Journal of the Institute of Conservation*. 33. no. 2 (2010): 131.

[90] Domenech-Carbo, p 2008, p. 122.

[91] Domenech-Carbo, p 2008, p. 122.

[92] Domenech-Carbo, p 2008, p. 122.

Derivatization Techniques for Natural Resins

Derivatization is a technique that transforms a chemical compound into a product of similar chemical structure, its derivative. While similar, the derivative has new chemical properties; it is rendered less polar, and thus more volatile, allowing for better separation and analysis by gas chromatography.[93] Techniques proposed by Domenech-Carbo include methylation using methanolic HCl (hydrogen chloride), esterification with DM (degree of methylation), TMSDM (trimethylsilyldiazomethane) to characterize components in both fresh and oxidized resins, ECF (ethylchloroformate), MCF (methylchloroformate), or TFTMAH (trifluoromethyl) phenyltrimethylammoniumhydroxide), or silyation reagents; improving separation and enhancing detection.[94] In their 2003 article, Marinach et al. described derivatization techniques and provide chromatograms of various types of shellac.[95] Unfortunately, the names identifying the types of shellac they studied seem arbitrary, follow no standard grading, and cannot be identified in terms of type, processing method, or wax content. As the chromatograms are printed with neither retention time nor intensity, they are not helpful as GC references for the identification of ingredients found in Lac resin.

Gas Chromatography-Mass Spectrometry (GC-MS)

GC coupled with Mass spectroscopic (MS) instruments are used extensively within the conservation field, as MS allows for a more accurate method of identification. MS instrumentation measures the mass-to-charge ratio of charged particles in a compound, determining the composition of the sample. Having already been vaporized to pass through the chromatographic column, a jet molecular separator separates the carrier gas from the compounds to be analyzed in the spectrometer. A mass spectrum is plotted with a relation of mass/charge ratio vs. percent (%) relative abundance.[96] In his 2010 study, Ken Sutherland concluded that GC-MS is an effective and sensitive method for characterizing shellac in aged and complex varnish samples.[97] By using this method of

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[93] *A Dictionary of Chemistry*. 6 ed. Oxford paperback reference. John Daintith. Oxford: Oxford University Press, 2008.

[94] Domenech-Carbo, 2008.

[95] Marinach, C., Papillon, M-C., Pepe, C., "Identification of binding media in works of art by gas chromatography-mass spectrometry." *Journal of Cultural Heritage* 5 (2004): 231-240.

[96] Stuart, 2007.

[97] Sutherland, 2010, p. 143.

analysis, Sutherland found that shellac bleached with sodium hypochlorite during processing still contains trace levels of chlorinated compounds up to a few percent in the finished product.[98]

In Summary

For the analysis of resins on objects of cultural heritage, IR spectrographic techniques are often employed and favored by conservators.[99] The principal advantages of Mid-IR-ATR-FTIR are: the sample can be re-examined; pre-treatment of the sample is limited; the time of analysis is short; sample size needed is very small, and the method has a comparatively low cost.[100] Limitations include; micro-samples can give spectra of low quality, or misrepresent the proportional make up of the whole; weak absorptions can get lost in instrumental noise; there can be overlapping, making it difficult to identify single components in a mixture; and it may be difficult to access and compare reference materials.[101] Although some quantitative calculations can be made, FTIR methods are mainly for qualitative studies. Gas chromatographic (GC) techniques have the potential for quantitative measurements, and when coupled with mass-spectrography (MS) gas chromatography can provide a more detailed description of a sample than spectroscopic techniques alone, making GC-MS a good complimentary method to FTIR Spectroscopy.[102] Sample preparation is relatively complex and time-consuming for GC-MS, thus monitoring alteration processes on a large number of samples may prove difficult.[103]

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[98] Sutherland, 2010, p. 134.

[99] Domenech-Carbo, 2008, p. 115.

[100] Domenech-Carbo, 2008, p. 115, 133-134.

[101] Domenech-Carbo, 2008, p. 115, 133-134. & Derrick et al., 1999, ch. 5.

[102] Domenech-Carbo, 2008, p. 121.

[103] Domenech-Carbo, 2008, p. 121.

Chapter 5

Mapping the Characteristics of Lac

The Physical Characteristics of Lac as a Film-Forming Finish

Shellac Survey

To analyze the physical differences between the varieties of shellac, it was necessary to first establish the characteristics themselves. For this purpose, the physical characteristics of film-forming finishes were named through conversations with Mitch Kohanek, Director of the National Institute of Wood Finishing. To evaluate the characteristics recognized in shellac, a survey was conducted and distributed to members of a professional finishers' network, with a return of 24 responses.[104]
The qualities identified were:

Adhesion
Compatibility (with other finishes)
Visual beauty (depth/birefringence/chatoyance)
Color
Ease of use
Flexibility
Durability (abrasion resistance)
Water resistance (in liquid form)
Sealing qualities (use as a barrier coating in a finishing schedule)
Use to reconstitute/amalgamate existing finishes
Reparability
Heat resistance.

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[104] For a summary of the survey's results, consult appendix 1. The respondents were asked to rank the above characteristics with respect to shellac, and assign a relative importance to them.

The Uses of Shellac for Finishing Wood

Shellac has traditionally been used on prized furniture and wooden objects, imparting a characteristic visual depth and warmth, and enhancing the wood grain. Once mastered and readily available, shellac is also prized for its ease of use and versatility, as it can be applied by brush, pad, or sprayed by an atomizing gun. It can be used as the sole product in a finishing schedule, or for a specific purpose in combination with other finishing products.

Shellac can be used as a sanding sealer on bare wood. By raising the wood fibers and holding them in place, a sanding sealer allows the user to "cut" the uneven face with fine sandpaper, leaving a smooth working surface. Since the shellac reactivates with alcohol as a solvent, the successive applications melt into the first, and there are no concerns about adhesion between the layers of finish. If other products are to be used as a topcoat, the light sanding of the shellac provides a ground for mechanical adhesion between coats.

Shellac can be used as a seal coat, as it has excellent barrier and adhesive properties. On surfaces with contamination that is difficult to remove, such as oil, wax or silicone, shellac can be applied as a barrier coat, to prevent interference problems, such as "fish eye", in the subsequent finishing procedure.

Used as a "wash" (or primer) coat, a thin application of shellac will lay the ground for an even application of color, on wood that may otherwise blotch. Shellac will also seal between layers of glazing, which is often done with a combination of oils and pigments and if desired, it can be tinted with dyes, and used as a toner. These techniques are used to harmonize colors, and create additional decorative effects.

For objects worthy of a high gloss finish, shellac can be built up to a filled-pore, mirror-like surface when applied with a French polish technique. Using oil as a lubricant, the shellac is applied in very thin layers, using a pad that fits in the palm of the hand. The pad can be a wad made of cotton or wool, which acts as a reservoir for the shellac. This core is then covered with a lint-free organic cloth (often linen) for direct contact with the surface. The application method varies from artisan to artisan, but consists of a combination of the correct wetness; amount of lubricant; speed of movement; squeezing of the pad; and strength of the arm against the surface. All these factors, when properly channeled into one continuous action, slowly build the much sought after, flawless surface of a true French polish.[105]

Uses of Shellac within Furniture Restoration-Conservation

For use within furniture restoration-conservation, there are many factors to consider when choosing a coating material. To make the connection between shellac's performance qualities and its component ingredients, the physical characteristics of shellac are compared to findings within conservation and chemical research literature. To evaluate shellac for use within conservation, standards and requirements as identified by conservators Shayne Rivers and Nick Umney are considered, and applied to shellac as a coating.[106] To answer further questions, selected characteristics have then been tested in the experimental section.

The Functions of a Coating

Within furniture restoration-conservation, coatings serve both aesthetic and protective functions, while covering both structural and decorative elements. In addition to considering these requirements, conservators must bear in mind ethical guidelines when contemplating which coating to use within a treatment plan for an object.[107] This section of the text presents the desired functions of a coating, from a conservation perspective, and explores how shellac relates to these functions.[108]

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[105] For a historical tutorial on French polishing, turn to Richard Bitmead, *French Polishing and Enamelling, A Practical Work of Instruction* (London: Crosby Lockwood and Son, 1910), Chapter III.

[106] Rivers, S. & Umney, N. *Conservation of Furniture*. Oxford: Butterworth-Heinemann, 2003.

[107] For more on the ethics of furniture conservation, turn to Walter Angst's, "Ethics in Scientific Furniture Conservation," *Proceedings of the Furniture and Wooden Objects Symposium, 2-3 July 1980*. Ottawa, Canada: Canadian Conservation Institute, 1980, pp. 123-135.

[108] For more on coatings and conservation, as well as a selected reading list, turn to Williams, D.C. Smithsonian Museum Conservation Institute, "Preserving and Restoring Furniture Coatings." Last modified July, 2003. Accessed June 22, 2012. http://www.si.edu/mci/english/learn_more/taking_care/coatings.html.

Aesthetic Functions

As the coating presents the first visual impression of an object, it should enhance the overall appearance of it. As laid out by Rivers & Umney, the important optical qualities of a coating are: clarity, gloss, and color.[109] Applying shellac as a finish on wood has the potential of creating a surface of unequivocal beauty, as it more than fulfills the criteria of bringing out all of the optical qualities of a wooden object.

Clarity

The clarity of a finish is its transparency, and depends on a constant refractive index throughout the film, allowing light to pass through it, without scattering. [110] Amorphous polymers are transparent as long as they do not contain impurities that absorb and scatter visible light.[111] Shellac has varying degrees of clarity, depending on its wax content. As the shellac resin mixture is an amorphous polymer, a dewaxed variety will have higher clarity, since the wax particles naturally present in shellac interfere with the passage of light through the film.[112] This interference becomes more visible the thicker a film is applied. Of professionals surveyed, 50% prefer using dewaxed shellac for general use.

Gloss

Although gloss is comprised of several kinds of reflection, the most common factor in describing the gloss of a surface is its specular reflection, the mirror-like reflection seen in the surface.[113] The gloss of a surface is generally measured by the degree of specular reflection (on a scale of 1 to 100); a matte surface having a low degree, while a glossy surface has a high degree of specular reflection.[114] The ability of the surface to reflect also depends on the topography of the surface being finished. The smoother the surface is, the glossier the reflection will appear. Shellac can create a glass-like surface, especially when applied with a French polish padding technique.[115] Of professionals surveyed, 84% value the ability of shellac to be French polished as important, or very important. A lower gloss

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[109] Rivers & Umney, 2003, p.135.

[110] Rivers & Umney, 2003, p.138.

[111] Rivers & Umney, 2003, p.138.

[112] For more information on transparency, see Rivers & Umney, 2003, p. 138.

[113] Hammond, H. Gloss, in J.V. Kolesky (ed.), *Paint and Coating Testing Manual*, ASTM: 1995. Ch. 41.

[114] Hammond, 1995. p. 37.

[115] For more on the procedure of French Polishing, turn to a Guide to French Polishing, by Wood Finishing Supplies, available at: http://www.woodfinishsupply.com/GuideToFrenchPolishing.pdf

surface can be achieved by adding matting agents (such as fumed silica) or by rubbing the dry film with a variety of abrasives, imparting fine scratches that hide small imperfections and scatter the reflection of visible light, creating a dull, but even sheen. This is known as rubbing out a finish. According to Rivers and Umney, a characteristic of an ageing finish can be the loss of gloss.[116] The experimental section explores how gloss is affected when varieties of shellac are exposed to artificial ageing.

Color

As described in Chapter 3, natural shellac contains both Lac dye (laccaic acid) and erythrolaccin. Lac dye is soluble in alkaline solution, and therefore most of the Lac dye is washed out by the sodium carbonate (pH 11.4) added to the wash-water during processing. Erythrolaccin is alcohol soluble, and therefore remains in the shellac, giving the various types of shellac their natural colors.[117] The natural colors of shellac span from a rich amber yellow, to a dark reddish-brown. As mentioned above, processing techniques influencing the color of shellac include the removal of color by activated charcoal filters during the solvent method, or the bleaching of color by sodium hypo-chloride, which makes a nearly colorless varnish. Of professionals surveyed, 91% value the color variety of shellac as important or very important.

Generally accepted ethics for conservation work dictate that treatment should not impart a new or inappropriate color to a surface. In addition to the inherent color of the coating, one must consider how it will change over time, and whether or not it will yellow. Rivers and Umney condemn the use of shellac as a varnish on painted or decorated surfaces without an alcohol insoluble barrier, as the shellac will yellow over time.[118] The insoluble barrier under the shellac layer, allows for the shellac coating to be removed and replaced without damage to the underlying surface.

Chapter 7 addresses the question of whether the various shellac types may age/yellow differently, with an experiment measuring the color change in various kinds of shellac exposed to artificial ageing.

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[116] Rivers & Umney, 2003, p. 587.

[117] Parry, 1935, p. 141.

[118] Rivers & Umney, 2003, p. 594.

Characteristics that Affect the Visualization of Color

The ability of a coating to wet the substrate also plays a part in how the color of the wood is visually perceived. Shellac wets the surface well, saturating it and accentuating the colors present in the substrate. As shellac saturates the wood surface when applied, there are no cracks or fissures under that film surface to catch and reflect light, and so the colors of the wood become enhanced.[119] By accentuating the crystalline grain figure in wood, shellac creates a three-dimensional shimmering quality known as birefringence (some refer to it as chatoyance) which changes with light and viewing angle. This quality is highly valued by users of shellac, as it creates unparalleled depth and beauty in wood, as evidenced by 91% of surveyed professionals who value this quality of shellac as important or very important.

In addition to being available in a range of colors, shellac easily tints with dyes to yield almost any color. Mixing with pigments gives more opaque qualities, as the pigments block and scatter visible light, and obscure the surface. Both dye tinting and mixing with pigments are valuable tools for in-painting, or when using shellac to make repairs and finish appropriate replacement parts for wooden objects or furniture.

Protective Functions

Being the outer layer of an object, the coating applied to a surface of a piece of furniture is essentially charged with protecting the entire piece. The three main ways of applying shellac are by brushing, padding and spraying.[120] When presented with the requirements set by preservation standards, Rivers and Umney deem shellac to be strong enough to wear well, while it is flexible enough to allow movement in the substrate.[121]

Hardness

According to Rivers and Umney (2003) coatings should resist abrasion and be hard enough to provide protection from soiling during handling, as well as dust and

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[119] Rivers & Umney, 2003, p.175.

[120] For more information on the application of shellac, turn to Donald Williams' "Shellac Finishing: A Traditional Finish Still Yields Outstanding Results." *Fine Woodworking*, July/Aug. 1988, 56-59.

[121] Rivers & Umney, 2003, p. 136.

atmospheric pollution.[122] As conservator Donald Williams points out, shellac was traditionally used as a coating for floors and bowling alleys, and it is certainly durable enough for conservation purposes.[123]

Reparability

Although modern synthetic finishes may create a surface able to withstand more abrasion and abuse, the reparability of shellac gives it a clear advantage. The ability to re-amalgamate a cured shellac film makes the coating reparable, and in some instances fully reversible.[124] Of professionals surveyed, 50% value the durability of shellac as important or very important, while 77% value the reparability of shellac as very important.

Rivers and Umney posed the concern that shellac will polymerize and crosslink over time, making it harder to remove the resin with alcohol, and leading to a need for harsher cleaning solvents in the future.[125] As there are free hydroxyl groups available for esterification within the structure of shellac, Mills and White found it likely that cross-linking continues after application, in the shellac film itself. [126] The experimental section explores the identification and monitoring of polymerization between varieties of shellac during ageing.

Barrier Properties

To avoid causing damage to an object, coatings should impede the passage of water vapor, as well as oxygen, and UV radiation, while allowing for subsequent removal, without causing damage to the substrate.[127] As Relative Humidity (RH) changes, all wood naturally expands and contracts. One important protective function of a coating from a conservation perspective is its ability to slow the permeation of water vapor, thus

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[122] Rivers & Umney, 2003, p.135.

[123] Williams, D.C. "Shellac Finishing: A Traditional Finish Still Yields Outstanding Results." *Fine Woodworking*, July/Aug. 1988, p. 56. For more on the mechanical properties of shellac, turn to Martin, p. 459.

[124] When areas of repair or in-painting are isolated with an alcohol insoluble barrier, the shellac repair can easily be removed. For more information on amalgamation qualities and techniques, see Mitchell, D. "Amalgamating Aged Finishes." *Papers Presented at the Wooden Artifacts Group, Vancouver 1987*. Washington, DC: American Institute for Conservation, 1987, 8 pages.

[125] Rivers & Umney, 2003, p. 594.

[126] Mills & White,1994, p. 103.

[127] Rivers & Umney, 2003, p. 586.

reducing the effect of sudden humidity changes which can lead to damage from swelling or shrinking of the wood. In severe cases, this can include crushing or splitting of the wood, as well as finish and/or glue failure.[128]

Shellac coatings will develop white marks or rings when directly exposed to liquid water for a length of time.[129] As Williams also points out, however, shellac generally performs quite well as a barrier against water vapor.[130] As most objects in a conservation setting will not be exposed to careless or accidental water use, shellac provides a sufficient barrier against the permeation of water vapor. The Journal of Agriculture and Food Chemistry reports that at Relative Humidity (RH) levels under 50%, shellac proves to be a better barrier (on fruit) for Oxygen (O_2) and Carbon Dioxide (CO_2) than cellulose acetate, polyethylene, or polypropylene.[131] Hagenmaier et al. also point out that the O_2 and CO_2 permeability of shellac varies depending on which solvent is used to prepare the coating.[132] Permeability is higher when the coating is prepared with an alkaline solution, than with ethanol, especially when RH is over 55%.[133]

In general, shellac should be applied under conditions with low RH. According to Gardner, if the atmosphere is excessively humid, the moisture can cause “blooming” or water vapor entrapment within the coating, after application.[134] The blooming may self-dissipate as the trapped water escapes with solvent evaporation, or be accelerated by applying pure alcohol to the surface. This technique is effective, but it can lead to reduced water resistance qualities in the film, and applications in humid conditions

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[128] Wachowiak, M.J. Smithsonian Museum Conservation Institute, "Biological Deterioration & Damage to Furniture & Wooden Objects." Last modified 2003. Accessed June 22, 2012. http://www.si.edu/mci/english/learn_more/taking_care/biodetwood.html.

[129] Further studies might include various shellac samples, and testing their reactions during exposure to liquid water.

[130] Williams, 1988, p. 57.

[131] Hagenmaier, Robert, and Philip Shaw. "Permeability of Shellac Coatings to Gases and Water Vapor." Journal of Agricultural and Food Chemistry. 39. no. 5 (1991), p. 827-829.

[132] Hagenmaier et al., 1991, p. 827.

[133] Hagenmaier et al., 1991, p. 828.

[134] Blooming can manifest itself as a grey or white cloudiness, and is most likely to occur when spraying shellac. If the substrate temperature falls below the dew-point, moisture in the air will condense on the substrate. Upon coating application, air from the spray gun and solvent evaporation can lower the surface temperature of the coating. The condensed moisture will cause the blushing reaction, getting trapped in the coating as it dries.

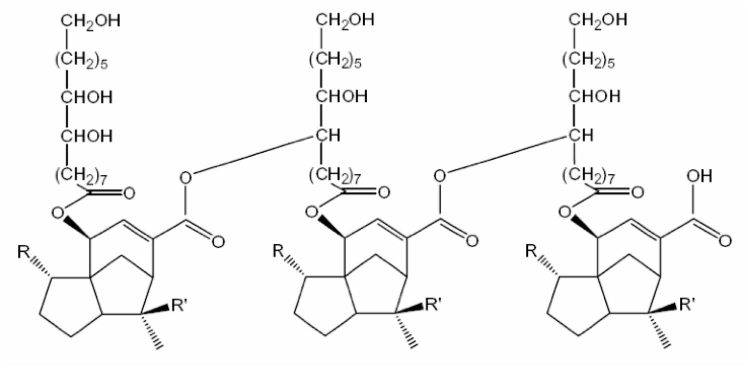
should be avoided.[135] An additional fact affecting the barrier qualities of shellac is that thick films retain more solvent than thin ones, and will actually lower the moisture resistance of the coating.[136]

Flexibility and Adhesion

It is important that a coating adheres well to the surface, but while providing cohesion, the coating must also allow sufficient elasticity to accommodate expansion and contraction caused by changes in humidity and temperature.[137] Although coatings impede the transmission of water vapor, they are not impervious barriers. When wooden substrates expand or contract, it is important that the chosen coating is flexible enough to allow for movement without cracking or failing (dislodging from the surface). If the coating does crack: dirt, ultra violet light, water vapor and other gaseous pollutants can cause damage to the surface of an object.

The Chemical Characteristics of Lac

As mentioned in Chapter 2, raw sticklac is composed of 70-80% resin, which in turn can be divided into two parts: 25% soft (ether-soluble) resin, and 75% hard (ether-insoluble) resin. According to John Mills and Stuart White, shellac is a terpenoid resin consisting of low molecular weight polymers (oligomers) formed by esterification of polyhydroxy carboxylic acids with one another.[138]



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[135] Gardner, 1941, p. 273.

[136] Gardner, 1941, p. 275.

[137] Rivers & Umney, 2003, p.135.

[138] Mills, J.S., & R. White. *The organic chemistry of museum objects.* Oxford: Butterworth-Heinemann, 1994, p. 101.

Fig. 1 The most plausible chemical structure of the pure Lac resin (hard resin) polyester (Singh et al., 1974, p. 3692. & Limmatvapirat et al., 2007, p.691).

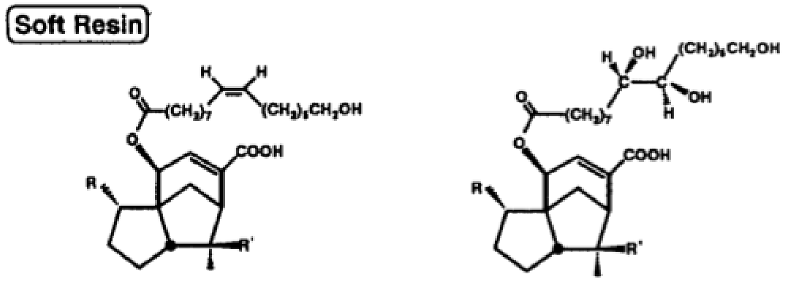

Fig. 2 The chemical structure of the soft resin component in shellac (Wang et al., 1999, p. 1317).

According to William Gardner, the soft resin portion of shellac acts as a natural plasticizer, while the hard resin is a brittle substance.[139] Cockeram et al. reported that the hard resin component, although brittle, has adherence properties exceeding those of shellac as a mixture.[140] The combination of flexibility and adhesion means that a shellac film adheres to the surface while it is flexible enough to allow for some movement without failing as a coating. Of survey respondents, 88% value the adhesion qualities of shellac as an important or very important characteristic; while 63% value the flexibility of shellac as important or very important. The superior adhesive qualities of shellac make it a favorite as a sealer/barrier coating when other coatings are to be used as topcoats, or to overcome surface problems, such as silicone contamination. Dewaxed shellac is generally suggested as a seal-coat under other finishes, as wax may lead to adhesion problems for the subsequent topcoat (if other than shellac). Waxy shellac is suggested when over-coating a contaminated surface, such as a surface impregnated with wax. The work of Ernest Parry suggests that wax-free shellacs lack mechanical strength, mainly in elasticity.[141]

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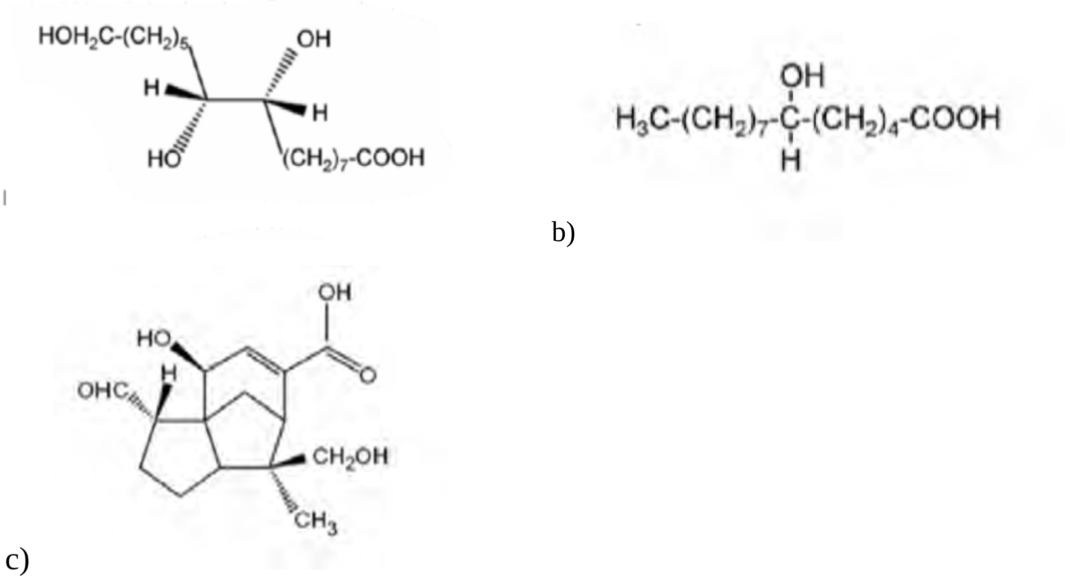
[139] Gardner, William Howlett. *Shellac and Other Lacs, in Protective and Decorative Coatings: Paints, Varnishes, Lacquers, and Inks,* Vol. 1, ed. Joseph J. Mattielo. New York: John Wiley & Sons, 1941, p. 266.

[140] Cockeram & Levine, 1961, p. 317.

[141] Parry, 1935, p. 179. Future studies should include extensive film technology studies testing the adhesive and flexibility qualities of various natural shellacs, as well as dewaxed and bleached varieties.

Although the composition of Lac seems to vary according to host tree, two acid groups have been identified in shellac; one being aleuritic and butolic acids, which are aliphatic compounds related to fatty acids; and the other being jalaric acid, an alicyclic compound of the sesquiterpene series.[142]



a) b)

c)

Fig. 3 The chemical structures of a) aleuritic acid, b) butolic acid, and c) jalaric acid (Farag, 2010).

