HIGHLIGHT

Oriental Lacquer, Poison Ivy, and Drying Oils

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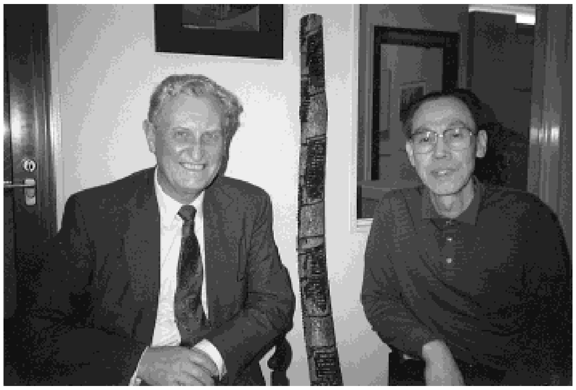
ABSTRACT: From the oriental lacquer tree *Toxicodendron vernicifluum*, a sap (emulsion) is obtained the oil-soluble components (urushiol) of which consist of a mixture of 3-n-pentadecylcatechols and very small amounts of 3-n-heptadecylcatechols. Urushiol is the basis of oriental lacquer. The sap is conditioned by removal of most of the water by specific techniques, and the clear liquid is called oriental lacquer. It is used in the Orient for coatings to produce exquisite art objects. Poison ivy also has as its active ingredients 3-n-pentadecylcatechols, but they have a high diene content, which does not cure effectively. In humans 3-n-alkylcatechols cause severe contact dermatitis. The components of drying oils are glycerin esters of fatty acids derived from the families of palmitic (hexadecanoic) and stearic (octadecanoic) acids. In the case of the urushiols, as well as of the glycerides of drying oils, high unsaturation (60%) in the form of trienes in the long aliphatic chains is essential for curing. J Polym Sci A: Polym Chem 38: 4327–4335, 2000

Keywords: lacquer tree (*Toxicodendron vernicifluum*); poison ivy; contact dermatitis; urushiol; 3-n-alkylcatechols; oriental lacquer; curing; lacquerware



OTTO VOGL SHIGERO TSUTSUMI
center: stump of a lacquer tree

Otto Vogl was born in Austria, where he attended the University of Vienna and received his Ph.D. in 1950. He served at the university as lecturer before he went to the United States in 1953. After his postdoctoral years at the University of Michigan and Princeton University, he joined the DuPont company in Wilmington, DE. In 1970 he was appointed professor at the University of Massachusetts and later held the endowed Herman F. Mark Chair at the Polytechnic University. A few years ago he retired and became Professor Emeritus at the University of

Massachusetts in Amherst, MA. Otto Vogl went to Japan for the first time in 1965 and in the Fall of 1968. There he spent one semester as Industrial Visiting Professor at the Department of Synthetic Chemistry at Kyoto University and the Department of Macromolecular Chemistry at Osaka University. At that time, he also served on the "Okamura" committee, which was responsible for selecting characteristic polymers of that period for the Time Capsule Expo '70 which was buried in Osaka Castle Park. Otto Vogl was the invited main lecturer several times at Annual Meetings and Annual Symposia of the Society of Polymer Science, Japan. In addition, he received the distinguished Medal of the Society and is now a life member. In 1996, while he was appointed for three months the Monbusho Professor at the Kyoto Institute of Technology, he received an honorary doctoral degree from Osaka University.

Otto Vogl's accomplishments in science, teaching, and professional societies have been recorded in two recent articles (J Polym Sci A: Polym Chem 2000, 38, 2293 and 2623).

INTRODUCTION

For centuries, actually for millennia, oriental lacquer has been used to coat objects of high artistic and pleasing beauty.[1,2] Oriental lacquer is produced from "urushi,"[3] the sap of the lacquer tree *Toxicodendron vernicifluum.*[4–6] The oleoresins of the sap consist of a mixture of 3-n-alkyl-substituted linear catechols of various degrees of unsaturation.[7,8] During several periods the chemical compositions of a few components of urushiol have been identified and studied.