According to Singh et al., pure Lac resin (hard resin) is derived from equimolar proportions of jalaric and aleuritic acids, while the soft resin is composed of jalaric and laccijalaric esters.[143] The secondary products of shellolic and laksholic acids, as well as epishellolic and epilaksholic acids are formed when jalaric acid is treated with an alkali solution.[144] From laccijalaric acid, laccishellolic acid as well as epilaccishellolic and epilaksholic acids occur.[145] As these secondary products occur under alkaline hydrolysis, it is likely that the secondary acid groups are developed during the processing from sticklac to seedlac. [146]

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[142] Mills & White, 1994, p. 101.

[143] Singh, A.N., Upadhye, A.B., Mhaskar, V.V., Dev, S., Pol, A.V., & Naik, V.G. "Chemistry of Lac Resin-VII: Pure Lac Resin-3: Structure." *Tetrahedron*. 30. (1974): 3689. & Singh, A.N., Upadhye, A.B., Mhaskar, V.V., Dev, S., "Chemistry of Lac Resin-VI: Components of Soft Resin." *Tetrahedron*. 30. (1974): 867-874.

[144] Mills & White, 1994, p. 101.

[145] Colombini et al., 2003, p. 358.

[146] An overview of mole percent distributions of 14 acidic compounds present in various types of shellac from India and Thailand is provided in Wang et al., 1999, p.1322.

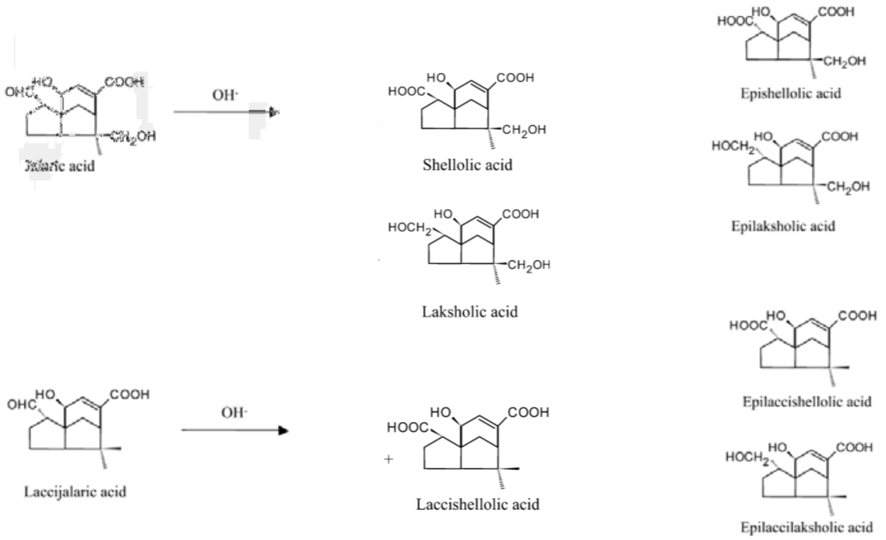

Fig. 4 The chemical structures of the major terpenic acid components of shellac, and the secondary products, which occur under alkaline hydrolysis, as reported by Colombini et al., 2003, p. 358.

According to the work of Ernest Parry, the presence of aleuritic and shellolic acids in shellac are a function of animal metabolism, making shellac a unique product in comparison with other natural resins used within conservation.[147] Cockeram et. al have pointed out that Lac resin is a viscous, colorless liquid when first exuded by the Laccifer Lacca, becoming harder and darker as esterification takes place.[148]

As the varieties of shellac have natural compositional differences on account of host trees, there is a potential for great variation in the flexibility and adhesion qualities between types of shellac. It was noted by Gardner that the hard and soft resins in Lac are not secreted at the same rate by the Lac beetle, the rate of the soft resin being irregular, and reaching its maximum content a month later than the hard resin.[149] It is unknown to what extent these compositional differences might affect the adhesion and flexibility of shellac as a coating. One hypothesis is that if sticklac is prematurely harvested, this could lead to a marked difference of properties in the finished shellac product.

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[147] Parry, E. J. *Shellac, Its Production, Manufacture, Chemistry, Analysis, Commerce and Uses*. London: Sir Isaac Pitman & Sons, Ltd., 1935, p. 140-141.

[148] Cockeram, H.S., Levine, S.A. "The Physical and Chemical Properties of Shellac." *Journal of Cosmetic Science*. 12. no. 6 (1961) p. 316.

[149] Gardner, 1941, p. 269.

Ageing or being exposed to photochemical deterioration will change the physical properties of a film coating. Shellac undergoes polymerization as it ages, eventually becoming insoluble in alcohol. Cockeram and Levine concluded that even if shellac has undergone extensive esterification, its adherence and coherence properties will prevail, due to remaining free hydroxyl and carboxyl groups.[150] The experimental section performs an industry standard cross hatch, pull-off tape test to determine whether there are changes in the adhesive qualities of various shellac types, before and after undergoing ageing and curing procedures.

The Esterification of Shellac

As mentioned in Chapter 1, the polymerization of shellac takes place by esterification and the expelling of water (H_2O), resulting in blocking and reduced solubility. Figure 5 shows the reaction of self-esterification that happens in shellac as it ages.

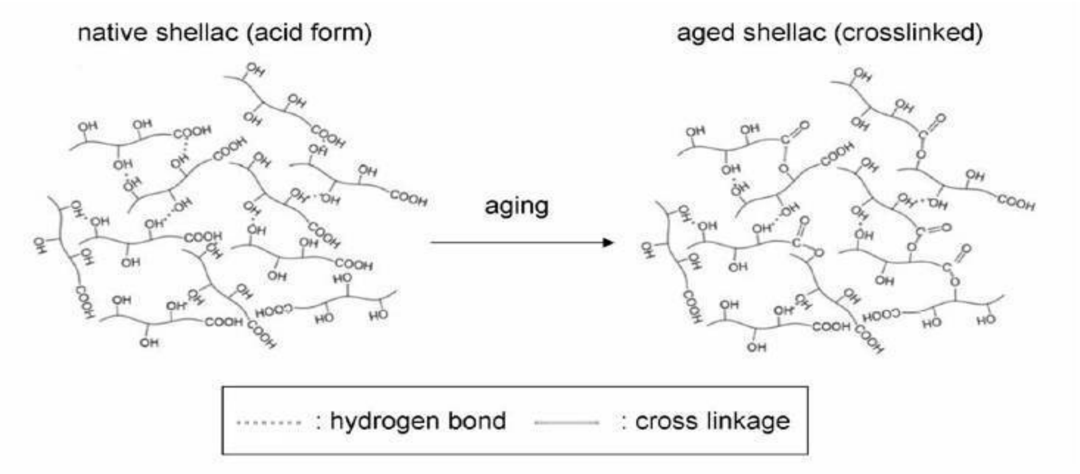

Fig. 5 The schematic description of the process of esterification, which takes place during aging of shellac (Farag, 2010, p. 15).

As mentioned above, the polymerization of shellac takes place by way of esterification, as shellac ages. As pointed out by P.K. Bose, shellac deteriorates with gradual loss of alcohol solubility, increase in melting point, and rise in alcohol insolubility, decreasing life and fluidity testing, as well as darkening in color.[151]

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[150] Cockeram & Levine, 1961, p. 318.

[151] Bose, P.K., Y. Sankararanarayanan, and S.C. Sen Gupta. *Chemistry of Lac*. Namkum, India: Indian Lac Research Institute, 1963, p.156.

The testing referred to are standard tests developed by the IINRG for the industry to determine the freshness of bulk shellac product. One of these tests is called the "*Flow Test*", and measures the fluidity of shellac at a certain temperature, assigning a value to the quality, from the highest rating of 95, down to the minimum workable value of 50.[152]

The polymerization process is accelerated when shellac is exposed to heat. When shellac is heated above its melting point of 120-130℃, it becomes 70% insoluble in alcohol very quickly, before the rate of reaction slows down, leaving only 5-10% alcohol-soluble when fully cured.[153] As the level of alcohol insoluble material rises, splitting of water vapor occurs, gradually eliminating water from the molecular structure of the shellac.[154] The test devised to measure how quickly shellac polymerizes when exposed to heat, is called the "*Life Under Heat*" test. Shellac goes from being soluble in alcohol and fusible with heat in stage A, to a rubbery consistency in stage B, until it becomes impervious to alcohol, hard and horn-like at stage C.[155] The third standard test in the industry gives shellac an *Acid Value* number; a higher number indicating freshness, as there is more acid present that is not yet polymerized.[156]

Chapter 6 includes an experiment devised with samples of shellac cured to the C stage, to identify and monitor polymerization in various shellac varieties, and investigate whether or not there are variances attributable to processing method.

In a conservation setting, these tests would only be useful as an indication of the freshness of shellac as a bulk product, and to determine whether or not the product is too old for use in a treatment schedule. There is good reason for monitoring the age and polymerization of products in use at the conservation laboratory. According to Gardner,

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[152] Baboo, B. & Goswami, D. N. *Processing, Chemistry and Application of Lac,* Indian Council of Agricultural Research, New Delhi, India: Chandu Press, 2010, p. 64. See appendix 4 for more on this test.

[153] Baboo & Goswami, 2010, p. 81.

[154] Baboo & Goswami, 2010, p. 82.

[155] Bose et al., 1963, p. 157. This reaction is reversible, as B-stage shellac can be converted to A-stage shellac by heating under pressure in the presence of water, for example in an autoclave. Baboo & Goswami, 2010, p. 82.

[156] Baboo & Goswami, 2010, p. 162. See appendix 4 for a description of this test.

esterification reduces the film's resistance to water, and when the process has gone too far, the surface will remain tacky after application, and never dry to a hard film.[157] This can also be seen if dry shellac flakes have become "blocked" (clumped) or will not dissolve in alcohol.

Baboo and Goswami indicated that Lac exhibits a decrease of flow and heat polymerization time, as well as an increase in alcohol-insolubles at levels of high relative humidity, suggesting that these conditions cause rapid cross-linking within the structure of Lac.[158] Goswami et al. concluded that storing shellac at room temperature (14-25 ℃), in a paper bag, and under dry conditions (60-65% RH), is the best way to avoid unnecessary polymerization of shellac product.[159] An additional contribution to rapid esterification, is made by the addition of oxalic acid during the processing from seedlac to shellac. Goswami et al. concluded that the oxalic acid reacts with OH groups in shellac, accelerating the degradation of shellac during storage, and should be avoided.[160]

Degradation Issues within Conservation

The photochemical degradation of a coating can cause changes in optical (yellowing, opacity, loss of gloss), physical (brittleness, crazing/cracking/adhesion) and chemical properties (crosslinking, oxidation).[161] Such losses can severely affect the ability of a coating to protect an artifact, and could in turn lead to the degradation of the object itself. The experiments in Chapter 6 were devised to identify color change, loss of gloss, crosslinking, as well as adhesion, and additionally investigate whether these characteristics vary among different types of shellac.

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[157] Gardner, 1941, p. 272.

[158] Baboo & Goswami, 2010, p. 81.

[159] Goswami, D.N., Prasad, N., Baboo, B., Kumar, K.K., & Ansari, M.F. "Degradation of Lac With Storage and a Simple Method to Check the Same." *Pigment & Resin Technology*. 38. no. 4 (2009): p. 211, 216. Although this may be room temperature conditions in some climates, they are only achievable with air-conditioning in India, a luxury that is often unavailable/unaffordable.

[160] Goswami et al., 2009, p. 212-13.

[161] Rivers & Umney, 2003, p. 587.

Chapter 6

Experimental

This section describes in detail the procedures used to conduct a series of five experiments using 10 varieties of shellac processed by various methods, to investigate whether differences in the samples indicate distinctive performance characteristics when used as coatings for objects of cultural heritage.

Experiment 1: Investigates whether ten certified varieties of shellac processed in a number of different ways, exhibit marked differences in their spectra when examined by FTIR.

Experiment 2: Analysis of the FTIR data to determine whether differences in processing methods such as the chemical removal of color, or removal of wax are detectable.

Experiment 3: Investigates the effects of ageing and deterioration of a shellac film applied to a wooden substrate, testing the characteristics of adhesion, color and gloss.

Experiment 4: Investigates the polymerization of a shellac film subjected to natural and artificial ageing methods.

Experiment 5: Employs GC-MS analysis to quantify the components of the samples, facilitating a correlation between varieties of shellac, their chemical components, and their physical characteristics as a coating.

Experiment 1: Investigating Whether Certified Varieties of Shellac Exhibit Unique FTIR Spectra.

As mentioned in Chapter 1, (10) samples of shellac were selected to represent the array of shellac processing methods.

10 selected samples of shellac

1 De-waxed/bleached Jethua, from Tajna Industries.
2 Full wax/bleached, made from Thai seedlac, by Tajna Industries.
7 De-waxed/carbon color removal (solvent/evaporated) Superfine, Ernst P.
14 Full wax/color content-hand stretched Lemon (coal heat) Renshel Exports.
18 Full wax/color content-machine rolled Lemon (steam heat) Ernst P.
19 De-waxed/full color content (solvent/evaporated) Recto, Ernst P.
24 Kusmi Sticklac- not treated.
36 Full wax content-buttons (coal heat) washed for1hr- Aloak Kusmi
37 Full wax content-buttons (coal heat) washed for 2hr- Aloak Special Kusmi
38 Full wax content-buttons (coal heat) washed for 3hr- Aloak Super Kusmi

Sample Preparation

Samples were cast on glass slides, and were prepared by fully dissolving 5mg shellac in 20ml ethanol (200 proof). This ratio is termed a *2 pound cut* (2 pounds shellac: 1 gallon alcohol), and is an industry standard for use as a coating. The solution was filtered to remove remaining insoluble solids. Using a pipette, 3ml of this shellac solution was disbursed on a glass slide previously cleaned with ethanol. The glass slides with shellac solution were set under a ventilation hood at room temperature (ca. 23 degrees Celsius) for 70 hrs, ensuring ethanol evaporation, leaving dry cast film samples.

Samples were scanned by ATR-FTIR (Attenuated Total Reflectance).

ATR-FTIR Procedure

Instrument: Thermo Nicolet 6700 Fourier transform infrared (FTIR) spectrometer
Resolution: 1 cm^{-1}
Sampling accessory: Golden Gate ATR with diamond crystal, single bounce, 45º

Detector: DTGS (Deuterated Triglycine Sulfate)
Number of scans: 64
Correction: ATR corrected
Spectrum range: 4000-450 cm^{-1}

Samples for ATR-FTIR were scraped with a scalpel and placed directly on the diamond crystal of the ATR accessory before compressing. A piece of aluminum foil was used to back the sapphire anvil to eliminate any sapphire absorption in the IR spectrum.
Spectra were collected using Omnic software version 7.2.

Experiment 2: Comparing and Contrasting Selected Spectra, Searching for Evidence of Processing Methods.

Sample Preparation/Procedure

Sample Preparation and FTIR method was the same as in Experiment I. Using the list of 10 selected samples of shellac, comparisons were made between FTIR spectra of the samples. Spectra were collected using Omnic software version 7.2, then manipulated and imported to Word, using Spekwin 32 software.

Comparing Samples 1 and 2-

Although both these samples are bleached, only Sample 1 is dewaxed. These samples were compared to identify differences due to wax content.

Comparing samples 7 and 19-

Samples 7 and 19 are both processed by solvent treatment, but Sample 7 was treated with activated carbon filters to remove the coloring matter, erythrolaccin, from the mixture. These samples were compared to find evidence of differences related to color removal by activated carbon.

Comparing Samples 14 and 18-

Both samples contain wax and come from the same seedlac, but sample 14 is exposed to lower heat and stretched by hand, while sample 18 is exposed to steam heat and rolled by mechanical rollers. This comparison was made to gather information about whether FTIR reveals a difference between hand and machine made shellac.

Sample 24 is not processed or heat treated, and is a standard of the raw resin product before the interference of processing.

Comparing samples 36, 37, and 38-

These samples are all from the same seedlac, but have been washed at various increments. Samples 36 through 38 were compared to search for evidence of the effects of different washing times within the same batch of original material.

Experiment 3: Testing Qualities of Adhesion, Color, and Surface Gloss.

Shellac samples on wooden slats were prepared and exposed to artificial ageing as well as heat and steam curing.

Wooden slat sample preparation

40 wooden slats were prepared from the same piece of flat sawn maple, sized 20cm x 15cm x 2cm, and sanded with garnet sandpaper grit sequentially: 120, 150, and 180. The slats were then divided into 4 sets of 10; labeled 1-1, 1-2, 1-7, 1-14, 1-18, 1-19, 1-24, 1-36, 1-37, 1-38 (and 2-1, 3-1 etc. in 4 sets), matching the shellac sample numbers. Set 4 was stored in a dark storage unit, as a control set. Set 1 was exposed in the Weather-Ometer, while set 2 was dry-cured, and set 3 was steam-cured.

Shellac solutions were prepared by fully dissolving 5mg shellac in 20ml ethanol . This ratio is termed a *2 pound cut* (2 pounds shellac: 1 gallon alcohol), and is an industry standard for use as a coating. The solution was filtered to remove remaining insoluble solids. One taklon artist brush was designated for use with each shellac type, numbered to correspond to the shellac samples, to avoid any cross-contamination between samples. Brushes were not washed out with alcohol between uses.

Wooden slat sets 1 through 3 were prepared following a finishing schedule as one might prepare a wooden object/piece of furniture, in the following manner:
Each slat was prepared using a dedicated piece of 320-grit sandpaper, to avoid cross-contamination by sanding dust. Each slat was marked with the sample name and finished with its corresponding shellac sample. Each shellac sample had a designated brush, so not

to cross-contaminate shellac resins. To each slat, 1 coat sanding sealer was applied.[162] The raised grain was then lightly sanded off with the designated 320-grit sandpaper, passed over the surface 3 times, cutting the raised grain and giving a smooth surface. Two coats of shellac were then applied to each slat and allowed to dry for one hour, after which the 320-grit paper was passed 2 times across the surface. This was done to ensure an even surface application, and then followed by two additional coats of shellac applied in the same manner. The finished wooden slats were left under a ventilation hood for 1 week, to ensure complete drying by solvent (ethanol) evaporation.

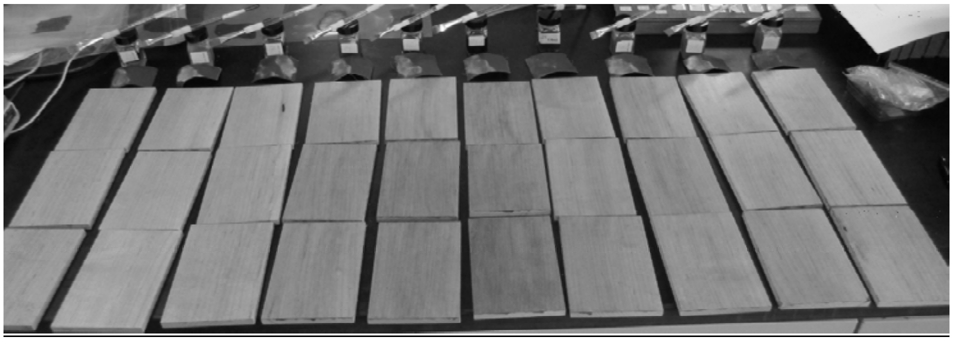

Image 19: Wooden slats prepared with respective shellac samples.

Procedure

Set 1 of the wooden slats finished with shellac (samples 1-38) were mounted to aluminum beds to allow for loading and securing in the Atlas Ci4000 Xenon Weather-Ometer.[163] Aluminum foil strips (3cm wide) were drawn across the wooden slats, to monitor color changes in the wood substrate itself.

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[162] Sanding sealer is the first coat of shellac on the bare wood. The application of this coat hardens the grain of the wood, allowing it to be sanded smooth.

[163] Samples were exposed to the equivalent of three months in the Weather-Ometer. See chapter 1 for limitations and details on mechanical failure.

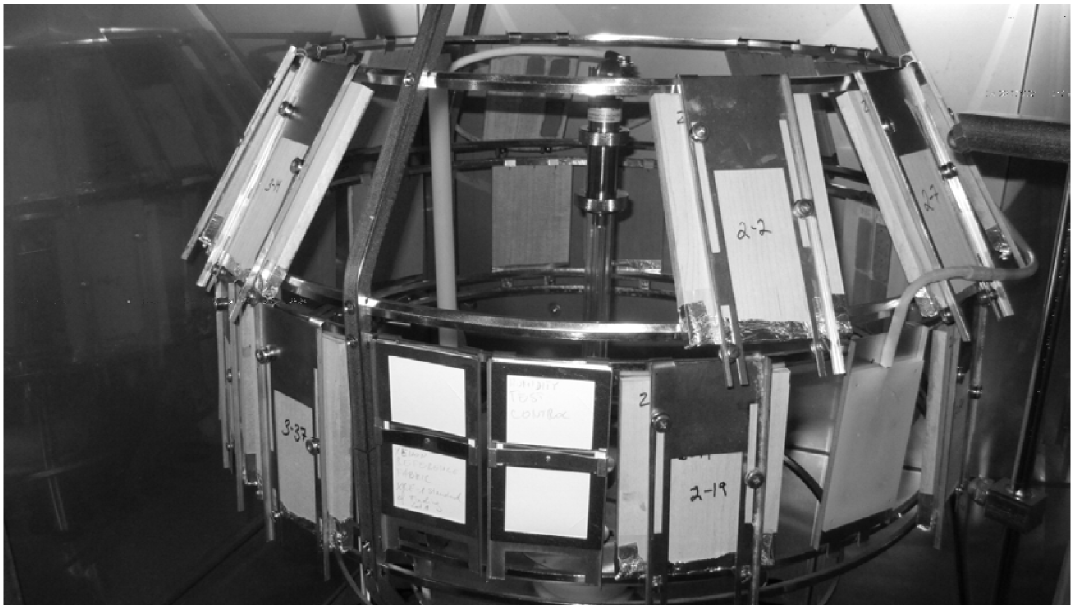


Image 20: Wooden slats and glass slides mounted in the weatherOmeter, for artificial ageing.

Set 2 of the wooden slats was dry-cured in an oven, 95℃ for 400 minutes.
Set 3 of the wooden slats was steam-cured in a steamer, 95℃ for 400 minutes.

All of the wooden samples were marked to enable 3 gloss measurements along the grain, ensuring that the measurements would be made on the same spot before and after artificial ageing/curing, to show any changes in the shellac surface gloss. Surface gloss was measured by gloss-meter before and after exposure, with the Micro-TRI-gloss, by BYK-Gardner. The device was set to measure at a 60% angle of incidence, as the samples have a semi-glossy surface, per the manual (p.46).

Image 21: Measuring surface gloss with the Micro-TRI-gloss.

One set of glass slides was prepared with shellac samples 1-38 (same preparation method for solution), for the purpose of measuring changes in color. Color change was measured by the visible light spectrophotometer MiniScan XE Plus, by HunterLab. See appendix 5 for experimental setup, and information on measuring color. Adhesive qualities were tested by a standard tape test, conducted on all three sample sets, before and after exposure.

Experiment 4: Identifying and Monitoring Polymerization in Shellac, Comparing Spectra Before and After Ageing/Curing.

Sample Preparation

Four sets of 10 glass slides were covered with aluminum foil and prepared using shellac samples 1-38 in solution, as in Ex. 1.

Set 1 (1-1 through 1-38) was tested as unchanged samples, for comparison.

Set 2, (2-1 through 2-38) samples were aged in room temperature (ca. 23℃), for 6 months.

Set 3, (3-1 through 3-38) samples were "heat-cured":

Samples were placed in a stable-temperature, dry oven, at 150℃ for 90 minutes.

Set 4, (4-1 through 4-38) samples were "steam-cured":

Samples were exposed to steam at 95℃ for 180 minutes.

Procedure

Sample sets 1-4 were sampled by same ATR-FTIR set up as in Ex. 1. The cast sample films were attached to the aluminum foil wrapped around the glass slides, allowing easy introduction of the sample, by placing the entire foil of aluminum backing to the sapphire anvil and compressing. Spectra were collected using Omnic software version 7.2.

Image 22: Glass slides wrapped in foil, heat cured in a GC oven.

Experiment 5: Quantifying the Components of Shellac by GC-MS.

GC-MS (Gas Chromatography-Mass Spectrometry)

Instrument: Agilent 6890N gas chromatograph with 5975 quadrupole mass spectrometer (GC-MS) and 7683 automated liquid sampler

Carrier gas: He, constant flow mode, at 1.5 mL/min.

Column: Agilent J&W HP-5MS, 30m x 0.25mm x 0.50µm

Inlet T: 300ºC splitless mode

Injection volume: 2 µL

Transfer line T: 280ºC

Column oven program: 50ºC for 1 min, 10ºC/min to 320ºC, hold 12 min

MS: EI, ion source 230ºC, quadrupole 150ºC, measuring masses from 50 to 650

Sample Preparation

Samples were taken from both bulk and from cast slides. Cast samples were prepared as in Experiment I. Sample amounts of ~0.2 mg were weighed out using a Sartorius Ultra Microbalance, the exact mass was recorded and the sample deposited in GC vials with 200 µL micro vial inserts, labeled and screw-capped shut. A derivitization solution was made of 1 mL Meth-Prep II (m-trifluoromethylphenyl trimethylammonium hydroxide (TMTFTH)), 0.5 mL of methanol and 0.5 mL toluene). To each sample 100µL of derivitization solution was added, the vials sealed, and placed in a 60℃ oven for 1 hour. After cooling the derivitized samples were analyzed by GC-MS. A blank sample of toluene was run on the GC-MS between each sample, to detect any sample carry-over between samples (sample residue left in column or injector, which might cross-contaminate samples. No such carry-over was detected).

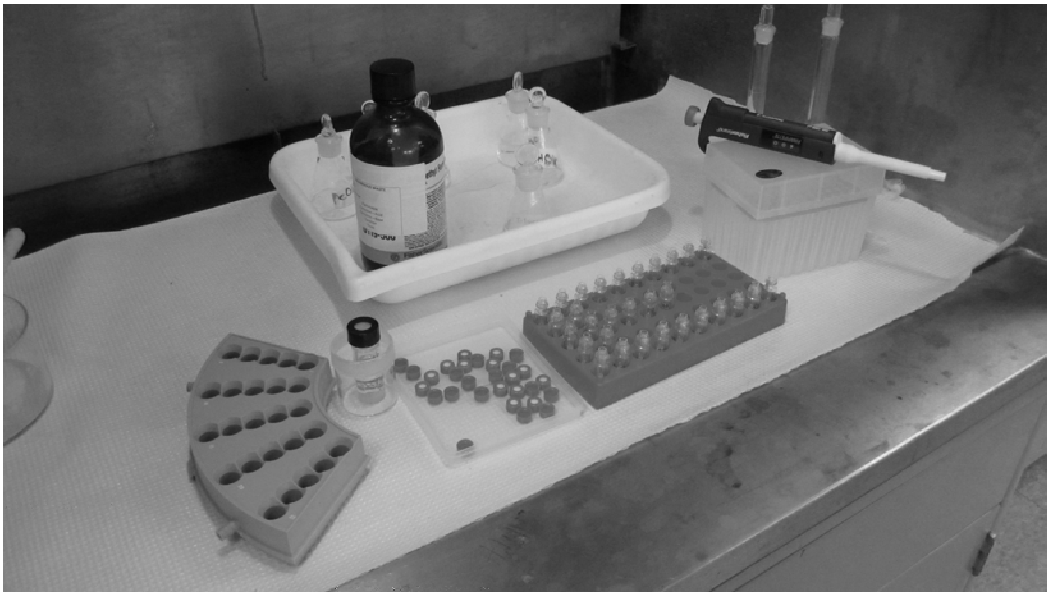


Image 23: Preparing GC samples.

Chapter 7

Results and Discussion

This chapter will present and discuss the results of the experiments conducted and described in chapter 6, including tabular presentations and graphs, as well as selected shellac spectra. For a complete set of spectra, consult appendix 6. All spectra have been baseline corrected to 0.0 and normalized at 1.0 intensity in absorbance mode, at the characteristic C-H stretching bands shared by all samples at 2934-2920cm-$_1$, unless otherwise noted. This is to facilitate visual comparison and indications of functional group intensities between spectra.

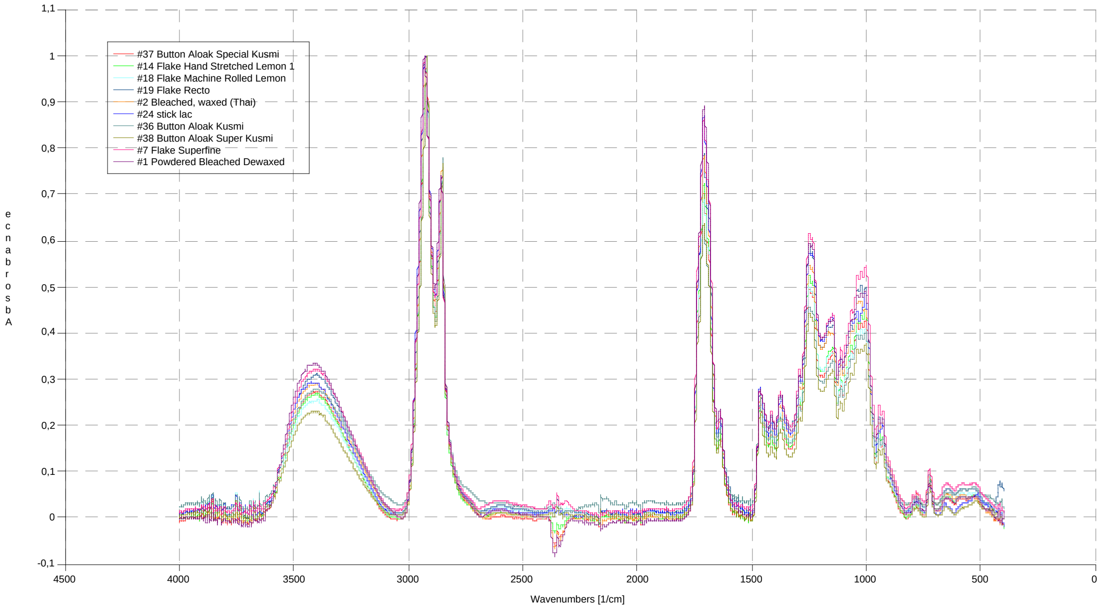
The following table presents the characteristic peaks of shellac when scanned by FTIR. The table is meant as a reference tool when discussing and reviewing spectra obtained for this study.

Table 8: Characteristic peaks for shellac

Molecular motion	Identified by Derrick et al.(cm-$_1$)	cm-$_1$ possible (in)	functional group
O-H stretch		3550-3200	hydroxyl
C-H stretch	2930	2940-2860	alkanes
C-H stretch	2857	2960-2940	alkanes
C=O stretch (fresh shellac)	1730-38	1740-1720	sat. aldehyde (ester)
C=O stretch	1715-22	1720-1710	sat. ketone (acid)
C=C stretch	1636	1680-1630	alkenes
CH_2 bend	1466	1470-1350	alkanes
C-O stretch	1240	1250-970	alkanes-from ester
C-O stretch	1163	1250-970	alkanes-from acid
C-O stretch	1040	1250-970	alkanes-from alcohols
C-H stretch/CH_2	945	995-880	alkenes
C-H stretch/CH_2	930	995-880	alkenes
CH_2 rocking	730/720	720-25	alkanes-shellac wax

Table 8 presents characteristic peaks for shellac, corresponding molecular motions and the range possible within the corresponding functional groups. (compiled with data from MSU, Infrared Spectroscopy, Scheinmann, 1970, pp. 123-143, & Derrick, 1999, p.107)

Experiment 1: Investigating Whether Certified Varieties of Shellac Give Unique FTIR spectra.

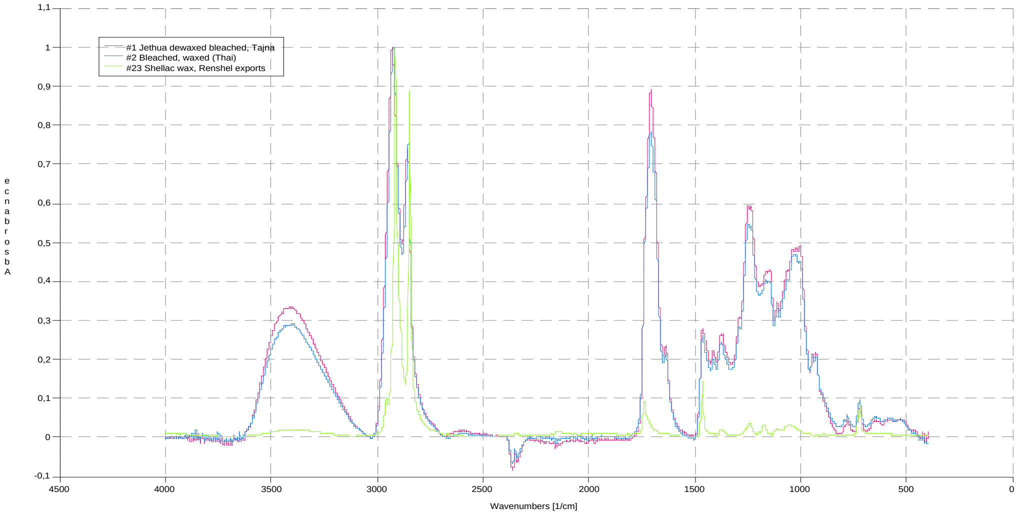


Spectrogram 1: A spectrogram of all 10 shellac samples

By overlaying the spectra of all 10 shellac samples, one can see that there is little peak variation between the types of shellac, though there are variations in peak intensity. A broad hydroxyl band is shared between 3400-3300cm-$_1$, as well as the C-H stretching bands at 2934-2920cm-$_1$ and 2857cm-$_1$. The carbonyl band from ester formation is visible at 1730cm-$_1$, while the band at 1715cm-$_1$ corresponds to acid groups. An olefinic band from C=C stretching is present at 1630cm-$_1$, while C-O bands from ester, acid and alcohol groups are present at 1240, 1163, and 1040cm-$_1$, respectively. The similarities in the distribution of peaks in the spectra indicate that various types of shellac share a common chemical structure, with varying intensities of individual components. As the peak distribution between the various shellac samples is so similar, it is not possible to identify each individual sample by its FTIR spectrum.

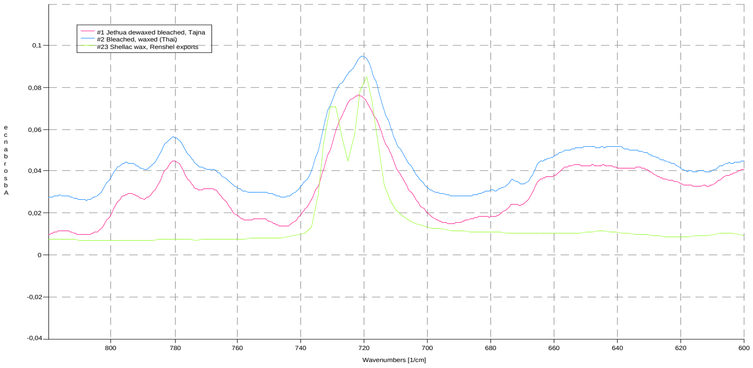
Experiment 2: Comparing and Contrasting Selected Spectra, searching for evidence of processing methods.

Comparing samples 1 and 2 with 23 (shellac wax)



Spectrogram 2: Samples 1 (pink), 2 (blue), and 23 shellac wax (green)

Samples 1 (dewaxed bleached) and 2 (waxed bleached) are both shellac samples that have been bleached with sodium hypochlorite. Additionally, sample 1 has been dewaxed, while sample 2 contains 3-5% wax.[164] In figure 7 sample 1 and 2 are compared with a spectrum of pure shellac wax, sample 23. Figure 8 takes a closer look at the spectra, focusing in on a section in the fingerprint region. Shellac wax (23, green) shows a characteristic doublet at 720 and 730cm-$_1$ which corresponds to shellac wax, and is the underlying structure of the peaks in both samples 1 and 2. Sample 2 contains wax, and shows a higher intensity than sample 1. Although most of the wax in sample 1 has been removed, there are still traces detectable within the sample.



Spectrogram 3: A closer look at samples 1,2 &23 at 720 and 730cm-$_1$

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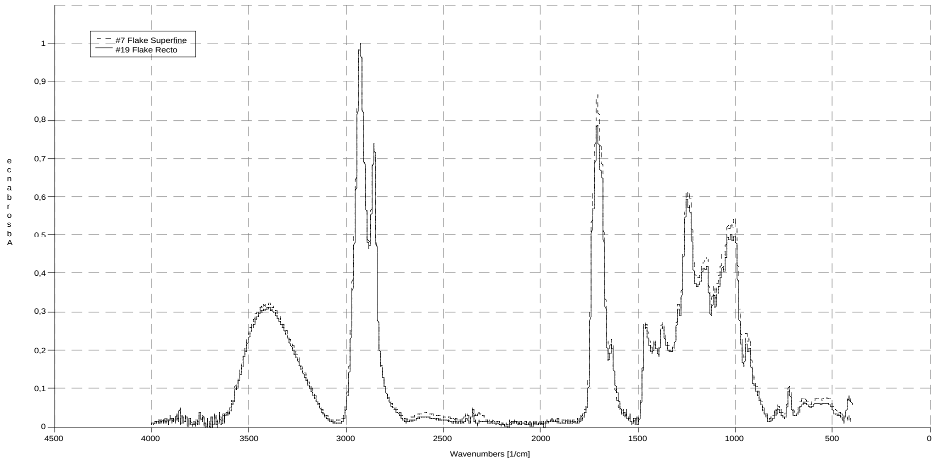
[164] The wax content in sample 2 is visible, as the shellac solution is cloudy. Sample 1 is transparent.

In this case, one can identify the presence of shellac wax in the samples, while the peak intensities indicate that sample 2 has a higher quantity of wax present. One is, however, not able to quantify the wax content in the sample by viewing the spectrum.

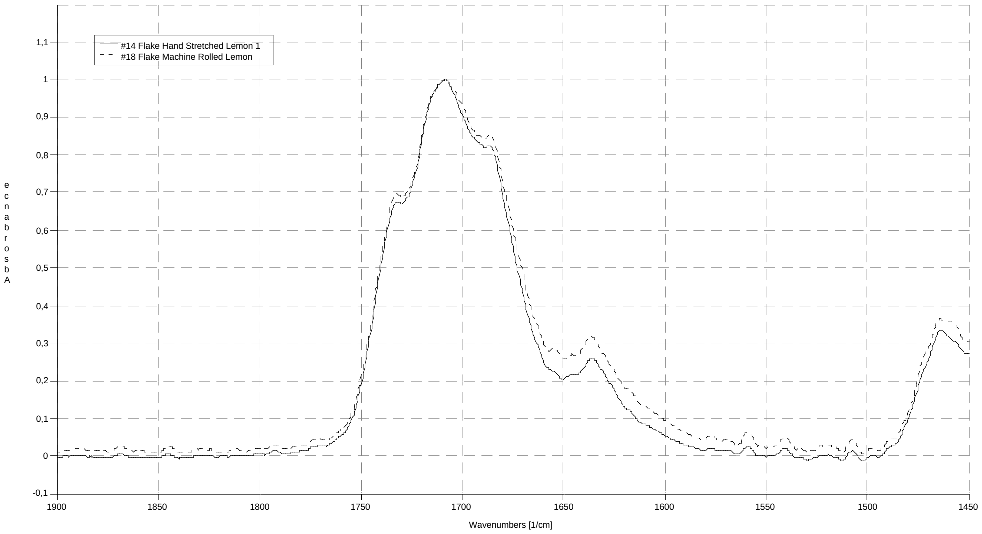
Comparing 7 and 19.



Spectrogram 4: Comparing sample 7 (dotted line) and sample 19 (solid line)

Overlaying 7 (erythrolaccin removed by activated carbon filtration) and 19 (full color content) for evidence of removing erythrolaccin gave two almost identical spectra. Although there is some peak intensity variation, the higher intensity bands belong to sample 7. Hence, it is not possible to identify or differentiate erythrolaccin content between the two shellac samples with this FTIR comparison.

Comparing 14 and 18.



Spectrogram 5: Comparing sample 14 (solid line) and sample 18 (dotted line)

In figure 10, sample 14 (hand-stretched Lemon) and 18 (machine-rolled Lemon) have been compared for evidence of heat differentiation during processing, resulting in two almost identical spectra. As exposure to heat hastens polymerization by esterification, one would expect the carbonyl bands corresponding to ester groups to be higher in the sample exposed to a higher heat source during processing. When the samples are normalized to the band at 1708cm-$_1$ (corresponding to acid groups), one can see that the relative intensity of the ester groups at 1730cm-$_1$ in sample 18 is higher than that of sample 14. This shows that the shellac exposed to higher heat has the taller peak, and is the more polymerized sample (in accordance with Derrick et al.)[165]

Comparing 36, 37, and 38.

Spectrogram 6: Compares samples 36 (brown), 37 (orange), and 38 (yellow) showing the progression of color in the samples. Sample 6 (Lac dye) is added in purple.

Samples 36 (washed 2 hrs), 37 (washed 2.5-3 hrs) and 38 (washed 4 hrs) have been compared in search of evidence of different amounts of lac dye, corresponding with washing time (with soda ash) during the conversion from sticklac to seedlac. The three spectra alone give the impression that the samples have an almost identical expression, with slight variation of peak intensity. When sample 6 (lac dye) was added, a shared

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[165] Derrick et al., 1999, p. 105.

triple peak between 1465cm-$_1$ and 1300cm-$_1$ became evident as the only shared area between the samples. This may be the indication of lac dye in the samples, as it shows the progression of washing out the dye in the correct sequence.

Experiment 3: Testing Qualities of Color, Surface Gloss and Adhesion.

Measuring Color Change

Table 9: Spectrophotometric measurements of color shift in shellac samples after artificial ageing

	Lightness decrease	hue shift	chromaticity	visual appearance
Sample 1	-0.93	0.13 towards green	increase	cooler
Sample 2	-2.01	-0.76 towards yellow	increase	warmer
Sample 7	-0.83	-0.22 towards yellow	increase	warmer
Sample 14	-1.76	-1.30 towards yellow	increase	warmer
Sample 18	-1.62	-1.06 towards yellow	decrease	warmer
Sample 19	-2.40	-1.69 towards yellow	increase	warmer
Sample 24	-3.19	-0.83 towards yellow	increase	warmer
Sample 36	-0.63	2.29 towards green	decrease	cool, to grey
Sample 37	-2.55	-1.01 towards yellow	increase	warmer
Sample 38	-2.24	-0.88 towards yellow	increase	warmer

Table 9 is compiled from appendix 5.

Samples 2, 24, 36, 37, and 38 showed a significant color difference. For other samples color difference is barely perceivable. All the samples showed some brightness decrease (24, 37 and 38 darkened the most). 8 out of 10 samples have gone warmer in color, while samples 1 and 36 have gone cooler. Sample 36 changed its optical properties the most. There is no evident link between samples 1 and 36 to explain their shift in hue, towards green. Samples 2, 24, 37 and 38 all contain wax, but are otherwise processed in different manners. The sample with the darkest initial color, sample 19, yellowed the most.

Measuring Gloss Change

The following table shows changes in surface gloss on wooden samples finished with shellac, measured at two marked points, before and after ageing. The degrees of difference were combined and averaged to yield this result.

Table 10: Changes in surface gloss after artificial ageing

	Average Starting gloss level	Average gloss change
Sample 1	39.4	-18.3
Sample 2	36.7	-6.6
Sample 7	50.9	+5.8
Sample 14	41.4	+5.5
Sample 18	46.8	+14.2
Sample 19	35.5	-12.1
Sample 24	44.5	-5.9
Sample 36	45.3	-0.5
Sample 37	32.6	+13.3
Sample 38	37.4	+17.2

Table 10 is compiled from appendix 7.

The results of the gloss meter readings show that sample 1 changed the most with –18.3 degrees, while sample 36 changed the least with –0.5 degrees. Samples 7, 14, 18, 37 and 38 all show increased degrees of gloss, while samples 1, 2, 19, 24 and 36 decreased in degrees of gloss. There is no clear pattern as to why the samples increased or decreased in gloss as a result of ageing/curing. It is interesting to note that the initial gloss levels of wax-containing varieties were not significantly lower than dewaxed varieties. As discussed in chapter 5, the visual difference between the two, is on account of attributes such as visual clarity.

Adhesive Changes in Shellac Samples After Curing

The following table shows changes in adhesive qualities of shellac samples as a freshly applied shellac (allowed to dry 1 week), dry-cured in an oven (95℃ for 400min.), and steam-cured (95℃ for 400min.). The fractions denote fragments pulled off by the tape, from a 100 square grid, 1cm by 1cm.

Table 11: Adhesive changes in shellac, measured by pull-off test

	Fresh	Dry-cured	Steam-cured
Sample 1	none	3/100	11/100
Sample 2	none	1/100	8/100
Sample 7	none	5/100	14/100
Sample 14	none	3/100	14/100
Sample 18	none	0	10/100
Sample 19	none	5/100	14/100
Sample 24	none	0	14/100
Sample 36	none	0	12/100
Sample 37	none	1/100	15/100
Sample 38	none	1/100	17/100

After dry-curing the sample surfaces do not have visible cracking or crazing, but an intact film coating. After steam-curing, the sample surfaces are visibly cracked as a result of the expansion and contraction of the substrate during exposure to steam.

The results show that there is very little loss of adhesion after dry-curing. Of the dry-cured samples, 18, 24 and 36 had no loss of coating, while sample 7 and 19 had the most. Samples 7 and 19 are both dewaxed. Dewaxed shellac is often used as a sealer, since the natural wax is thought to lessen adhesion qualities of subsequent film coatings. Although this test shows that the dewaxed varieties had the most loss, it may also be that the wax in the other samples prevented adhesion to the tape, and therefore was not pulled off. A test combining adhesion and surface tension testing, correlating to combined abrasion resistance and tendency to dislodge from the surface should be conducted to check this. The results show that there is some loss of adhesive qualities of shellac after being exposed to steam. Sample 2 had the least loss, while sample 38 had the most. There is no clear pattern of degradation of adhesive qualities due to processing method.

Experiment 4: Identifying and Monitoring Polymerization in Shellac by Comparing Spectra Before and After Aging/Curing. (Spectra for each sample group are compiled in Appendix 8.)

Identifying the polymerization process by heat-curing (D) and steam-curing (W) shellac samples (a comparison of sample sets 3 and 4).

Polymerization of shellac happens by esterification, while water vapor is released from the molecular structure. The peak related to ester in shellac, is located at 1730cm-1, while the main OH peak (thereby showing fluctuation of water content) is located between 3464-3387cm-1. To identify the process of polymerization analytically, shellac samples were exposed to: dry heat-curing (150℃ for 90 minutes), denoted by a “D”; and to steam-curing (95℃ for 180 minutes), denoted by a “W”. As Baboo and Goswami contend that the esterification of shellac is reversible, it was hypothesized that this should also be visible in the spectra. Theoretically, the ester peak should increase during heat-curing (while OH decreases) and decrease during steam-curing (while OH increases). Samples were exposed to steam to visualize whether water would be absorbed into the sample, and to monitor any changes in ester/OH peak relationships.

When comparing heat-cured and steam-cured samples, the theory of esterification is visible in all but one sample in both instances. After heat-curing samples, the general trend is that the ester peak rises in intensity, while the OH peak decreases. After steam-curing, the general trend is that the OH peak rises in intensity, while the ester peak decreases.

Ester peak intensity (Graph. 1).

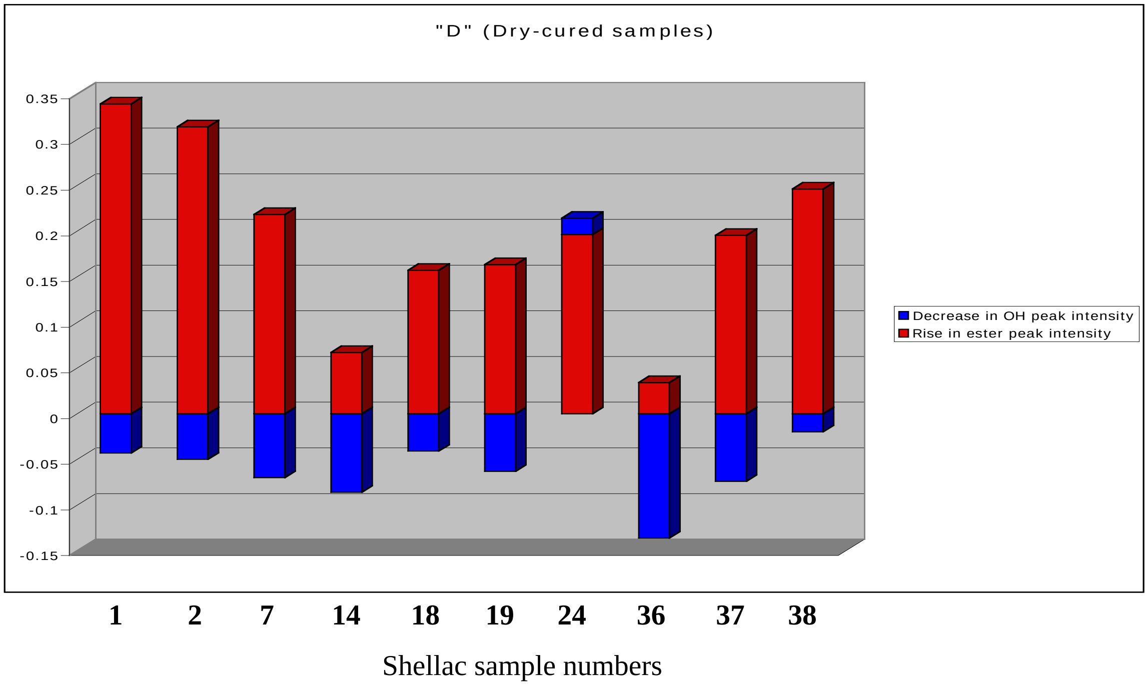
After heat-curing the spectra were compared and the rates of change in peak intensities of ester and OH in sample set 3 were compiled into a bar graph, showing the changes that took place as a result of the curing process. The peak intensities of sample set 1 were used as a baseline (at 0) in the graph. All the shellac samples showed increases in ester peak intensities as a result of heat-curing. All shellac samples showed OH peak decreases during heat-curing, except sample number 24, the raw stick lac. Stick lac is the only shellac sample that has not been processed by heat or refined in any way.

OH peak intensity *(Graph. 2).*

After steam-curing the spectra of sample set 4 were compared and the rates of change in the ester and OH peaks were compiled into a bar graph, presenting the changes taking place during steam-curing. The peak intensities of sample set 1 were used as a baseline (at 0) in the graph. In this case, sample 2 showed a decrease in OH peak intensity, while every other sample showed increases in the same, and decreases in ester peak intensity.