The first studies were early in the 19th century by R. Majima at Tohoku University in Sendai, Japan.[9–11] Majima had access to the sap of the lacquer tree because lacquer trees grow in the region around Sendai. In the 1950s, C.W. Dawson, at Columbia University in New York,[12–18] studied synthetic aspects and exactly identified 3-alkyl and 3-n-alkenylcatechols. He was interested primarily in poison ivy; the chemistry of the components of the poison ivy sap is similar to that of urushi. Two decades later, Jun Kumanotani of the University of Tokyo, with Yumin Du of Wuhan University, Wuhan, China,[19–26] became the primary investigator of the components of the sap of the lacquer tree. He introduced simple chromatographic techniques for the identification of the oleoresins of urushiol.

In the 1990s we reinvestigated the urushi problem and introduced combinations of modern instrumental techniques.[27–36] Today we know much more about the composition of urushi and have established techniques and combinations of techniques that allow us to isolate and characterize the oleoresins of urushi exactly and rapidly. Because of the chemical similarities, we now also can analyze the components of the sap of poison ivy and other *Anacardiaceae* species.

We also have developed polymerizable ultraviolet stabilizers of the 2(2-hydroxyphenyl)2H-benzotriazole family that can be copolymerized (co-cured) with oriental lacquer and drying oils.[37]

BOTANY OF THE FAMILY *ANACARDIACEAE*

The *Anacardiaceae* is a moderately large family of about 80 genera and about 600 species.[4–6] The plants of a few genera produce a sap that is suitable for use as the basis of exquisite coating materials for art objects.[2,3] To the *Anacardiaceae* family belongs the genus *Toxicodendron* and the species *Toxicodendron vernicifluum.* The varnish or lacquer tree is the main source of oriental lacquer.

The genus *Toxicodendron* grows in temperate climates and has been the subject of regular investigations by botanists and also by chemists and the medical profession.[38] In Asia, *Toxicodendron vernicifluum* trees grow in China, primarily in the Sichuan region, and in Japan. Similar species also grow in Vietnam, in Thailand, and in Taiwan.

After ten years of growth, the stem of the lacquer tree is mature enough to be cut, and a sap similar to that of the rubber tree oozes out of the tree. The difference between the sap of the lacquer tree and that of the rubber tree is that the rubber tree has *cis*-polyisoprene as the material of interest while for the lacquer tree the material of interest is urushiol, which consists of mixtures of substituted catechol derivatives (Fig. 1).

A number of Anacardiaceae species produce a sap that causes contact dermatitis in susceptible human beings. They include the cashew-nut tree, the varnish or lacquer tree, and poison ivy, which belongs to the sumac family.

Poison ivy (*Toxicodendron radicans*)[38] grows in North America and East Asia, but not in Europe and Africa, and is perhaps the best known member of this family.

Dermatitis due to contact with poisonous Anacardiaceae is the source of misery for millions.[39,40] It can be contracted by handling and ingestion of the sap. In the case of poison ivy, the offending oleoresins are present in virtually all plant parts with resin canals. The canals are

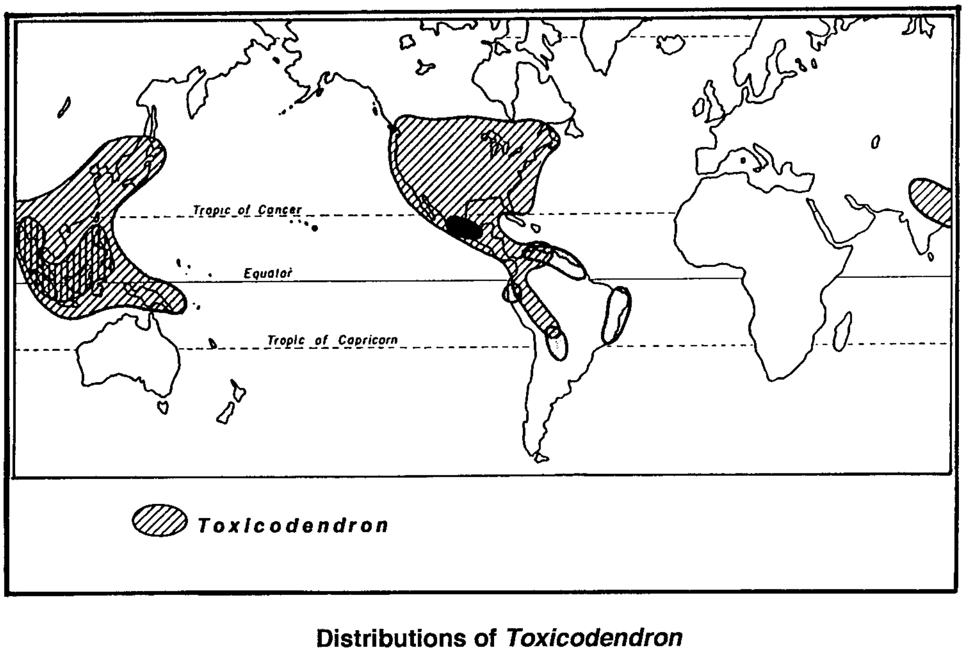


Figure 1. Distributions of *Toxicodendron*.

not open to the surface, and they must be injured in order to release the poisonous allergenic oleoresins.