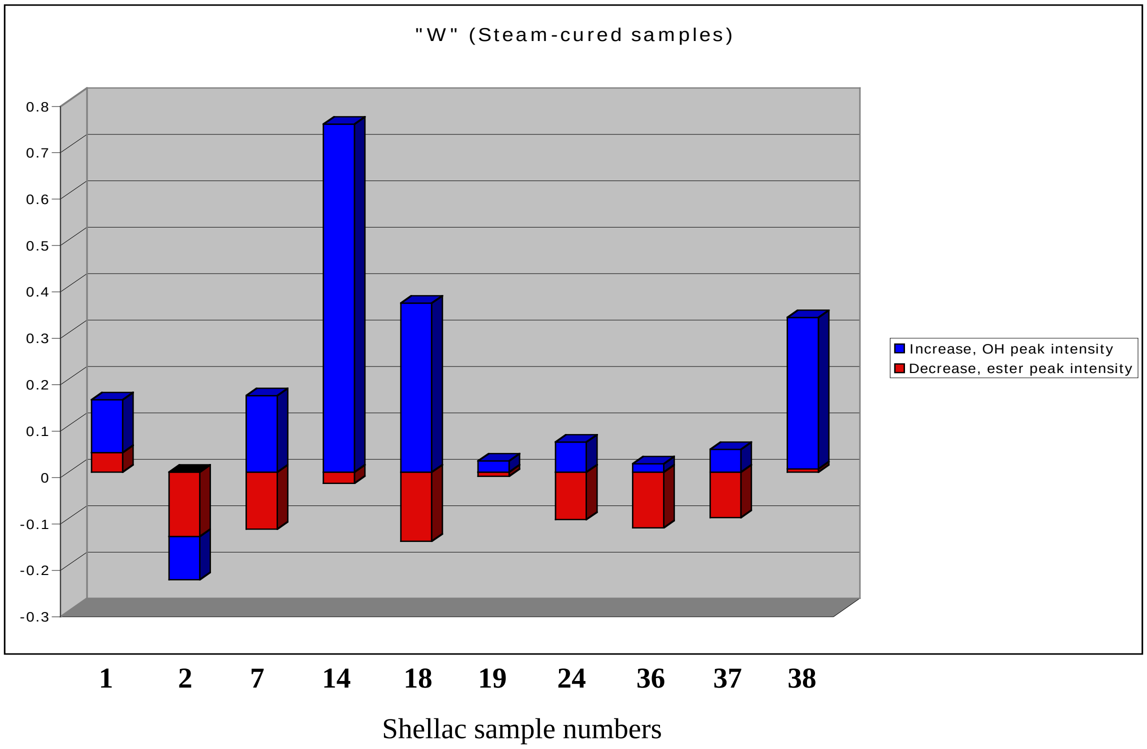
Graph 1: The increase in ester, the decrease in OH.

A bar graph representing the rise in ester peak intensity, with the simultaneous decrease in OH peak intensity of shellac sample set 3, which have been heat-cured (polymerized).



Graph 2: The increase in OH, the decrease in ester.

A bar graph representing the increase in OH peak intensity, with the simultaneous decrease in ester peak intensity of shellac sample set 4, which have been steam-cured.



Monitoring polymerization by comparing fresh film samples (set 1) to heat-cured (D-set 3) and steam-cured (W-set 4) samples.

FTIR scans were conducted of the original samples, as well as the “D” and “W” samples, then viewed together, to monitor the esterification process. Samples were compared to see if esterification could be identified, and to see if any patterns could be deduced, by considering the processing methods of the shellac samples.

Ester peak intensity (Graph 3)

The initial peak intensities of sample set 1 are shown in black, the increases of ester peak intensity after heat-curing (set 3) are red, while the decreases in ester peak intensity after steam-curing (set 4) are shown in blue (below zero).

Of the ten (10) types of shellac, sample numbers 1 and 2 had the highest increase in ester peak intensity during heat-curing, while samples 14 and 36 increased the least. Samples 1 and 2 are both bleached shellac, while 14 and 36 are both processed by traditional, coal heated battha ovens. Samples 14, 19 and 38 had the smallest decreases of ester during steam-curing, while sample 1 had an increase in ester intensity. There is no obvious link between these three samples: sample 1 is bleached and dewaxed; sample 19 is dewaxed and refined by solvent method, samples 14 and 38 contain wax and are refined by coal oven heat.

Comparing samples 36, 37 and 38, one can see a that the sample washed only two (2) hours in soda ash (sample 36) has the lowest increase in ester peak intensity during curing and the most decrease in ester peak during steam-curing, while sample 37 (washed 3 hours) has a higher increase during curing, and less of a decrease during steaming. Sample 38 (washed 4 hours) has the highest increase of the ester peak during dry-curing, as well as a very small increase during steaming. This trend could lead one to hypothesize that the more a shellac sample has been washed with water and soda ash, the more susceptible it is to esterification, with less and less reversibility of the process.

OH peak intensity (Graph 4).

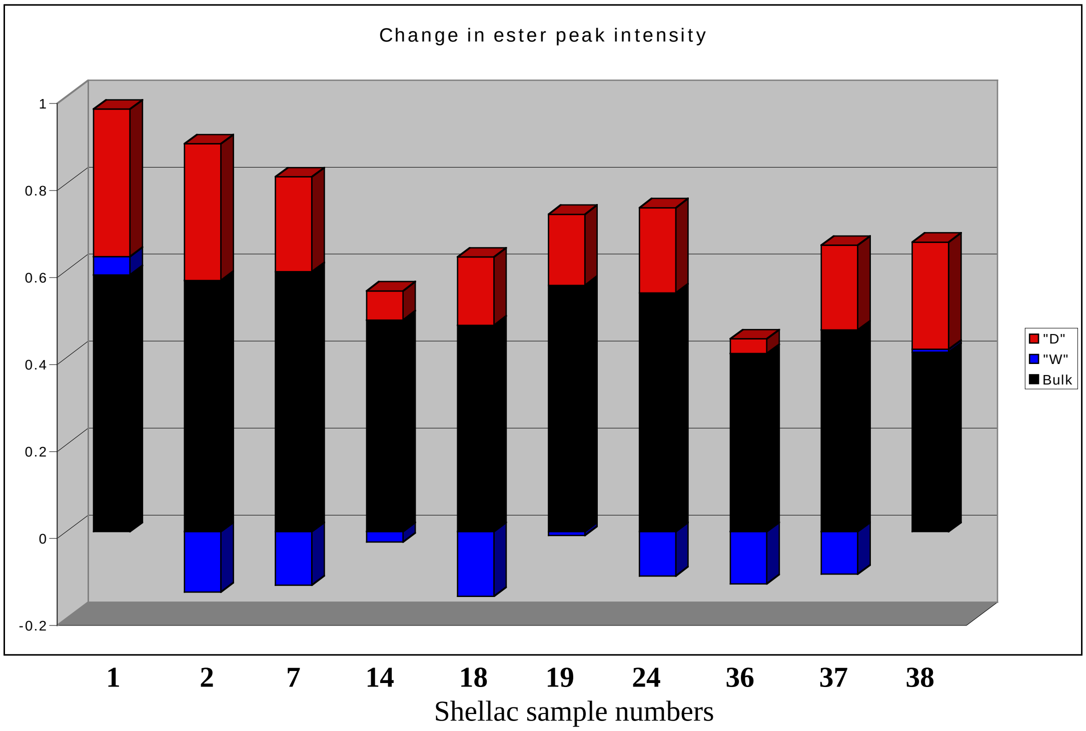
The initial peak intensities of sample set 1 are shown in black, the increases of OH peak intensity after steam-curing (set 3) are blue, while the decreases in OH peak intensity after steam-curing (set 4) are shown in red.

All shellac samples which have undergone any type of heat processing, showed decreases in OH peak intensity after heat-curing, and increases in OH peak intensity after steam-curing, with variable rates. Sample 24 (raw sticklac), however, displayed increases during both curing treatments. Both types of curing are the first time the sticklac is exposed to any heat treatment.

Comparing samples 36, 37 and 38, one can once again see a progression. The sample washed only two (2) hours in soda ash (36) absorbs the least amount of water during steam-curing, while it loses the most during heat-curing. Sample 37 absorbs more water, but looses less during heat-curing, and sample 38 absorbs the most water during steam-curing, while losing the least amount during heat-curing. The more a shellac sample has been exposed to water-washing, the more OH it seems to reabsorb during steam-curing, and the less it loses during heat-curing. This presents itself as counter-intuitive, since shellac washed longer could or should have higher moisture content, and thus have more integrated water to lose. Instead, one might conclude that shellac treated longer with water during processing, is more receptive to reabsorb it later. The implications this trend might have for the physical attributes of certain shellac types and coatings technology is uncertain, but may be an interesting question to pursue in further research.

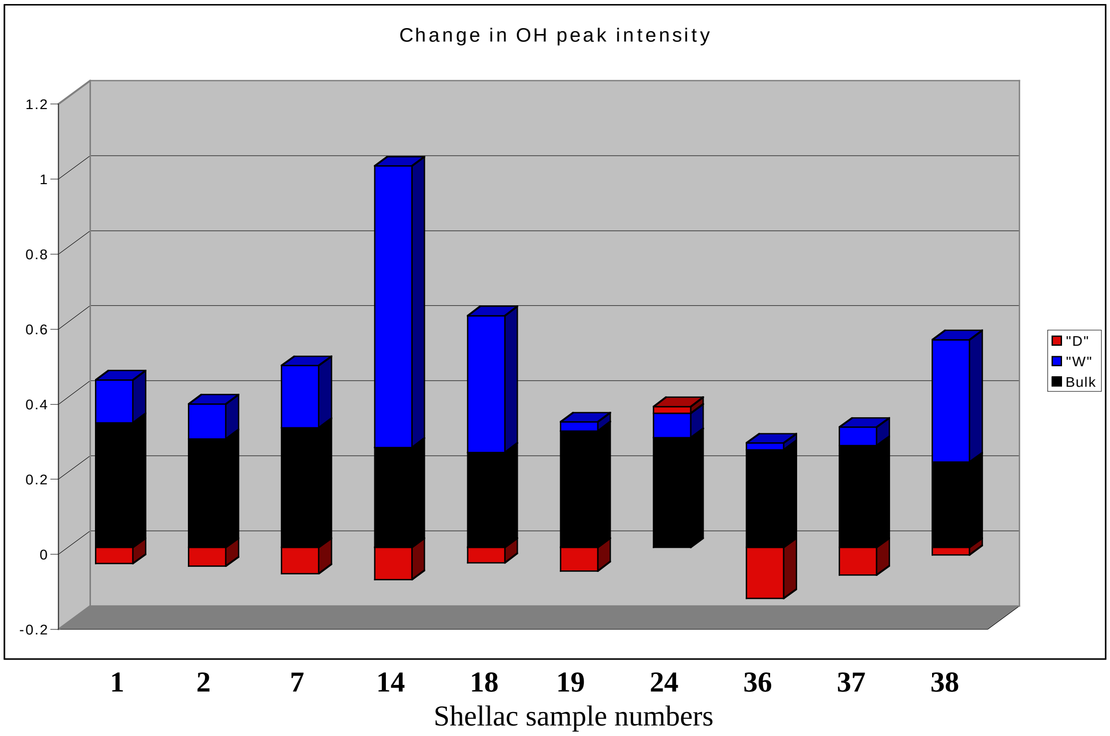
Graph 3: Change in ester peak intensity.

A bar graph showing the change in intensity in the ester peak of each shellac sample's spectrogram after curing, noted as "bulk" (set 1, freshly cast shellac film), "D" (set 3, heat-cured), and "W" (set 4, steam-cured).



Graph 4: Change in OH peak intensity.

A bar graph showing the change in intensity in the OH peak of each shellac sample after curing, noted as "bulk" (set1, freshly cast shellac film). "D" (set 3, heat-cured), and "W" (set 4, steam-cured).



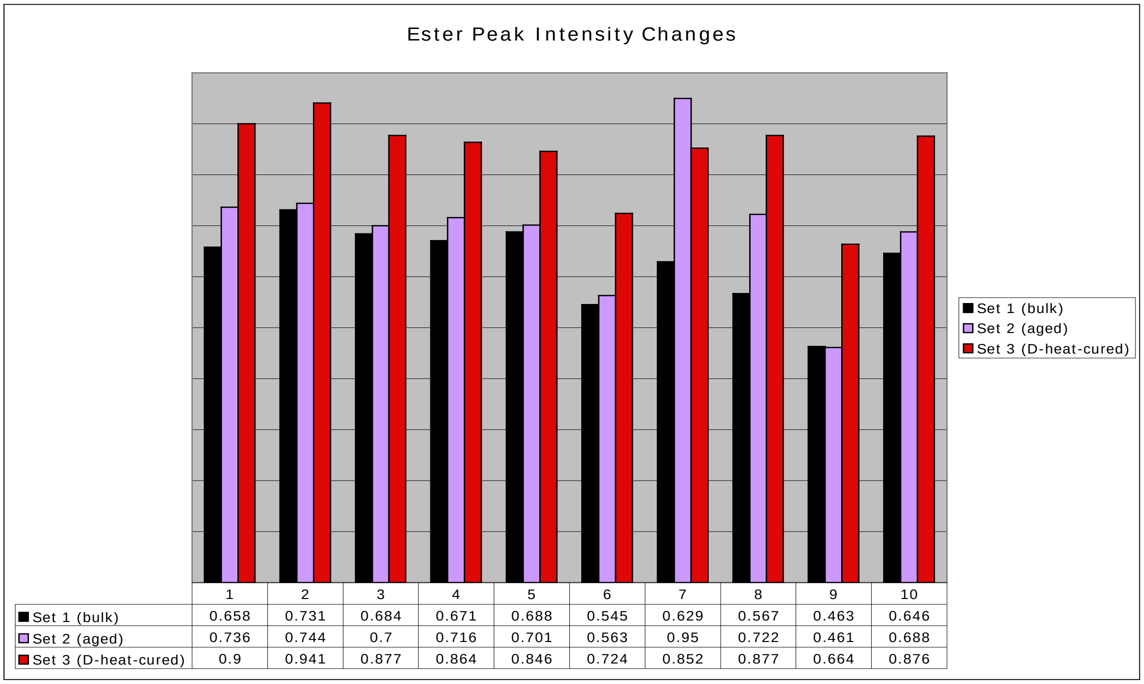
<u>Monitoring polymerization by comparing fresh film samples (set 1) to aged (set 2) and heat-cured (D-set 3) shellac samples.</u>

Shellac samples were aged and heat-cured to see whether the progression of polymerization by esterification would be visible in comparison with bulk product, by FTIR analysis. All but one sample showed increases in ester peaks after aging; sample 37 exhibited a .002 decrease in intensity. All samples but one showed further increases when heat-cured: sample 24 exhibited a lower increase during heat-curing than during aging. Sample 24 is the only sample that has not been exposed to any heat treatment or processing. The fact that sample 24 increased in ester intensity so strongly when exposed to ageing (including UV exposure), makes me wonder whether exposure to heat and the subsequent polymerization level makes the processed products more resistant to UV deterioration. This may be an avenue for further exploration and study.

Based on the FTIR measurements of the samples, it is evident that most aged shellac samples show increases in the intensity of the peaks associated with ester, at 1730cm-1. Further, all samples show a significant increase in ester development when cured.

Graph 5: Ester peak intensity changes.

A bar graph showing the Intensity changes in Ester peaks after ageing and curing.



	1	2	3	4	5	6	7	8	9	10
■ Set 1 (bulk)	0.658	0.731	0.684	0.671	0.688	0.545	0.629	0.567	0.463	0.646
■ Set 2 (aged)	0.736	0.744	0.7	0.716	0.701	0.563	0.95	0.722	0.461	0.688
■ Set 3 (D-heat-cured)	0.9	0.941	0.877	0.864	0.846	0.724	0.852	0.877	0.664	0.876

1 2 7 14 18 19 24 36 37 38

Shellac sample numbers

Concluding Remarks

Through documenting the background and processing of Lac in Part 1, it is evident that the host tree, the beetle strain, as well as the various refining methods, play important roles in the composition, the physical, and chemical characteristics of shellac. Traditional melting and hand stretching techniques yield waxed varieties of buttons and flakes, while more modern methods allow for the bleaching of color, as well as the removal of both color and wax.

In Part 2, sections dedicated to the chemistry of Lac have explained how the polymerization of shellac happens by esterification and the expelling of H_2O. We have seen that prolonged exposure to temperatures above shellac's melting point results in the polymerization of the product. One can hypothesize that higher temperatures during manufacturing also facilitate a more rapid esterification process. It stands to reason that products rendered under lower temperatures, such as traditionally produced buttons and hand stretched varieties of shellac, should have lower initial rates of polymerization due to less exposure to excessive heat. Through analytical testing, however, the conclusion is that these initial qualities are not positively detectable through FTIR scanning of various shellac samples.

As shown in experiment 1, the ten (10) selected samples of shellac do not exhibit marked chemical differences when scanned by FTIR spectrometry. The samples do, however, exhibit some variation in intensities of similar ingredients. Experiments were then devised to test the hypothesis that these variations could potentially change the physical performance-characteristics of the various shellac types. The chemical esterification process was simultaneously identified and monitored by FTIR analysis.

The physical and chemical characteristics of shellac and its components have been explored through available literature, as well as a survey. Experiment 2 indicated that the removal of laccaic acid and wax are detectable by FTIR, although not quantifiable. Experiment 3 confirmed that aged shellac has a slight tendency to yellow. While it is clear that some types of shellac change more than others, there are no clear patterns relating this function to methods of production. The same is true when trying to establish an explanation for why the surface gloss of various shellac types increased or decreased as a result of artificial aging. The adhesive qualities of shellac were shown to be remarkably stable after dry-curing, and though dewaxed samples failed to a higher degree, there was no clear pattern to explain why some varieties showed more signs of deteriorating adhesion after steam-curing.

Experiment 4 set out to identify the polymerization process in shellac by monitoring the peaks related to esters and OH in various shellac samples during curing procedures. The results show that the progressive polymerization process, via esterification, is identifiable with FTIR analysis, though there are no clear patterns of differentiation between varieties, based on processing method.

Experiment 5 produced chromatograms of the varieties of shellac, but they are at this time not identifiable. These chromatograms have been included as Appendix 11, and I encourage any comments or enquiries for further study. My hope is that future research can make use of the chromatograms as reference tools.

Recommendations for the use of shellac in a restoration-conservation setting.

When choosing shellac as a component in a treatment schedule, there are several aspects to consider. Variations in color and wax content of shellac make an aesthetic and protective difference when choosing a product for a specific object. Additionally, ethical guidelines for conservators should influence which coatings are deemed acceptable for use on furniture and objects of cultural heritage. Using waxed shellac provides a coating with additional flexibility, following the movements of the substrate. If exposed to liquid water, however, waxed shellac will develop white rings to a greater extent than dewaxed shellac. Dewaxed and waxed shellac will both build to a glossy surface, but dewaxed shellac will build to a film with higher clarity. All shellac samples show excellent adhesion qualities, and though dewaxed shellac should be chosen as a seal coat under other finishes, waxed shellac is likely to withstand more abrasion as a topcoat.[1] If one wishes to use a historically correct coating, care should be taken to use shellac rendered by traditional methods. Multiple applications of thin layers are preferable, as thick films retain more solvent, and leave the coating less resistant to moisture. It is up to the individual conservator to consider the environment in which the object will exist, and the needs of each object.

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[1] For more on the mechanical properties of shellac, consult Martin, p. 462.

It is important to choose shellac with a known production date. As esterification reduces the film's resistance to water, and solubility in alcohol, a conservator should use a product offering optimal protection. Shellac should be prepared fresh for use whenever possible, and mixed shellac in solution should be used or discarded within six months.

As shellac can easily and safely be prepared in alkaline solution, some users of the product are exploring this constitution as an option for finishing with shellac. Considering the results by Hagenmaier et al. further studies on film hardness and durability may be prudent before using shellac prepared with alkaline solution (water borne) in a conservation setting.[2]

Bleached shellac should be avoided in a conservation-restoration setting, as introducing trace elements of chlorine to an object is undesirable. Additionally, the use of sulfuric acid to precipitate shellac out of solution during the bleaching process creates a catalytic situation, which results in rapid esterification of the carboxylic acids present in shellac. As the rate of polymerization is brought to an advanced state by the processing method itself, the long term durability of the product is already compromised. It should be specified that a product where oxalic acid has been added during processing is also undesirable, as this exponentially speeds the rate of esterification.

Shellac that has been decolorized by charcoal filtration is a more suitable alternative when additional color is undesirable, although personal experience and survey responses cite that this product is also prone to blocking and alcohol insolvency after relatively short storage time. A date of production should always be requested for this product as well, to insure optimal freshness.

Further Possibilities for Study

As shown through FTIR analysis, shellac's components are detectable down to 1% of the total composition of a sample, and in light of the consistent results from the experimental data, it is clear that the compositional building-blocks of different shellac products are very similar. Therefore, to further determine the quantitative variations between various types of shellac, other methods must be utilized and perfected. Coordinating an experiment using GC-MS

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[2] Waterborne shellac is, however, useful in the application of aquarelle or gouache colors for retouching smaller, damaged areas of an object. For a discussion and guide on making aqueous solutions of shellac, consult Martin, p 459-462.

methods of analysis to quantify the individual components of shellac may be the key to correlating compositional values to the physical and chemical characteristics of shellac. Significant compositional variations could be due to either the taxonomy of the host tree, the strain of Lac beetle, or the many processing techniques. To minimize the variables, it would be necessary to maximize the number of samples sourced from each host tree, harvest time, Lac beetle strain, and processing method, gathering enough data to make a valid statistical comparison. In the area the performance of shellac coatings, an avenue for further study of the physical characteristics is whether or not the dry film thickness or method of application appreciably changes the protective qualities of the cured shellac film.

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Appendix 1

Survey of professionals/ frequent users of shellac
Distributed to over 100 professional finishers, 24 responses.

1. Application Method

Brush	1111111111111111111111
Spray	1111111111111111111
Pad	111111111111111

2. Type of shellac used

Orange/Amber	1111111111
Dewaxed (specifically)	111111111
Garnet	1111111
Blonde	111111
Dewaxed Blonde	111111
Dewaxed Garnet	1111
Clear	111
Bysaki	11
Dewaxed Orange	11
Lemon	11
Gold dust (powdered Lemon #1)	11
Kusmi	11
Seedlac	1
Angelo	1
Dewaxed Platina	1
Dewaxed Ruby	1
Siam	1

Use for dewaxed

General Use	1111111111111
Seal/barrier coat	1111111
Top Coat	111
Toner	1

Use for waxed

On waxed/contaminated surfaces	1111
French Polish (skates)	111
General Use	11
Top Coat	11
Building coat (flow)	1
Used for high wood movement	1
Touch-up	1

Either-Color as determinant for use	11

3. Experienced not dissolving/blocking/clumping

Yes	11111111111111
No	11111
N/A (does not mix their own)	11111

Type blocked

Garnet	111
Blonde	111
Orange	11
Super Blonde	11
Dewaxed varieties	1
Dewaxed Lemon	1
Gold Dust (powdered Lemon #1)	1
Amber	1
Dewaxed Orange	1
Dewaxed Blonde	1
Bleached	1
Kusmi Buttonlac	1

4. Concentration/cut used

General use	1.5-2 lb cut	111111111111111
Touch-up	1-1.5 lb cut	1
Seal	1-1.5 lb cut	11
Brush	2 lb cut	111
Brush	3 lb cut	11
Pad (French)	2 lb cut	11
Spray	2 lb cut	11
Spray	1 lb cut	1
Spray	3 lb cut	11
Stock 3 lb cut (dil. as needed)		1
No response		1

5. Alcohol used

Denatured alcohol	111111111111111
Ethyl Alcohol 200 proof	111111111
No response	1

Characteristics valued by frequent users of shellac

Adhesion-

Very Important	11111111111111111
Important	1111

Not Important	
No response	111
Compatibility-	
Very Important	111111111111111111
Important	111
Not Important	
No response	111
Use for French Polishing-	
Very Important	1111111111111111
Important	1111
Not Important	1
No response	111
Gives visual beauty/depth/ bi-refringence/chattoyance-	
Very Important	111111111111111
Important	111111
Not Important	
No Response	11
Use as a barrier/sealer-	
Very Important	111111111111111
Important	11111
Not Important	1
No response	11
Color-	
Very Important	11111111111
Important	1111111111
Not Important	1
No response	11
Use as top coat-	
Very Important	1111111111
Important	1111111
Not Important	111
No response	111
Ease of use-	
Very Important	11111111
Important	11111111111
Not Important	1
Not easy to use	11
No response	111

Use to reconstitute/amalgamate/ on top of old finish-

Very Important	1111111111
Important	1111111
Not Important	11
Not used for this	1
No response	1111

Repairability-

Very Important	111111111
Important	1
Not Important	
No response	111

Flexibility-

Very Important	111111
Important	111111111
Not Important	111
Not seen as flexible	1
No response	1111

Durability-

Very Important	1111
Important	11111111
Not Important	111111111
No response	111

Water resistance-

Very Important	11
Important	111111111
Not Important	1111111111
No response	111

Heat resistance-

Very Important	
Important	1111
Not Important	11111111111111111
No response	11

Other qualities/free text:

Versatile	11111
“Green” coating	1111
Safe coating	111
Quick Drying	111
High UV light protection	11
Stability over time	11
Food safe coating	1
Hypoallergenic	1
Low VOC/HAP	1

Comments:

Sets practitioner aside from competition	111
Easy to color with dyes/pigments	111
Matches look of aged color well	11
The most beautiful coating	11
Adds warmth/enriching	11
Storage seems to be the problem for blocking	11
Creates multi layer presentations	1
Somewhat inconsistent in quality	1
Surface manipulation possible (variety of rub-out)	1
Helps preserve the historical integrity of a piece	1
Waxed and dewaxed shellacs have different looks	1
Waxed and dewaxed feel different when padding	1
Dewaxed resists water marking better	1
Dewaxed needs grinding and constant stirring to dissolve	1
Would appreciate adherence to dating product	1
Enjoy the smell of shellac	1
Our secret weapon	1
Shellac has the ability to bring people together who live so far apart	1

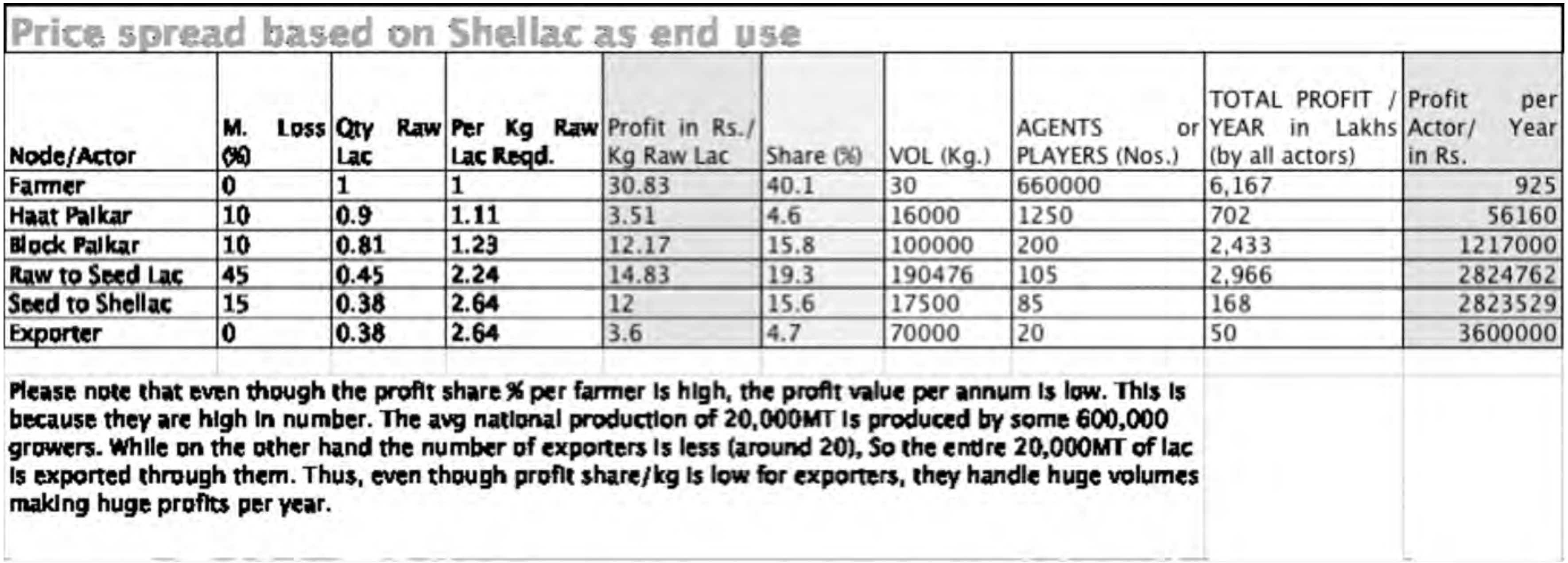
Appendix 2.

List of Total Shellac Samples Collected.

mple mber	Shellac/ By-product	Type of sample	Heat Treatment (coal vs. steam)	Stretched/rolled/ evaporated	Solvent treatment	Waxed/ dewaxed	Color removal carbon/bleach	Comments (name, producer, importer)
1	shellac	powder	unknown	none	yes	dewaxed	bleach	Bleached, Jethua, Tajna.
2	shellac	powder	unknown	none	yes	waxed (?)	bleach	Bleached, Thailand, Tajna.
3	shellac	powder	unknown	none	yes	dewaxed	bleach	Bleached shellac, Renshel.
4	shellac	powder	unknown	none	yes	unknown	unknown	Schellack mit Borax
5	shellac	flake	unknown	presumed evaporated	yes	dewaxed	carbon	Dewaxed super blonde, Renshel
6	By-product	powder	unknown	unknown	yes	N/A	N/A	Lac dye, Tajna.
7	shellac	flake	unknown	presumed evaporated	yes	dewaxed	carbon	Superfine, Ernst P.
8	shellac	flake	unknown	L.H.S.	unknown	unknown	unknown	From Bessels (more than 20 yrs
9	shellac	flake	unknown	L.H.S.	no	waxed	no	Lemon 1, Kremer.
10	shellac	flake	coal	Hand Stretched (H.S.)	no	waxed	no	Rangeenie #5, West Bengal.
11	shellac	flake	coal	L.H.S.	unknown	unknown	unknown	Red, from NIKU, before 2000
12	shellac	flake	steam	Machine rolled (M.R.)	unknown	unknown	unknown	From Mobelverkstedet
13	shellac	flake	unknown	M.R.	unknown	waxed	unknown	MM Lemon 1, Renshel.
14	shellac	flake	coal	H.S.	no	waxed	no	Hand stretched lemon 1, Rensh
15	shellac	flake	steam	M.R.	unknown	waxed	unknown	MM TN-Waxy, Renshel(thin flak
16	shellac	granules	unknown	none	yes	dewaxed	unknown	Dewaxed Bona 106, Renshel.
17	shellac	granules	unknown	none	yes	dewaxed	unknown	Dewaxed Beige 152, Renshel.
18	shellac	flake	unknown	M.R.	unknown	waxed	unknown	Lemon, Ernst P
19	shellac	flake	unknown	presumed evaporated	yes	dewaxed	no	Recto, Ernst P (thick flakes)
20	shellac	flake	unknown	L.H.S.	unknown	unknown	unknown	Orange, Mob.verkst.(thin flakes
21	shellac	flake	unknown	presumed evaporated	unknown	yes (?)	unknown	Ruby, Kremer (thick flakes)
22	By-product	granules	coal	unknown	yes	unknown	N/A	Black TN (for auto gaskets)
23	By-product	wax	unknown	N/A	yes	N/A	N/A	Shellac Wax, Renshel, India
24	Sticklac	bulk-thin layer	none	none	no	no	no	West Bengal, 2010. Raw produc
25	Seed Lac	seedlike-thin layer	none	none	no	waxed	no	With Oxalic acid, Balrampur.
26	Seed Lac	seedlike-thin layer	none	none	no	waxed	no	Not polished, Balrampur.
27	Seed Lac	seedlike-thin layer	none	none	no	waxed	no	Kusmi, Balrampur.
28	Seed Lac	seedlike-thin layer	none	none	no	waxed	no	Renshel, India
29	shellac	Button-thin layer	coal	none	no	waxed	no	Kusmi, West Bengal.
30	shellac	Button-thin layer	coal	none	no	waxed	no	Kusmi Special, West Bengal.
31	shellac	Button-thin layer	coal	none	no	waxed	no	West Bengal.
32	shellac	Button-thin layer	coal	none	no	waxed	no	Dark Bysakhi, Renshel.
33	shellac	Button-thin layer	coal	none	no	waxed	no	Kremer, India.
34	shellac	Button-thin layer	coal	none	no	waxed	no	Kusmi, West Bengal.
35	shellac	Button-thin layer	coal	none	no	waxed	no	Kusmi, Renshel.
36	shellac	Button-thin layer	coal	none	no	waxed	no	Aloak Kusmi, Balrampur, 1hr/sc
37	shellac	Button-thin layer	coal	none	no	waxed	no	Aloak Special Kusmi, 2hr/soda

Appendix 3

Price Spread on Shellac.



Price spread based on Shellac as end use

Node/Actor	M. Loss (%)	Qty Raw Lac	Per Kg Raw Lac Reqd.	Profit in Rs./ Kg Raw Lac	Share (%)	VOL (Kg.)	AGENTS or PLAYERS (Nos.)	TOTAL PROFIT / YEAR in Lakhs (by all actors)	Profit per Actor/ Year in Rs.
Farmer	0	1	1	30.83	40.1	30	660000	6,167	925
Haat Paikar	10	0.9	1.11	3.51	4.6	16000	1250	702	56160
Block Paikar	10	0.81	1.23	12.17	15.8	100000	200	2,433	1217000
Raw to Seed Lac	45	0.45	2.24	14.83	19.3	190476	105	2,966	2824762
Seed to Shellac	15	0.38	2.64	12	15.6	17500	85	168	2823529
Exporter	0	0.38	2.64	3.6	4.7	70000	20	50	3600000

Please note that even though the profit share % per farmer is high, the profit value per annum is low. This is because they are high in number. The avg national production of 20,000MT is produced by some 600,000 growers. While on the other hand the number of exporters is less (around 20), So the entire 20,000MT of lac is exported through them. Thus, even though profit share/kg is low for exporters, they handle huge volumes making huge profits per year.

From Binju Abraham, PRADAN. Ranchi, India. April, 2012.

Appendix 4.

Tests of quality for shellac, as specified by the IINRG.

Flow Test

Determining the flow of shellac or seedlac, is an industry standard for testing the freshness or quality of the product, ranging from a high value of 90 or 95, to the minimum workable value of 50.[1] Higher flow numbers indicate a fresher or better quality product. The IINRG reports that Kusmi shellac does have better flow as compared to Rangeeni shellac, the value decreasing with age, due to molecular polymerization and cross-linking within the resin component.[2]

The following is a simplified rendition of the *flow test*, as defined by the IINRG: Shellac is ground to powder, and a predetermined amount is placed into heat resistant test tubes. The test tubes are immersed into a bath kept at -+ 100 degrees Celsius, for three minutes, at which time the tubes are turned cork side down, and fixed at a 15degree angle. The distance traveled by the melted material in the course of 12 minutes, is the test result.[3]

Life Under Heat Test

The *life under heat* procedure tests how quickly the product polymerizes when exposed to heat, which is also called the *heat polymerization time*.[4] Fresh product will have a higher value of life under heat, as will a better quality of shellac. When shellac is heated, it first softens, then melts, becoming thicker and eventually turning into a rubbery mass, which upon cooling becomes tough, hard, and insoluble in alcohol, called cured shellac[5] This thermosetting development during the heating of shellac has been designated into three stages: Stage A is ordinary shellac which is soluble and fusible; Stage B is the rubbery stage, where shellac is still completely soluble; while Stage C is shellac in its cured state, infusible and impervious to alcohol.[6]

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[1] Baboo & Goswani, 2010, p. 64.

[2] Baboo & Goswani, 2010, p. 65.

[3] Baboo & Goswani, 2010, p. 160.

[4] Baboo & Goswani, 2010, p. 81

[5] Baboo & Goswani, 2010, p. 81.

[6] Bose et al., 1963, p. 157.

The method of testing consists of heating a sample of seedlac/shellac to 150 degrees Celsius in a test tube, and observing the time it takes for the substance to become rubbery, indicated by the spring back of a glass rod twisted in the mass.[7]

Acid Value Test

The Acid Value test gives the number of mg of KOH (Potassium Hydroxide) required to neutralize the free acid present in 1g of Lac sample. Higher numbers reflect fresher shellac, as polymerization and ester formation takes place during long term storage, resulting in tighter structural bonding within the product, reducing the amount of acid available to neutralize.[8]

The method consists of an alcohol solution of Lac being titrated with a solution of KOH until the free acid in the sample is neutralized, using Thymol Blue as an indicator.[9]

Range of quality test results on Lac:

Type	Flow	Life	Acid Value
All Lac			65-75
Rangeenie	35-55mm	30-50min	
Kusmi	60-100mm	45-70min	

[10]

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[7] Baboo & Goswami, 2010, p. 160.
[8] Farag & Leopold, 2009, p. 35.
[9] Baboo & Goswami, 2010, p. 162.
[10] Baboo & Goswami, 2010, p. 160-161.

Appendix 5.

Spectrophotometric examination of color change in shellac samples

By: Marta Doroszczyk and Juliane Derry, photos by Miriam Murphy

Introduction:

Spectrophotometry in visible light provides an instrumental evaluation of the color appearance of specimens examined. Tristimulous values XYZ correspond to the human perception of color (CIE 1931 Standard Observer). They match the response of the eye's conical cells with maxima in red, green and blue respectively. Y value was also chosen to represent the lightness. L*a*b* scale describes lightness and chromaticity of the color. L* stands for lightness and can have values from 0 (perfect black) to 100 (perfect light diffuser). Chromaticity coordinates a* and b* have no specific numerical limits and can have either positive or negative values. a* axis goes from green (negative) thru gray to red (positive). b* axis goes from blue (negative) thru gray towards yellow (positive). dE describes overall color change taking into account lightness and chromaticity. L*C*h scale is similar to L*a*b* but uses cylindrical coordinates instead of rectangular coordinates. C* describes chroma and goes from gray (0, center of the color wheel) to the saturated color. h is the hue angle and can have values from 0° to 360°. dL*, dC* and dH* describe the lightness, chroma and hue angle change respectively.

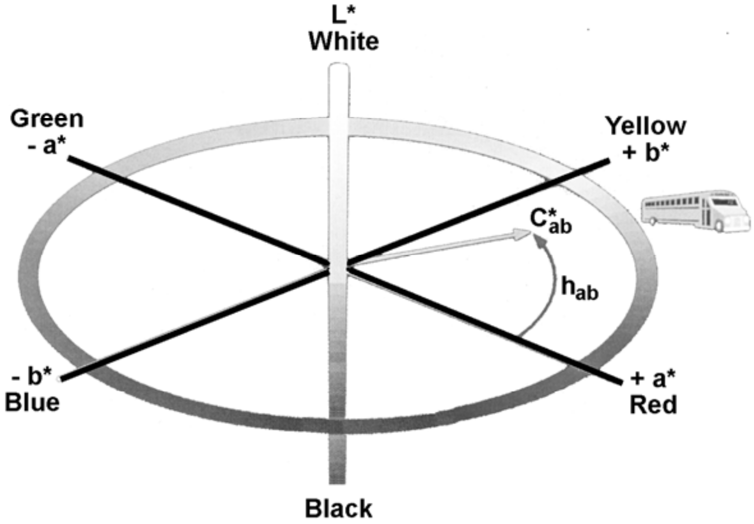


Figure 1: L*C*h color scale

Experiment setup:

Ten samples were measured before and after weathering using the visible light spectrophotometer MiniScan XE Plus by HunterLab. With a diffuse/8° geometry model the device has a 6 mm wide area of view. A combination of D65 illuminant and 10° observer was used. Samples of different kinds of the shellac on glass slides were placed on a standard white fabric and measured in the average mode. An average of three single measurements in three different places of the sample was taken.


Figure2: experiment setup

Results:

All the samples showed slight color change differing according to their composition.

Sample 1:

dL*= -0.93 dC*=0.58 dH*=0.13
Sample 1-2 showed a very little lightness decrease (-0.93) and a very little hue shift (0.13) towards green (color has gone cooler). Positive dC* shows a slight chromaticity increase (the color has gone more saturated).

Sample 2:

dL*= -2.01 dC*=5.12 dH*=-0.76
Sample 2-2 showed some lightness decrease (-2.01) and a little hue shift (-0.76) towards yellow (color has gone warmer). Positive dC* shows a chromaticity increase.

Sample 7:

dL*= -0.83 dC*=0.29 dH*=-0.22
Sample 7-2 showed a little lightness decrease (-0.83) and a very little hue shift (-0.22) towards yellow (color has gone warmer). Positive dC* shows a slight chromaticity increase.

Sample 14:

dL*= -1.76 dC*=-0.85 dH*=-1.30
Sample 14-2 showed some lightness decrease (-1.76) and a little hue shift (-1.3) towards yellow (color has gone warmer). Negative dC* shows a slight chromaticity decrease.

Sample 18:

dL*= -1.62 dC*=-0.43 dH*=-1.06
Sample 18-2 showed a little lightness decrease (-1.62) and a little hue shift (-1.06) towards yellow (color has gone warmer). Negative dC* shows a slight chromaticity decrease.

Sample 19:

dL*= -2.40 dC*=0.43 dH*=-1.69
Sample 19-2 showed a little lightness decrease (-2.40) and a little hue shift (-1.69) towards yellow (color has gone warmer). Positive dC* shows a slight chromaticity increase.

Sample 24:

dL*= -3.19 dC*=4.14 dH*=-0.83

Sample 24-2 showed slightly bigger lightness decrease (-3.19) and a little hue shift (-0.83) towards yellow (color has gone warmer). Positive dC* shows a slight chromaticity increase.

Sample 36:

dL*= -0.63 dC*=-16.88 dH*=-2.29

For sample 36-2 a change in the composition of the reflected spectrum is apparent: after the weathering sample reflects more light in 410-530 nm range (blue) and less light in 530-700 nm range (yellow and red). Sample 36-2 showed a little lightness decrease (-0.63) and some hue shift (2.29) towards green (color has gone cooler). Negative dC* shows a significant chromaticity decrease (color “moved” towards gray).

Sample 37:

dL*= -2.55 dC*=4.63 dH*=-1.01

Sample 37-2 showed slightly bigger lightness decrease (-2.55) and a little hue shift (-1.01) towards yellow (color has gone warmer). Positive dC* shows a chromaticity increase.

Sample 38:

dL*= -2.24 dC*=5.07 dH*=-0.88

Sample 38-2 showed slightly bigger lightness decrease (-2.24) and a little hue shift (-0.88) towards yellow (color has gone warmer). Positive dC* shows a chromaticity increase.

Conclusions:

Samples 2, 24, 36, 37, and 38 showed a significant color difference ($dE^* \geq 5$). For other samples color difference is barely perceivable. All the samples showed a little brightness decrease (24, 37 and 38 darkened the most). 8 out of 10 samples has gone warmer in color. 1 and 36 has gone cooler. Sample 36 changed its optical properties the most with an overall color change (dE*) of 17.05.

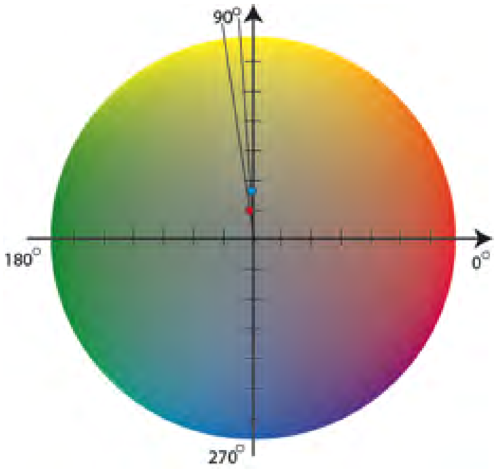


Figure : Chromaticity of sample 2 before (red dot) after weathering (blue dot)

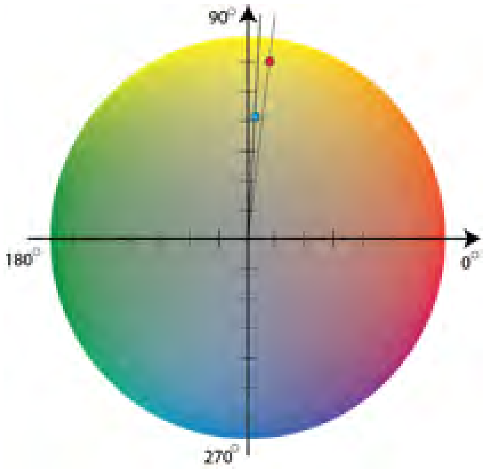


Figure : Chromaticity of sample 36 before (red and dot) and after weathering (blue dot)

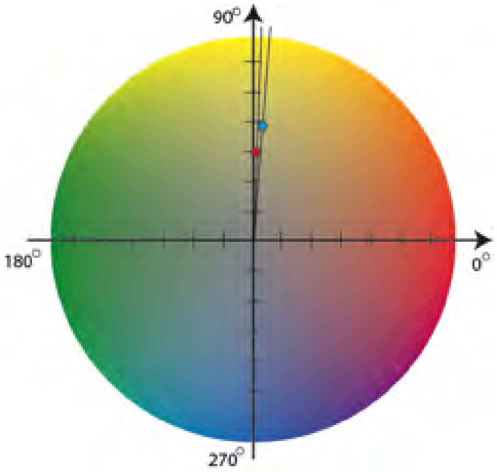


Figure : Chromaticity of sample 38 before
(red dot) and after weathering (blue dot)

References:

Hunter, R., Harold, W., *The measurement of Appearance*, second edition, A Wiley-Interscience Publication, pp. 143-152, 155-156

AATCC Evaluation Procedure 6-2008, Instrumental Color Measurement

AATCC Evaluation Procedure 7-2009, Instrumental Assessment of the Change in Color of a Test Specimen

http://www.hunterlab.com/appnotes/an07_96a.pdf L*a*b* scale description

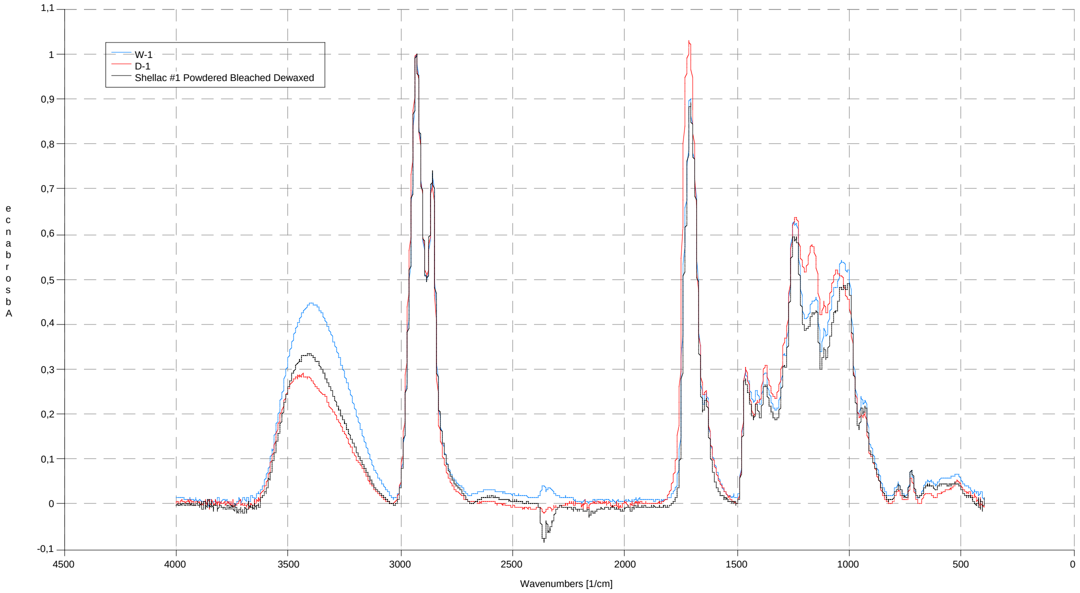
http://www.hunterlab.com/appnotes/an09_96a.pdf L*C*h scale description

Analysis performed: 11.22.2011 and 12.07.2011 Report date: 12.08.2011

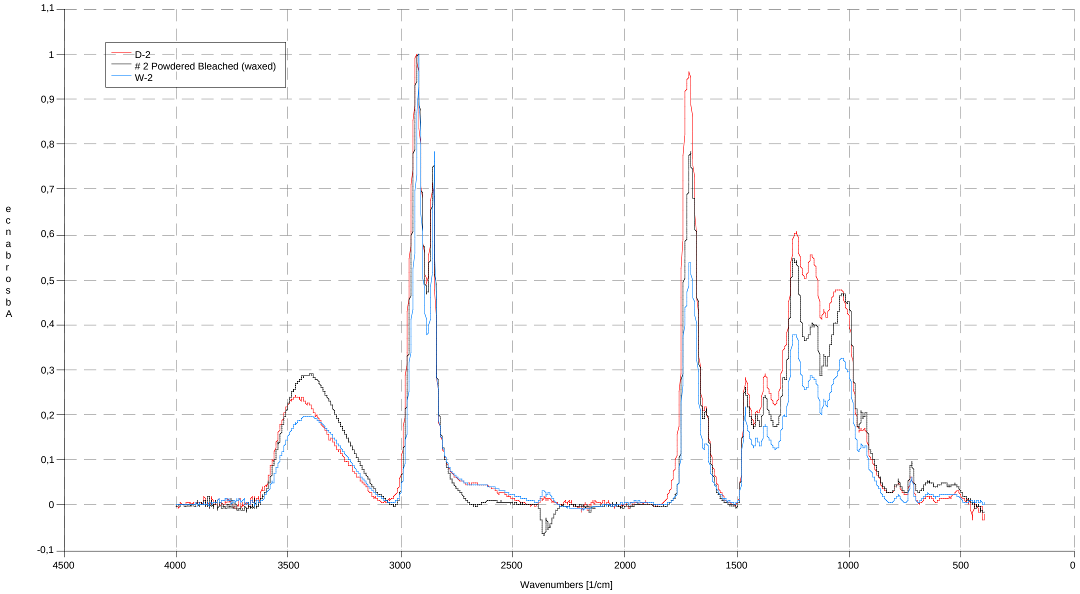
Appendix 6.

Spectral Groups, Bulk (black), Heat cured (red), and Steam cured (blue) overlayed.