The dermatologic activity depends on the phenol (catechol) component of the sap.[5,40] Also the unsaturation of the aliphatic side chain contributes to the effectiveness of the compounds. The dermatitis-causing activity requires that the aliphatic side chain be in the *meta* position to a phenolic group. A compound is formed between the urushiol components and a skin protein, which causes the immune reaction. Today no reliable antidote has been found to prevent *Toxicodendron*-caused dermatitis; only the effects can be treated.

CHEMISTRY OF URUSHIOL AND DRYING OILS

The oil-soluble fraction of the sap of the lacquer tree (urushiol) is a mixture of catechol derivatives substituted in the three position of the catechol with unsaturated (trienes, dienes, monoenes) and some saturated hydrocarbon chains—C_{15} and C_{17} chain lengths. The quality of the Japanese lacquer depends to a great extent on the quantity of the triene component. The composition of the urushiol varies and depends on the individual botanic species of the *Toxicodendron vernicifluum* tree from which the urushiol has been obtained, the location, the growing conditions, and the season of harvesting.

A number of techniques have been used to analyze and characterize the components of urushiol. Initially it was based on chemical reactions. Now they include regular[26] and capillary gas chromatography,[31] supercritical fluid chromatography,[32] high pressure liquid chromatography, and various techniques of high resolution NMR spectroscopy and two techniques of mass spectrometry, especially potassium ionization of desorbed species (K^+IDS) mass spectrometry.[28–32]

A number of individual compounds were found in urushiol samples by capillary gas chromatography, but many were present in amounts of less than 2%. Two compounds were present in over 80% in a ratio of 6:2. Mass spectrometry and NMR spectroscopy indicated that the peak with the retention time of 11.2 min was the triene, and the peak with the retention time of 12.2 min was the monoene.

Subsequently a careful study was carried out by a combination of ^{1}H and ^{13}C NMR and ^{1}H COSY NMR spectroscopy. Individual compounds were isolated by preparative HPLC of urushiol mixtures, and all the components and geometric isomers of the 3-n-alkylcatechols were isolated, identified, and characterized.

The desirable 3-(8-*cis*-11-*trans*-13-*cis*-pentadecatrienyl) catechol $[M]K^+ = 353$ (Fig. 2) was present in the various samples of urushiol in amounts of 55–68% while 3-(8-*cis*-pentadecenyl) catechol $[M]K^+ = 357$ Da was present between 15 and 25%. 3-(8-*cis*-11-*cis*-pentadecadienyl) catechol $[M]K^+ = 355$ Da was there in an amount less than 10%, and 3-(8-*cis*-11-*trans*-pentadecadienyl) catechol and 3-(pentadecanyl) catechol $[M]K^+ = 359$ Da were present in amounts of 2–4%. All other

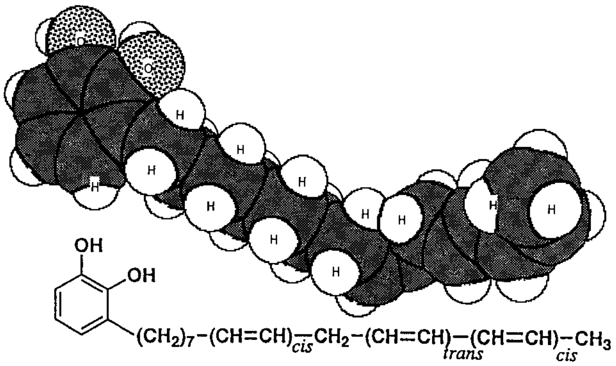
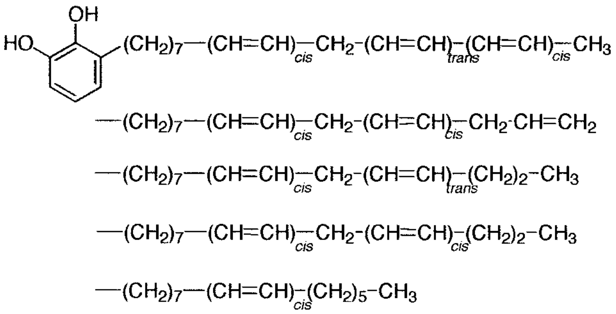


Figure 2. 3-(8-*cis*-11-*trans*-13-*cis*-pentadecatrienyl)-catechol.

components constituted less than 2%, usually only trace amounts.