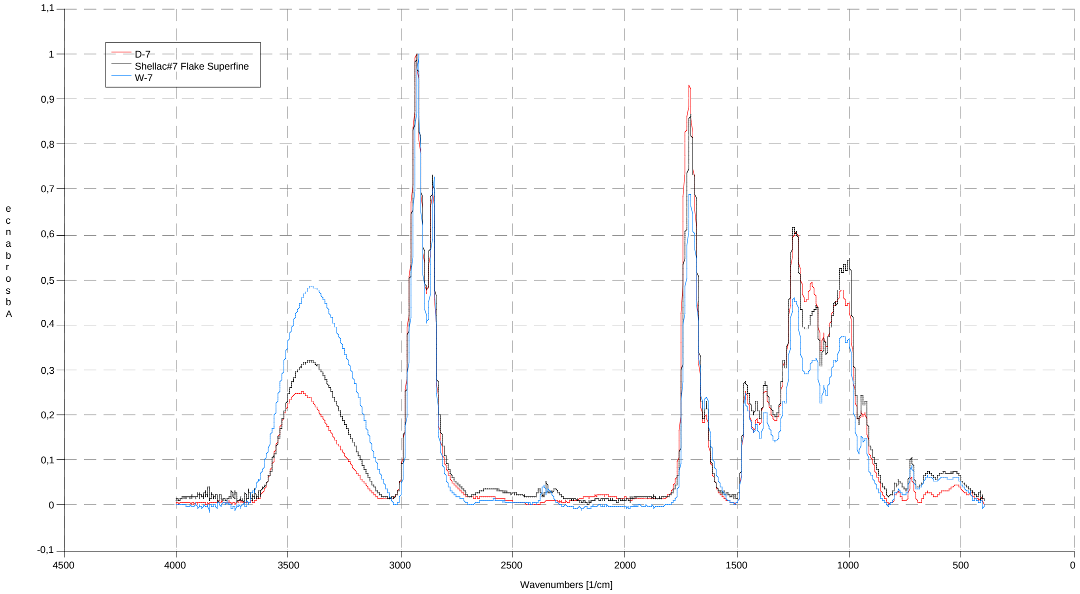
Group 1



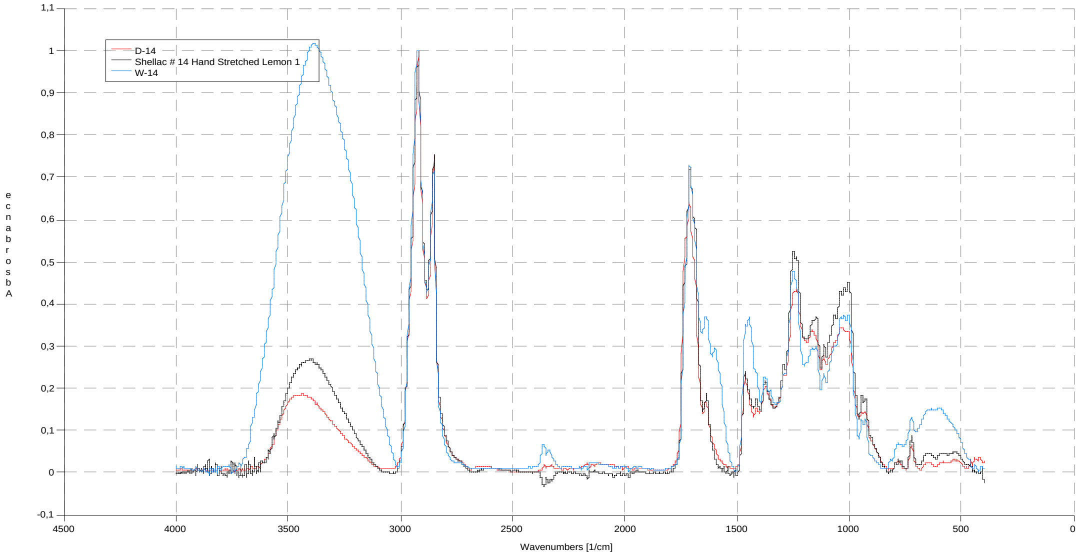
Group 2



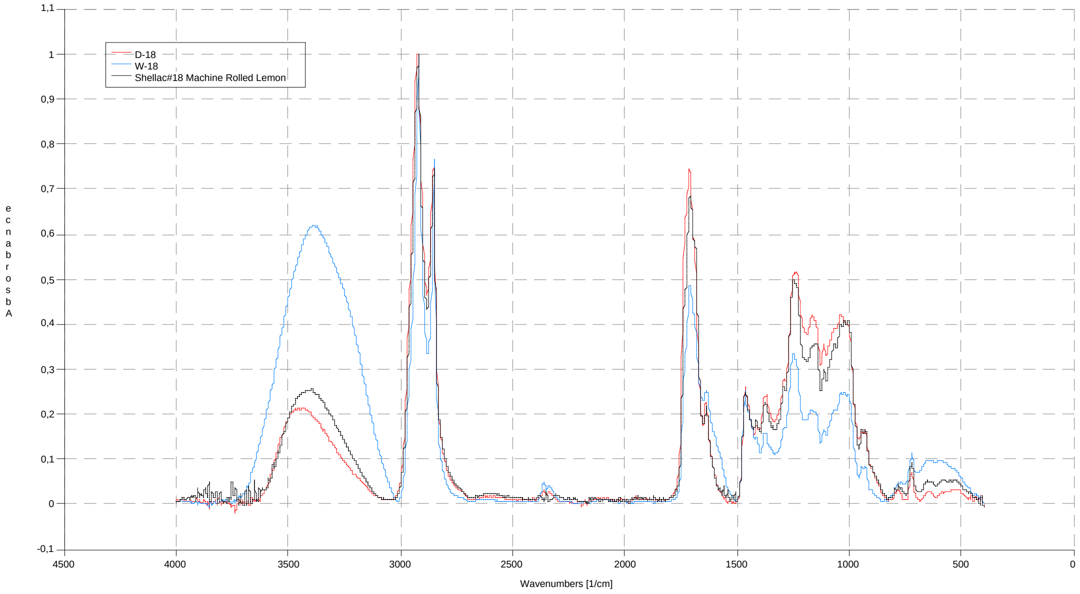
Group 7



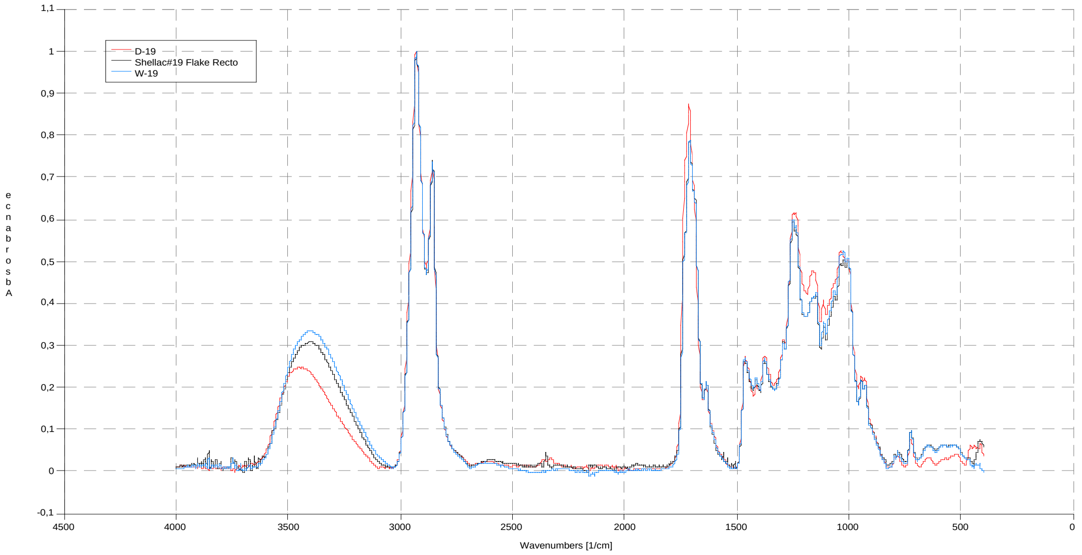
Group 14



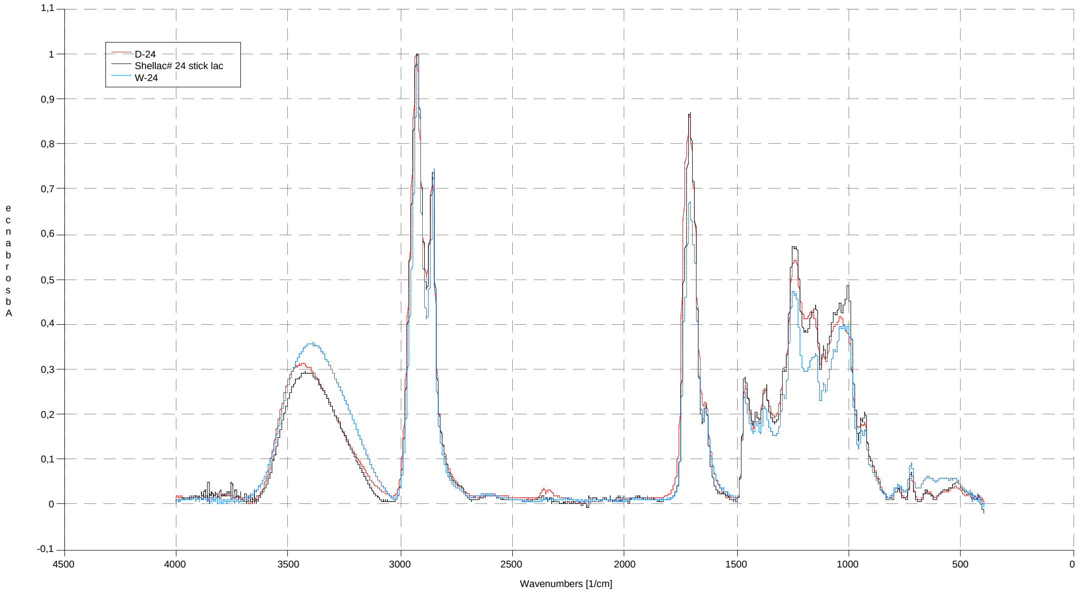
Group 18



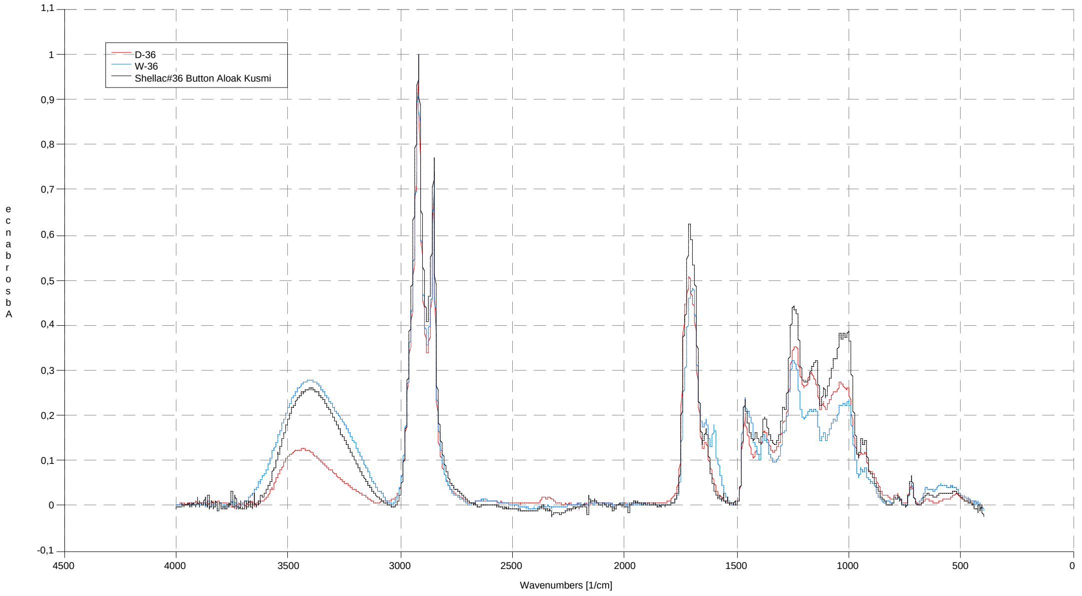
Group 19



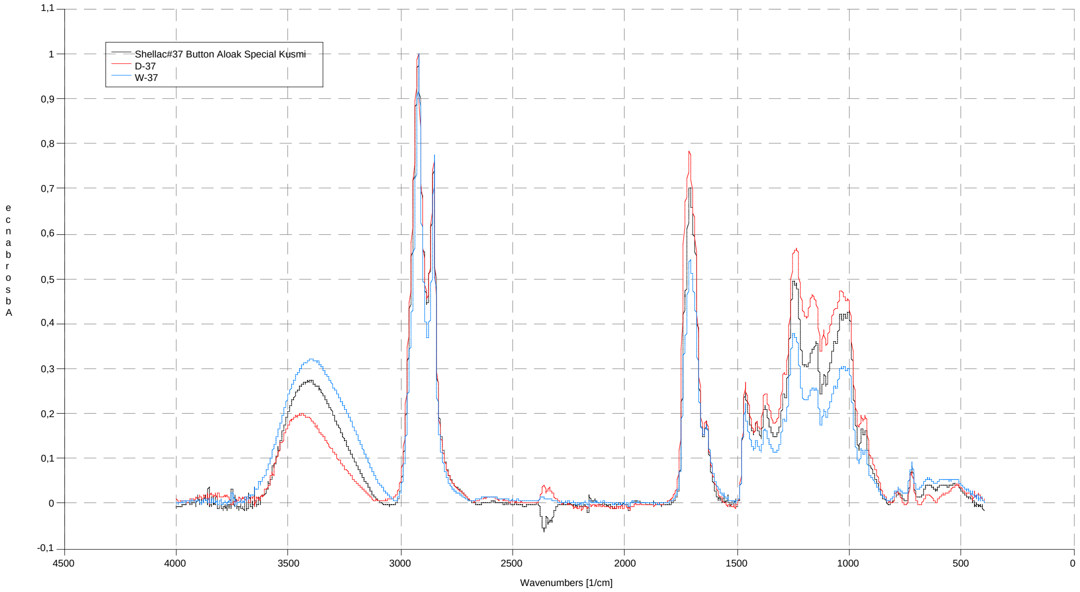
Group 24



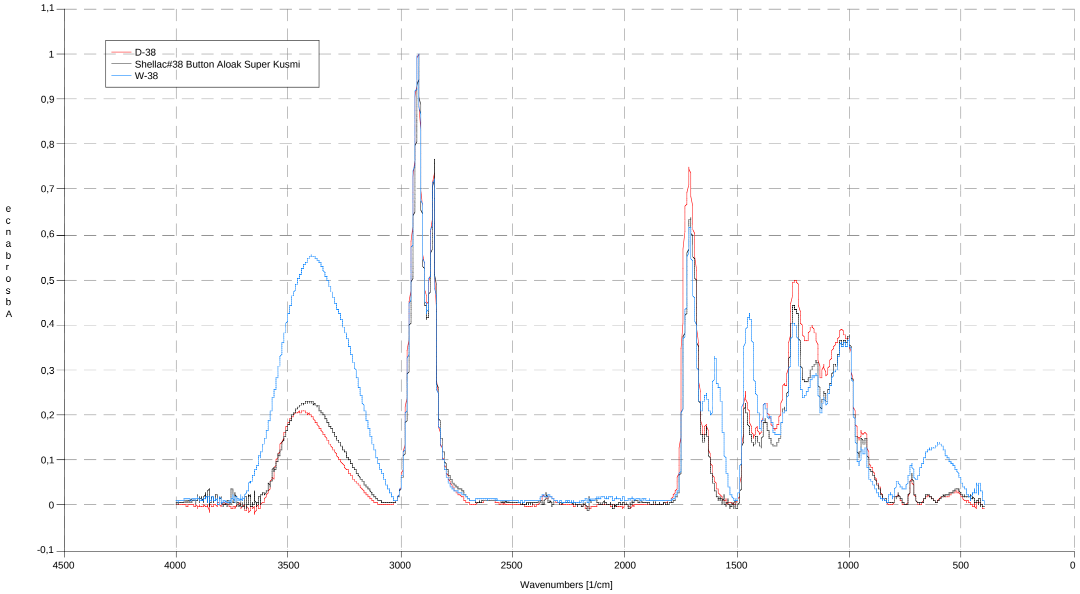
Group 36



Group 37



Group 38



Appendix 7.

Gloss Meter Readings, with a handheld, Micro-TRI-gloss, BYK Gardner.

Samples before and after ageing In positions 1 and 3.					Degrees difference		Average degree change
2-1 (before)			2-1 (after)				
1	3		1	3	1	3	
46.1	33.3		26.5	18.3	-20.9	-15.7	-18.3
44.7	33.1		26.2	17.6			
45.9	33.6		25.1	17.9			
45.0	33.5		23.1	17.2			
45.4	33.3		21.7	17.4			
45.4	33.4	average	24.5	17.7			
2-2 (before)			2-2 (after)				
1	3		1	3	1	3	
36.1	37.3		29.2	31.7	-6.8	-6.3	-6.6
35.9	37.2		29.5	30.8			
35.9	37.4		29.6	31.1			
36.0	37.4		29.4	30.8			
36.0	37.3		28.3	30.7			
36.0	37.3	average	29.2	31.0			
2-7 (before)			2-7 (after)				
1	3		1	3	1	3	
55.2	46.5		62.9	50.8	+7.2	+4.3	+5.8
55.2	46.5		62.5	50.7			
55.3	46.4		62.7	50.9			
55.3	46.5		62.0	50.7			
55.3	46.5		62.6	50.8			
55.3	46.5	average	62.5	50.8			
2-14 (before)			2-14 (after)				
1	3		1	3	1	3	
44.0	38.7		49.0	44.6	+5.1	+5.9	+5.5
44.0	38.8		49.1	44.7			
44.0	38.9		49.1	44.6			
43.9	38.9		49.3	44.8			
44.0	38.9		49.1	44.7			
44.0	38.8	average	49.1	44.7			
2-18 (before)			2-18 (after)				
1	3		1	3	1	3	
51.9	41.5		71.1	50.6	+19	+9.4	+14.2
52.1	41.5		70.4	50.9			
51.9	41.4		70.8	50.9			
51.9	41.5		71.5	51.6			
52.1	41.6		71.3	50.4			
52.0	41.5	average	71.0	50.9			

2-19 (before)			2-19 (after)				
1	3		1	3	1	3	
40.1	30.6		32.6	17.9	-11.3	-12.8	-12.1
39.6	30.9		28.1	17.3			
40.0	30.6		27.9	18.0			
40.4	31.3		27.4	18.8			
40.4	30.7		27.8	17.8			
40.1	30.8	average	28.8	18.0			

2-24 (before)			2-24 (after)				
1	3		1	3	1	3	
50.6	38.5		43.4	32.6	-6.3	-5.5	-5.9
50.4	38.3		43.8	33.1			
50.3	38.5		43.2	32.7			
50.3	38.4		44.2	33.4			
50.3	38.4		45.7	33.3			
50.4	38.5	average	44.1	33.0			

2-36 (before)			2-36 (after)				
1	3		1	3	1	3	
57.4	33.5		56.3	32.4	-0.4	-1.0	-0.5
57.0	33.4		57.1	32.4			
57.0	33.3		56.2	32.4			
57.0	33.4		56.8	32.6			
57.1	33.4		57.0	32.4			
57.1	33.4	average	56.7	32.4			

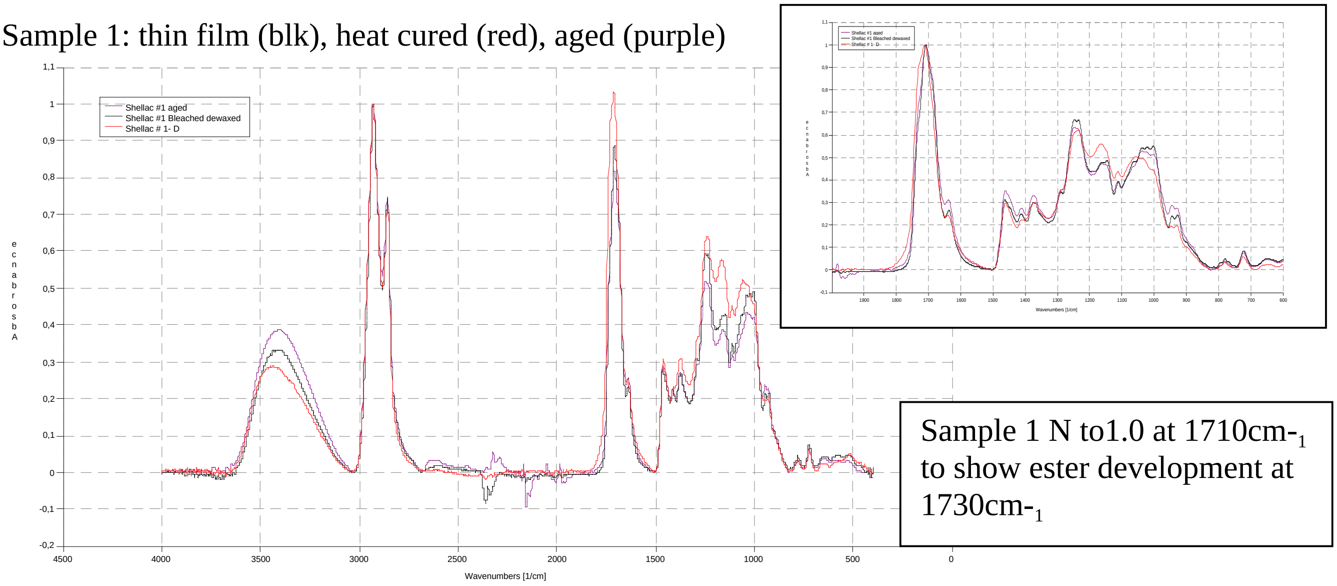
2-37 (before)			2-37 (after)				
1	3		1	3	1	3	
32.8	32.6		49.3	42.5	+16.8	+9.8	+13.3
32.7	32.5		49.7	41.9			
32.3	32.5		49.7	41.8			
32.3	32.6		49.3	42.2			
32.8	32.5		49.1	43.1			
32.6	32.5	average	49.4	42.3			

2-38 (before)			2-38 (after)				
1	3		1	3	1	3	
32.6	41.4		48.8	58.7	+16.6	+17.8	+17.2
32.2	41.2		51.7	59.5			
36.4	41.5		50.4	59.3			
33.1	41.5		49.0	59.6			
32.7	41.5		50.0	58.7			
33.4	41.4	average	50.0	59.2			

Appendix 8.

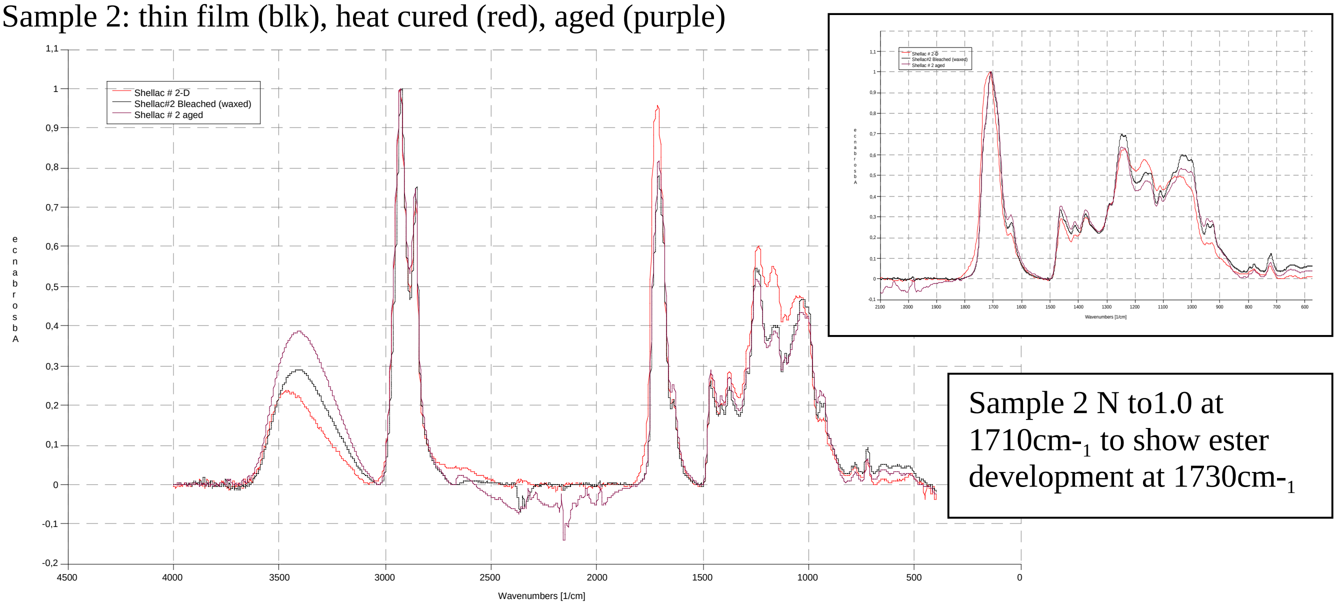
Aged Spectral Groups.

Sample 1: thin film (blk), heat cured (red), aged (purple)



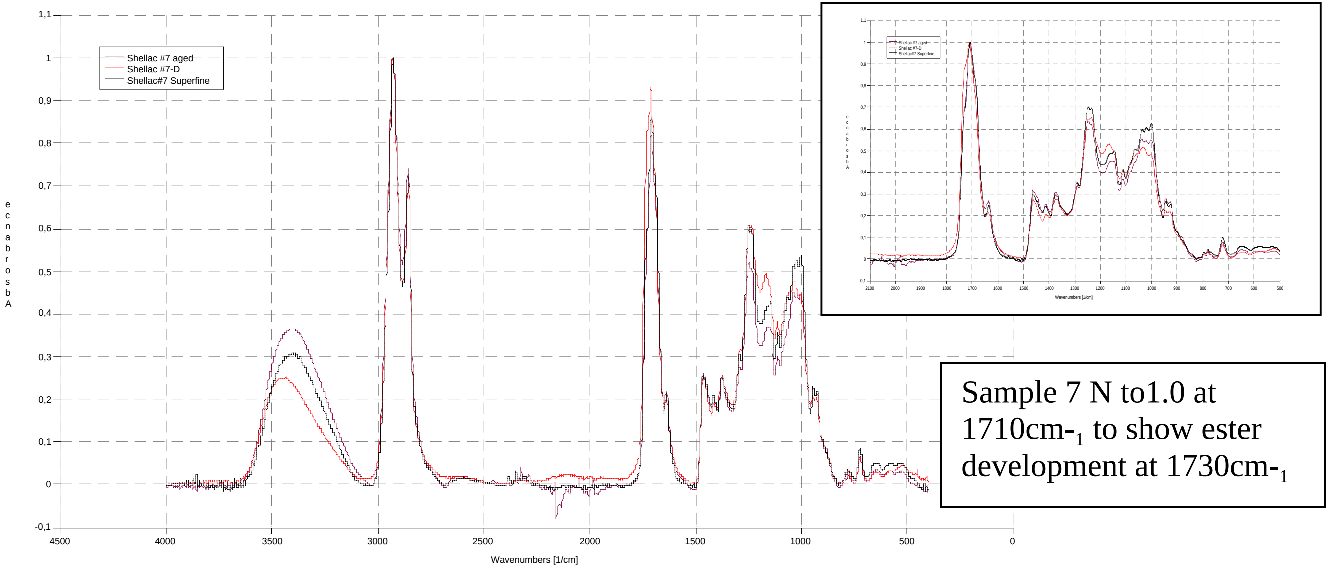
Sample 1 N to1.0 at 1710cm-$_1$ to show ester development at 1730cm-$_1$

Sample 2: thin film (blk), heat cured (red), aged (purple)



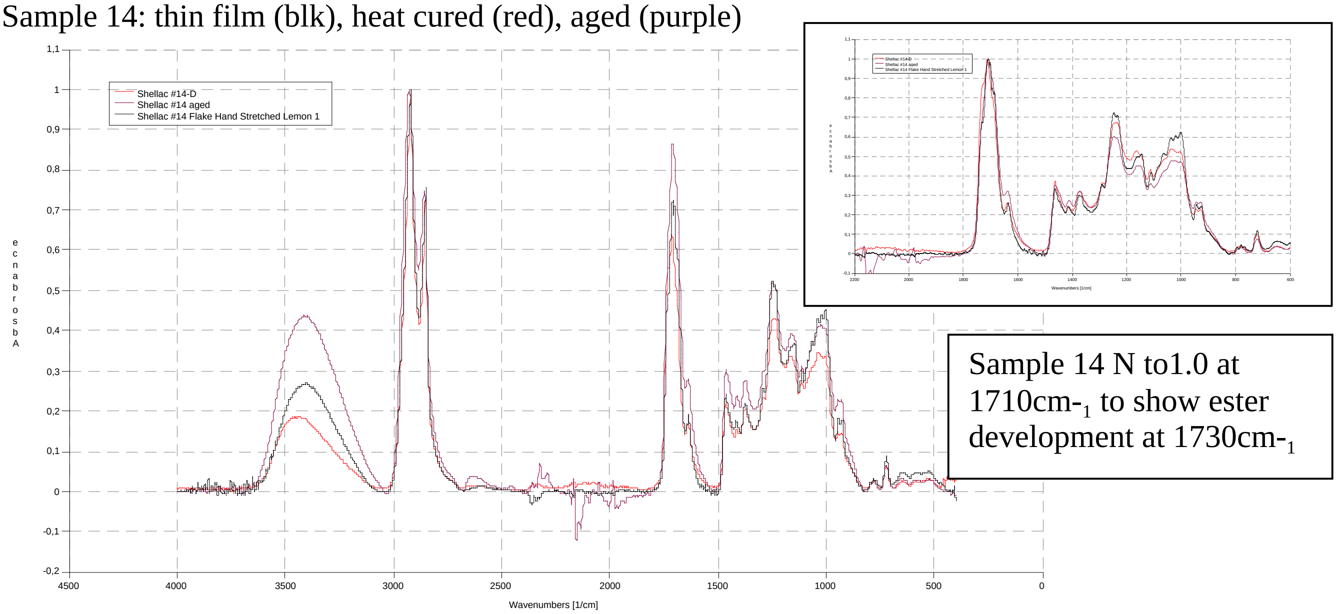
Sample 2 N to1.0 at 1710cm-$_1$ to show ester development at 1730cm-$_1$

Sample 7: thin film (blk), heat cured (red), aged (purple)



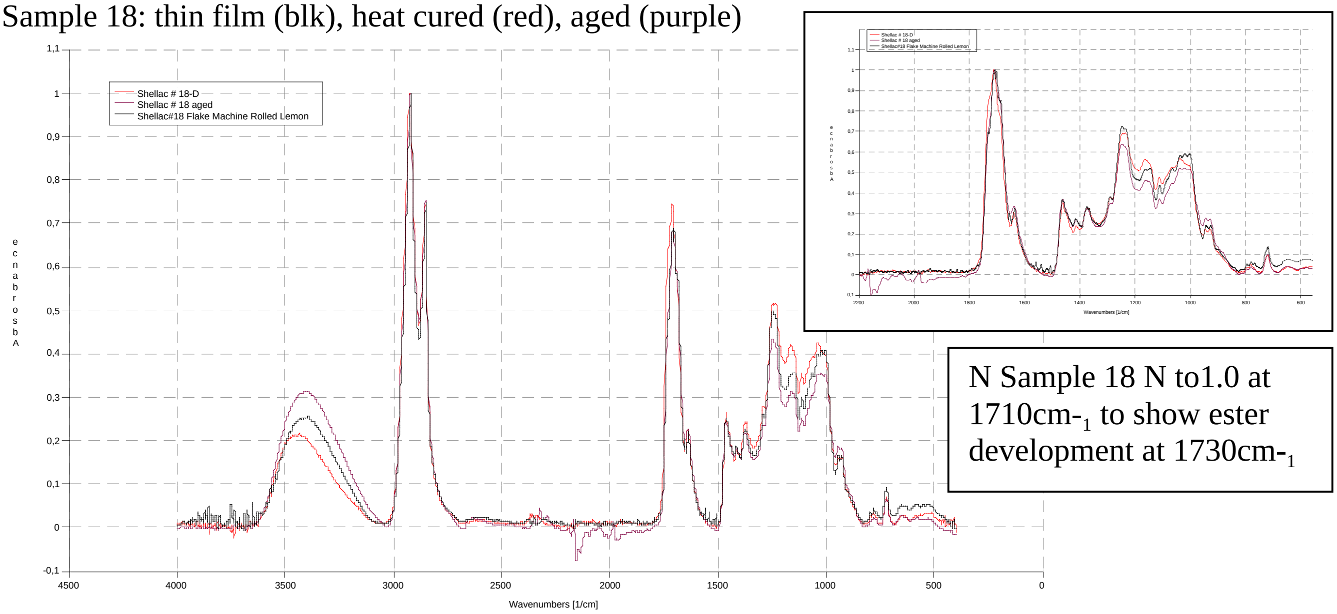
Sample 7 N to1.0 at 1710cm-$_1$ to show ester development at 1730cm-$_1$

Sample 14: thin film (blk), heat cured (red), aged (purple)



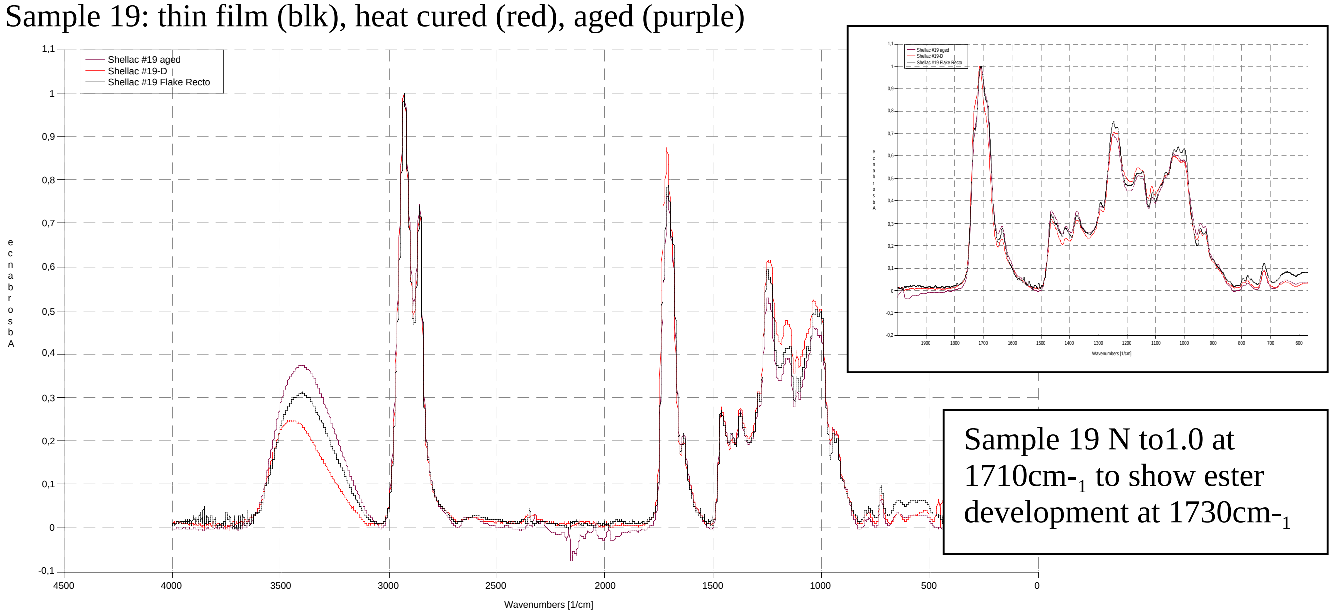
Sample 14 N to1.0 at 1710cm-$_1$ to show ester development at 1730cm-$_1$

Sample 18: thin film (blk), heat cured (red), aged (purple)



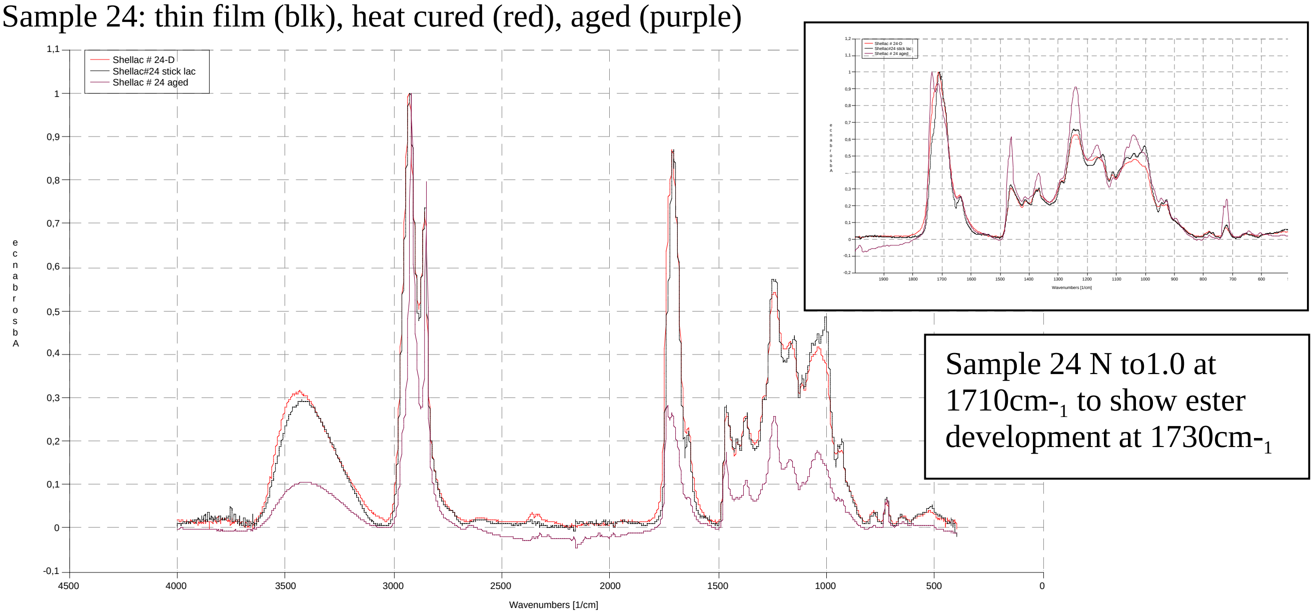
N Sample 18 N to1.0 at 1710cm-$_1$ to show ester development at 1730cm-$_1$

Sample 19: thin film (blk), heat cured (red), aged (purple)



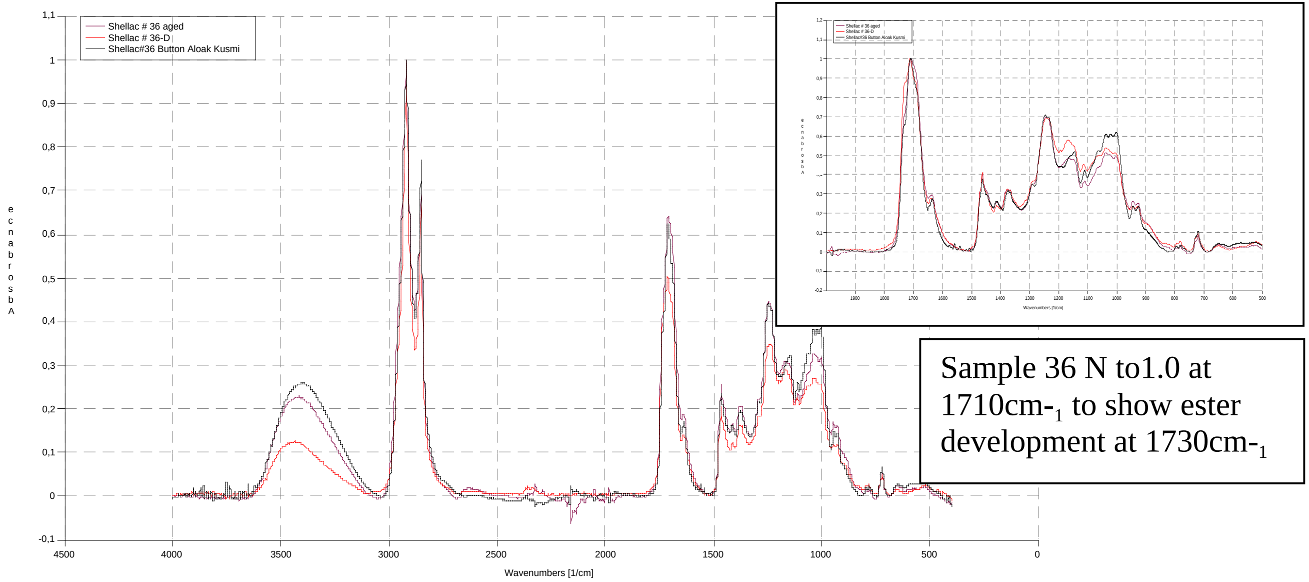
Sample 19 N to1.0 at 1710cm-$_1$ to show ester development at 1730cm-$_1$

Sample 24: thin film (blk), heat cured (red), aged (purple)



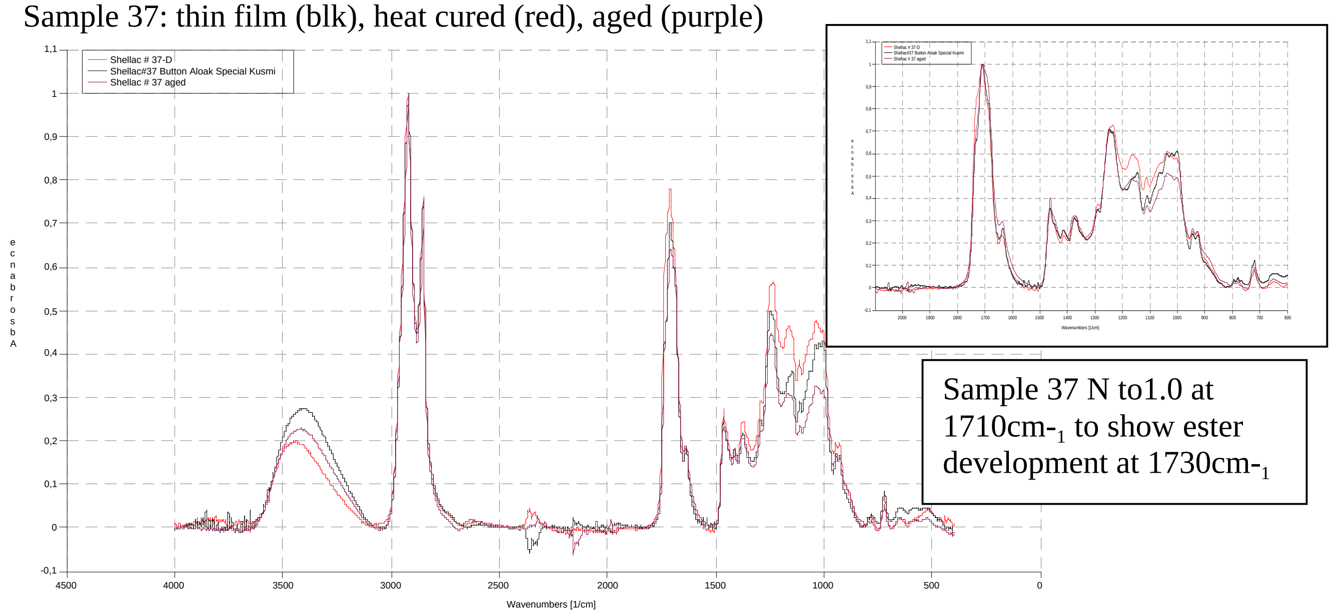
Sample 24 N to1.0 at 1710cm-$_1$ to show ester development at 1730cm-$_1$

Sample 36: thin film (blk), heat cured (red), aged (purple)



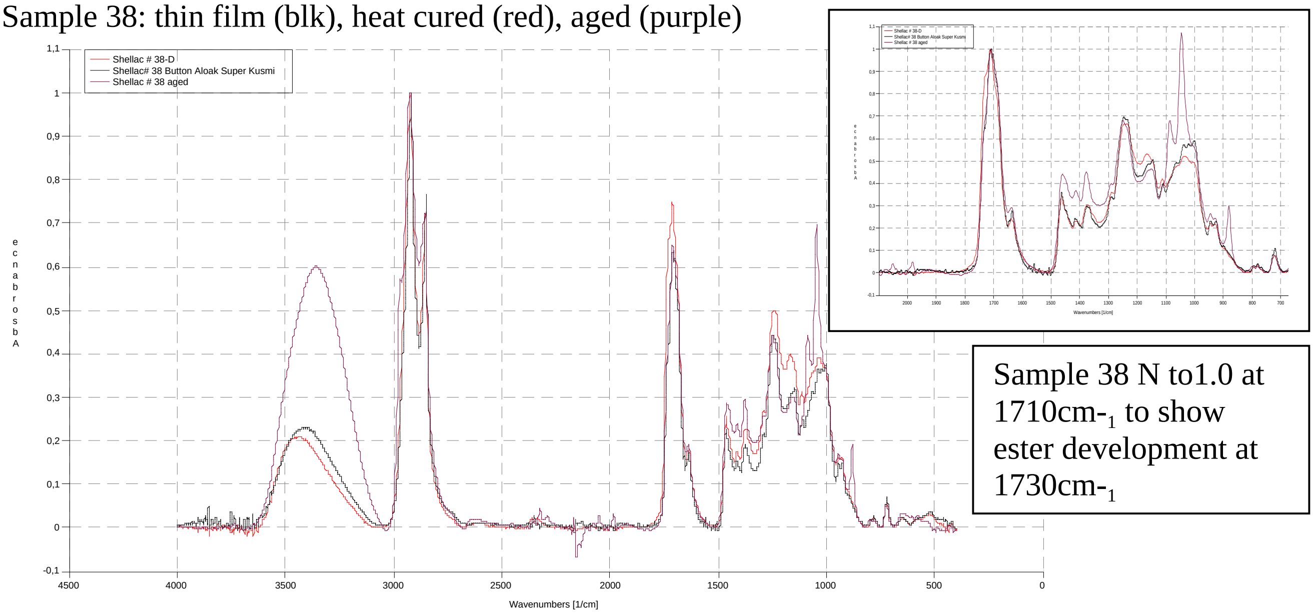
Sample 36 N to1.0 at 1710cm-$_1$ to show ester development at 1730cm-$_1$

Sample 37: thin film (blk), heat cured (red), aged (purple)



Sample 37 N to1.0 at 1710cm-$_1$ to show ester development at 1730cm-$_1$

Sample 38: thin film (blk), heat cured (red), aged (purple)



Sample 38 N to1.0 at 1710cm-$_1$ to show ester development at 1730cm-$_1$

Appendix 9.

Alcohol Solvency Test on Bulk and Cured Shellac Samples.

Alcohol solvency/reaction test on 3 sets each of 10 shellac samples. The sample numbers correspond to sample numbers used throughout the study. Shellac samples were tested by exposure to drops of alcohol (shellac solvent), one drop by pipette, and observed. The films were visually monitored, looking specifically for tidelines, made by the solvent. This would indicate a swelling reaction between the solvent and the film sample. The films were also manipulated/agitated with an alcohol soaked cotton swab, noticing whether cotton fibers would stick to the surface, indicating a dissolving effect by the solvent, on the film sample.

Set 1 is composed of shellac samples cast on glass slides, using method as previously explained.

Sample nr.	Reaction to exposure/swab agitation	Tidelines
1-1	Becomes tacky with exposure	Tidelines noticeable
1-2	Becomes soft with exposure	Tidelines not visible
1-7	Becomes soft with exposure	Tidelines noticeable
1-14	Becomes tacky with exposure	Tidelines noticeable
1-18	Becomes tacky with exposure	Tidelines noticeable
1-19	Become soft/rubbery with exposure	Tidelines noticeable
1-24	Becomes soft with exposure	Tidelines noticeable
1-36	Dissolves quickly with exposure	Tidelines noticeable
1-37	Becomes soft with exposure	Tidelines noticeable
1-38	Becomes slightly tacky	Tidelines barely visible

Set 2, “Dry-cured” is composed of shellac samples cast on glass slides covered with aluminum foil, using method previously explained. These slides were then baked in a stable pyrolysis oven, at 150°C, for 90 minutes.

Sample nr.	Reaction to exposure/swab agitation	Tidelines
2-1	No reaction with exposure	No tidelines visible
2-2	No reaction with exposure	No tidelines visible
2-7	No reaction with exposure	No tidelines visible
2-14	No reaction with exposure	No tidelines visible
2-18	No reaction with exposure	No tidelines visible
2-19	No reaction with exposure	No tidelines visible
2-24	No reaction with exposure	No tidelines visible
2-36	No reaction with exposure	No tidelines visible
2-37	No reaction with exposure	No tidelines visible
2-38	No reaction with exposure	No tidelines visible

Set 3, “Wet cured”, is composed of shellac samples cast on glass slides covered with aluminum foil, using method previously explained. These slides were then steamed at 93°C, for 180 minutes.

Sample nr.	Reaction to exposure/swab agitation	Tidelines
3-1	No softness/tackiness, but some material dislodges from substrate w/ agitation	Tidelines not visible
3-2	Rubber-like consistency w/ vigorous agitation	Tidelines not visible
3-7	No softness/tackiness, but some material dislodges from substrate w/ agitation	Tidelines not visible
3-14	No softness/tackiness, but some material dislodges from substrate w/ agitation	Tidelines not visible
3-18	No softness/tackiness, but some material dislodges from substrate w/ agitation	Tidelines not visible
3-19	Rubber-like consistency w/ vigorous agitation	Tidelines not visible
3-24	No softness/tackiness, but some material dislodges from substrate w/ agitation	Tidelines not visible
3-36	Dissolves somewhat, but less than uncured sample (set 1)	Tidelines barely noticeable
3-37	Rubber-like consistency w/ vigorous agitation	Tidelines not visible
3-38	Rubber-like consistency w/ vigorous agitation	Tidelines not visible

Appendix 10.

Chain of trade.

Report given by Binju Abraham, PRADAN. Nov. 19th, 2010.

International buyer >These two groups can be viewed as one unit.

International suppliers

Exporters -are always processors, have a good view of what is happening internationally.

Processor (not always exporters. Handles own factory, not speculative on the supply side)

Block Paikar/Agent (wealthy Intermediary-transport to processor, has possibility to speculate-info from both sides.) He provides logistics/transportation, sending agents to the large market with the raw material, which he has gathered from his Haat Paikars. Large/sudden ups and downs in the market are often because the block paikar is using his information to manipulate the market on one side or the other (supply/demand).

Haat (small market) Paikar Usually not wealthy, has contact with farmers and gathers product either from small local markets (haats), or door to door from the farmer (is strictly a middle man)**.**

Farmers –Live in remote areas, no transport possibilities (have no bargaining power)

The Market (Haat) (250 small markets/25 large in India)

Farmers produce crop of raw material (also called crude Lac, scraped Lac, sticklac).

Note: the term *sticklac* can be misunderstood in that some farmers sell the Lac still on the stick, just chopped up into pieces. The price for this product is half of the scraped material. The process from sticklac to seedlac is called the *primary processing*. The loss of material from seedlac to shellac is only 5%, and this loss is called *slag* (crude shellac material which is saved and used for melting and making things such as bangles, by the locals).

An agent brings trucks of raw material to the large market. The large market has a regulatory board, which oversees transactions. At market, the Lac is separated by strain, either Rangheenie, or Kusmi. The two strains are harvested at different times of the year, and easily distinguishable to the trained eye.

To determine the price for the raw product from the market, 6 random samples are taken from a truck load, mixed and then arranged in a circle (ca. 30cm diameter). This circle is divided in half, the one half is tested, while the other is kept in a locker with the agent's information. The sample is weighed. The testing consists of processing the raw material into seed Lac, and weighed again. The loss differential between products is calculated, and the percentage of seed Lac gleaned from the crude product is considered to be the resin content, or *Chowri*, of the raw material, that is, the usable material. This resin content is then reported and a price is given according to that content.

If the agent believes this report to be inaccurate or false, he can turn to the regulatory board of the market. The other part of the sample is tested, and compared to the first results.

Terms at market-

100Kg – 1 quinlat

40 Kg – 1 Mann

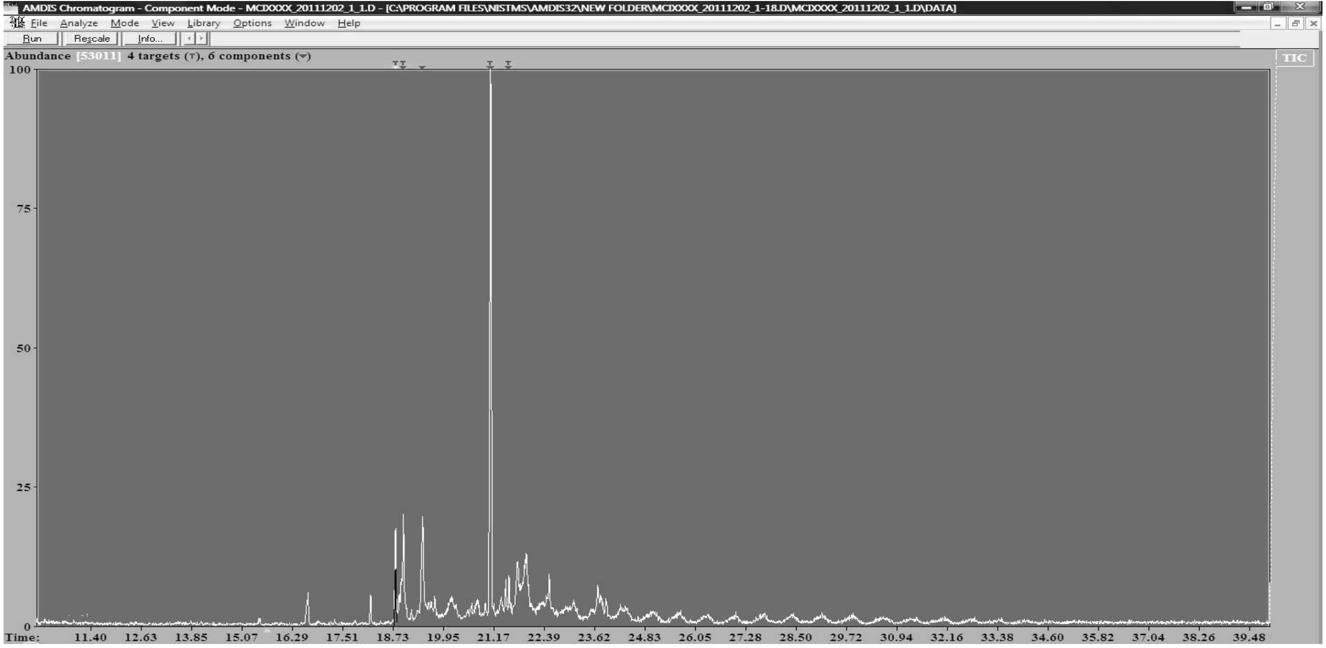
Internationally, there is a 40,000mt (metric tons) demand for shellac, annually. The worldwide production of Lac is at 30,000mt. (India supplies 20mt of this amount). There is no reason for fluctuating supply and demand, other than speculators making money on manipulating the market. The farmer has experienced a difference in price, ranging from 50 INR to 300 INR. This is demoralizing for the farmer, and creates an instability around Lac production.

Information from Binju Abraham, PRADAN. November 19, 2010. Ranchi, India

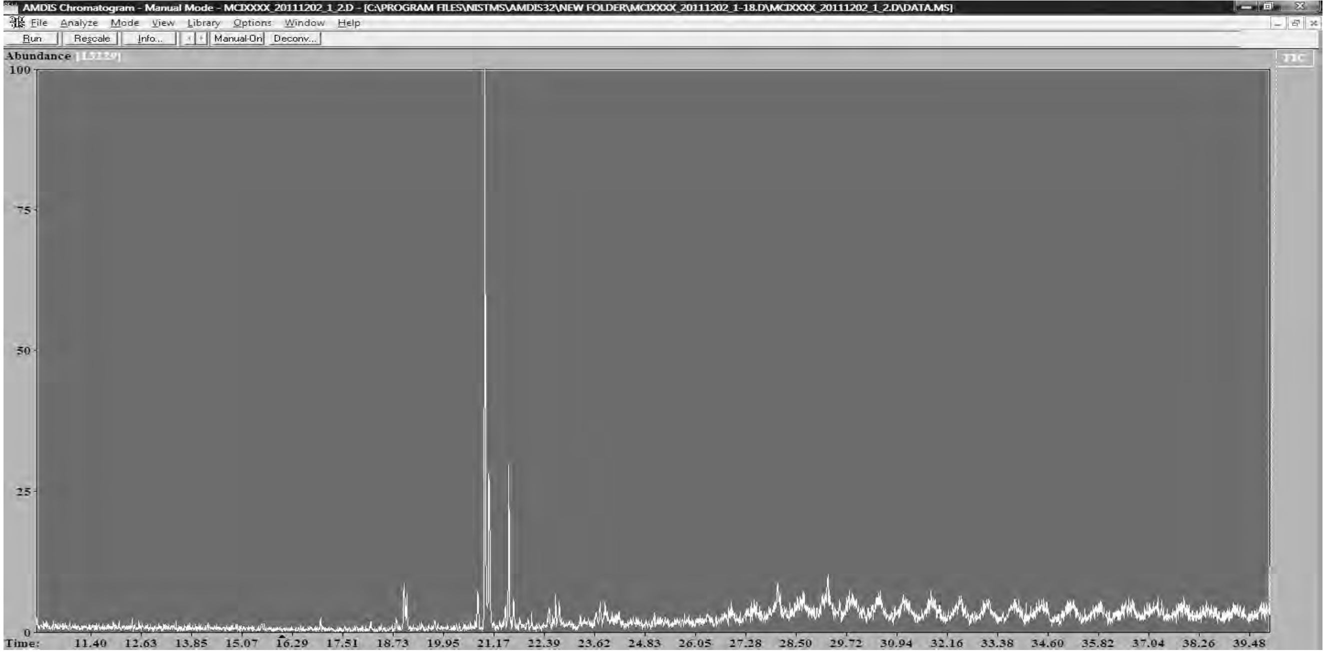
Appendix 11

GC Chromatograms of Shellac Samples.

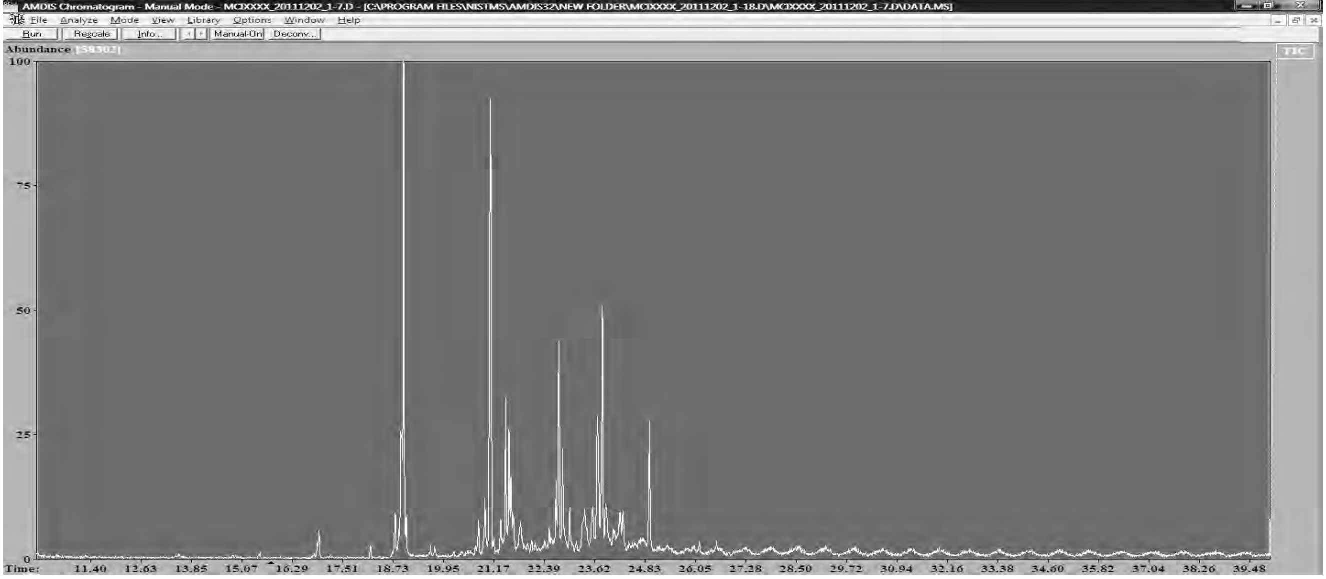
Sample 1



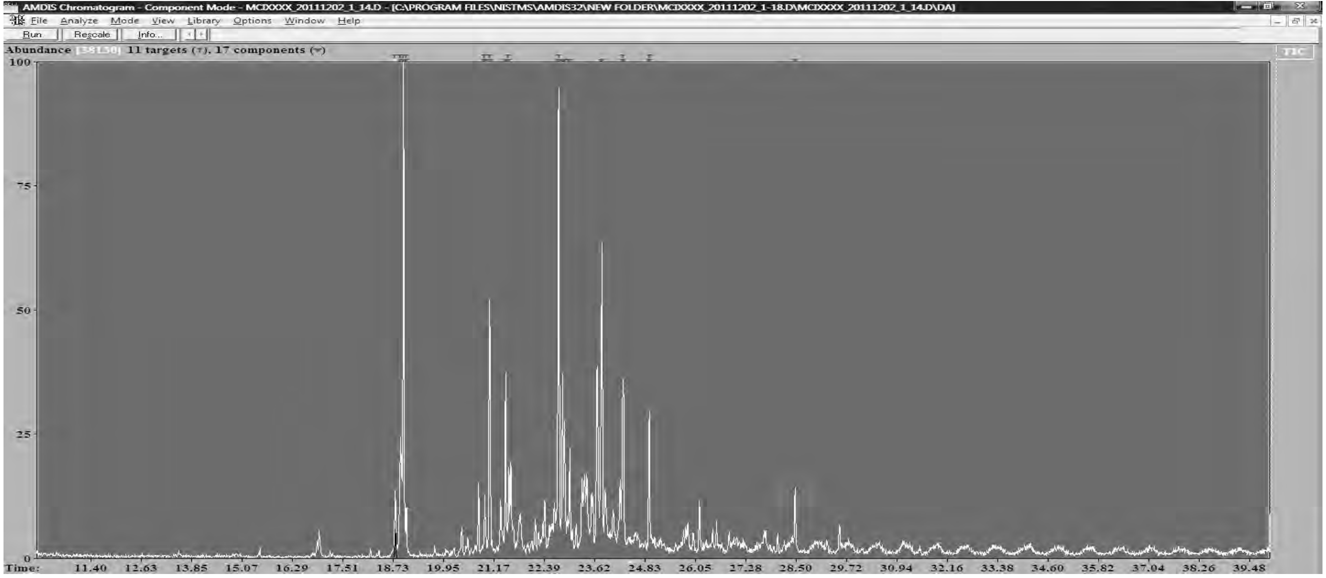
Sample 2



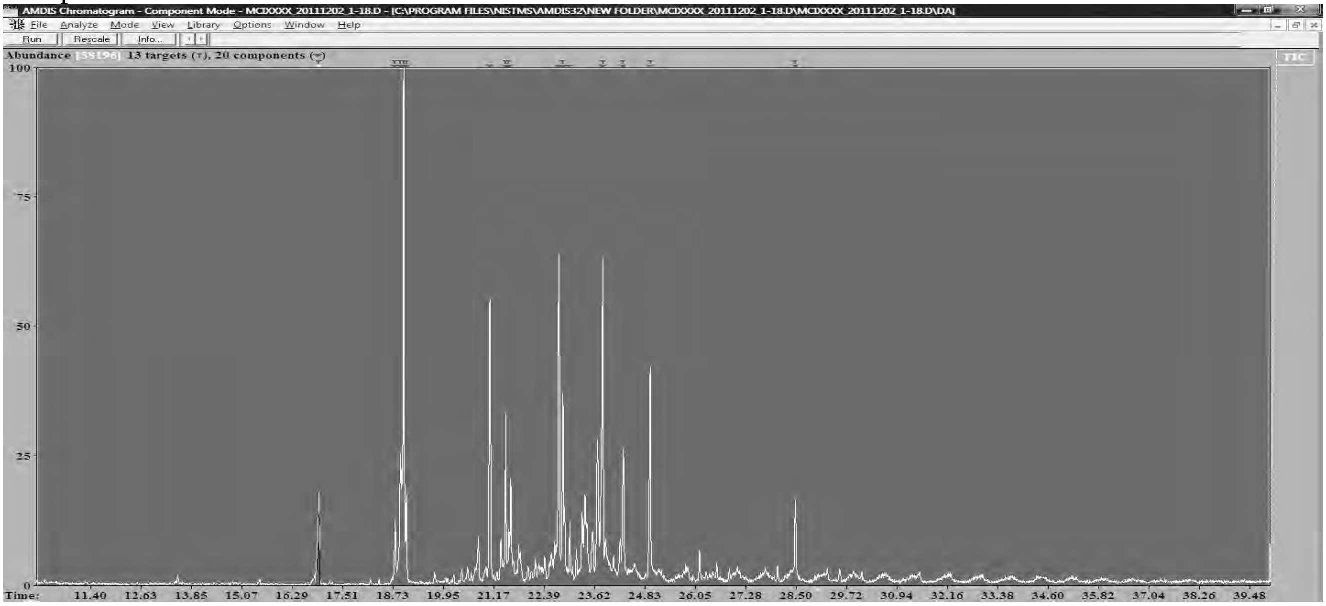
Sample 7



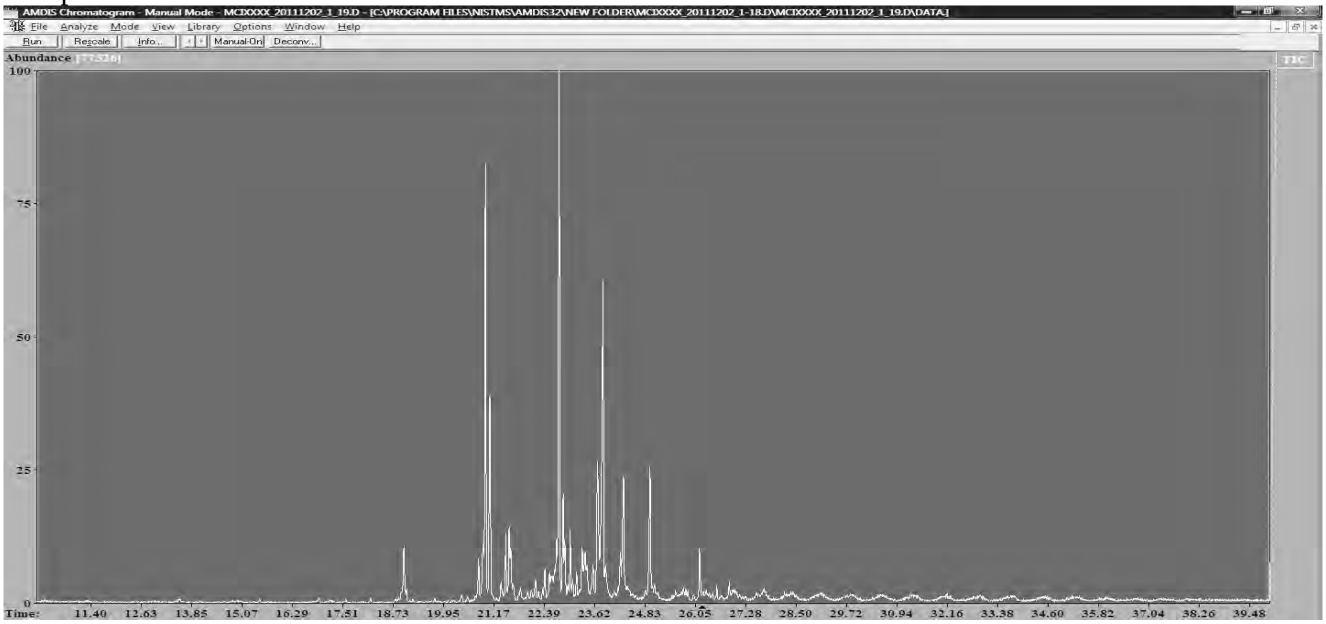
Sample 14



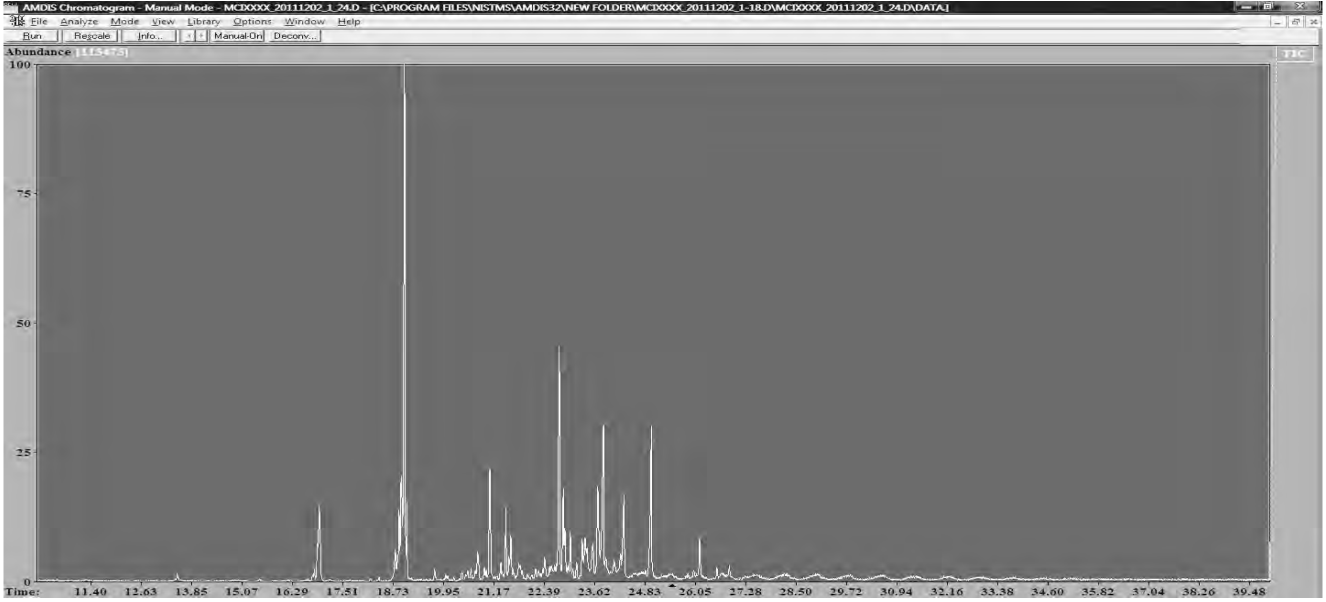
Sample 18



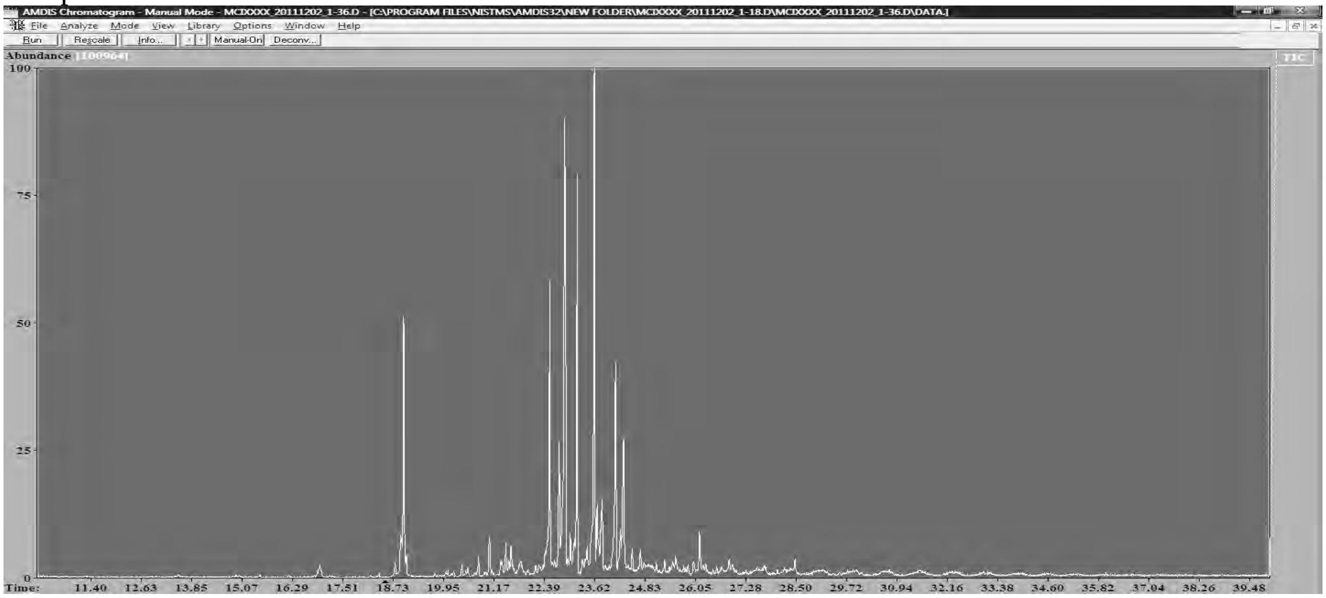
Sample 19



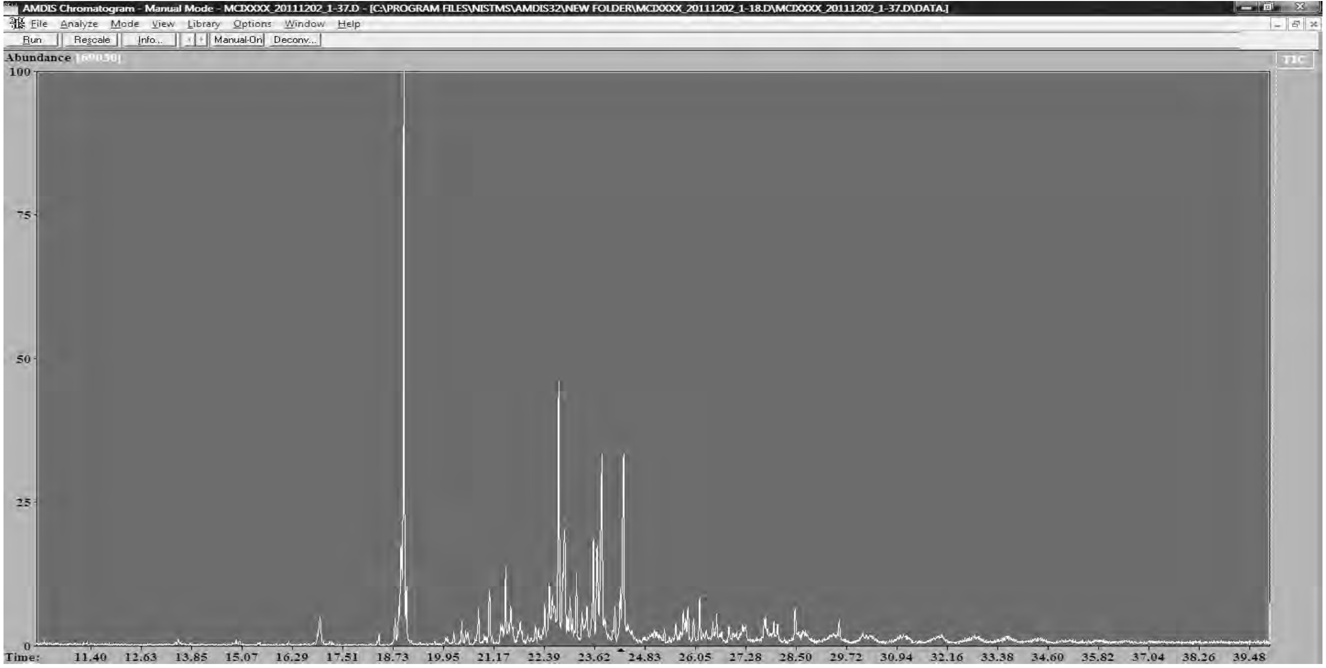
Sample 24



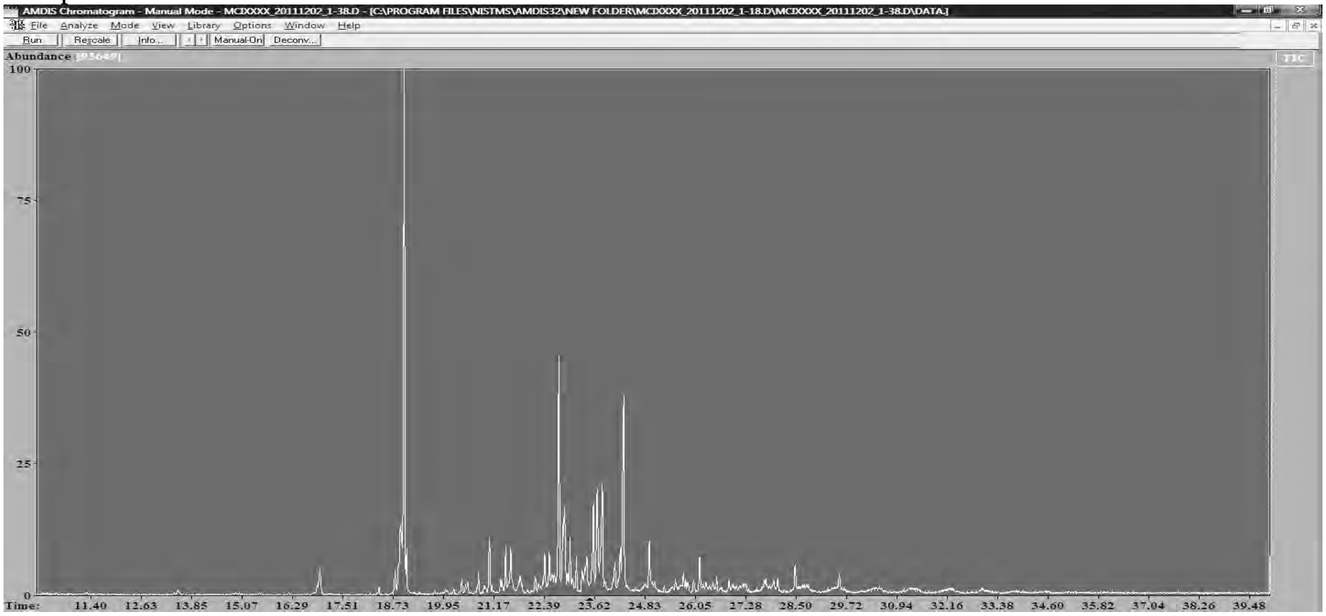
Sample 36



Sample 37



Sample 38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File Analyze Mode View Library Options Window Help
Run
Rescale
Info...
Manual-On
Deconv...
Abundance
TIC
100
75
50
25
0
Time:
11.40
12.63
13.85
15.07
16.29
17.51
18.73
19.95
21.17
22.39
23.62
24.83
26.05
27.28
28.50
29.72
30.94
32.16
33.38
34.60
35.82
37.04
38.26
39.48