For the 3-pentadecenylcatechol, only one geometric isomer, the *cis*-compound, has been isolated. Both geometric isomers of the dienes—3-(8-*cis*-11-*cis*-pentadecadienyl) catechol and 3-(8-*cis*-11-*trans*-pentadecadienyl) catechol—were found. Several geometric isomers of trienes $[M]K^+ = 353$ Da also were found in urushiol; the main component is 3-(8-*cis*-11-*trans*-13-*cis*-pentadecatrienyl) catechol.

From the chemical point of view, important for the curing process of the oriental lacquer is the methylene group in position 10. A methylene group in α-position to one or two additional double bonds also is needed, just as in the carboxylic acid portions of the glycerides that are used as drying oils.

In Table I we compare the compositions of the urushi of poison ivy and that of the lacquer tree. A significant difference is the presence of large amounts of the catechol of 3-(8-*cis*-11-*trans*-13-*cis*-pentadecatrienyl) catechol in the lacquer urushiol, which is needed for curing, while poison ivy has the 3-catechol of 8-*cis*-11-*trans*-pentadecadiene as the main component, which does not cure efficiently (Fig. 3).

Drying oils, such as tung and linoleic types,[41] are glycerol esters of fatty acids and are vehicles for a considerable volume of surface coating. Tung oil has as its main ingredient, in high percentage, eleostearic acid (9-*cis*-12-*trans*-14-*trans*-octadecatrienoic acid); linseed oil has linoleic acid 9-*cis*-12-*cis*-octadecadienoic acid and especially linolenic acid—9-*cis*-12-*cis*-15-*cis*-octadecatrienoic acid—as its main active components. The most important unsaturated acid, oleic acid, also has a *cis* double bond in the 9 position (9-*cis*-octadecenoic acid).

These fatty acids have similar structures to the aliphatic side chains in urushiol. The chain length of the linear hydrocarbon chains of these fatty acids is between 16 and 22, but the most important group has a chain length of 18 carbon atoms (stearic acid family). Linseed oil also consists of trienes, dienes, and monoene carboxylic acids. Part of the molecular structure and the positions and stereochemistry of the double bonds are similar to those of the trienes of the urushi.

The type of aliphatic side chains of some of the *Anacardiaceae* seem to be related to the fatty acids of natural fats. Natural fats[41] are triglyceride esters of palmitic and stearic acids, some of their lower homologues, and their unsaturated cousins. To the "stearic acid family" belongs not only stearic acid (octadecanoic acid) but also oleic acid (9-*cis*-octadedenoic acid), linoleic acid (9-*cis*-12-*cis*-octadecenoic acid), and linolenic acid (9-*cis*-12-*cis*-15-*cis*-octadecatrienoic acid) present in linseed oil. The primary component of tung oil is eleostearic acid (9-*cis*-12-*trans*-14-*trans*-octadecatrienoic acid).

It appears that the alkyl side chains of the catechols of urushi could have been formed by

Table I. Chemical Structures of the Allergenic Principles of *Toxicodendron* Species

Catechol Derivatives	Lacquer Tree[a] in %	Poison Ivy[b] in %
3-*n*-Pentadecyl	2–4	0–8
3-*n*-Pentadecenyl	13–28	3–42
3-*n*-Pentadecadienyl	7–16	18–83
3-*n*-Pentadecatrienyl	55–68	3–63
3-*n*-Heptadecyl	0–1	0–1
3-*n*-Heptadecenyl	1	0–2
3-*n*-Heptadecadienyl	1–2	0–22
3-*n*-Heptadecatrienyl	1–2	0–5
3-*n*-Heptadecatetraenyl	0	0

[a] *Toxicodendron verniciffuum*; [b] *Toxicodendron radicans*.

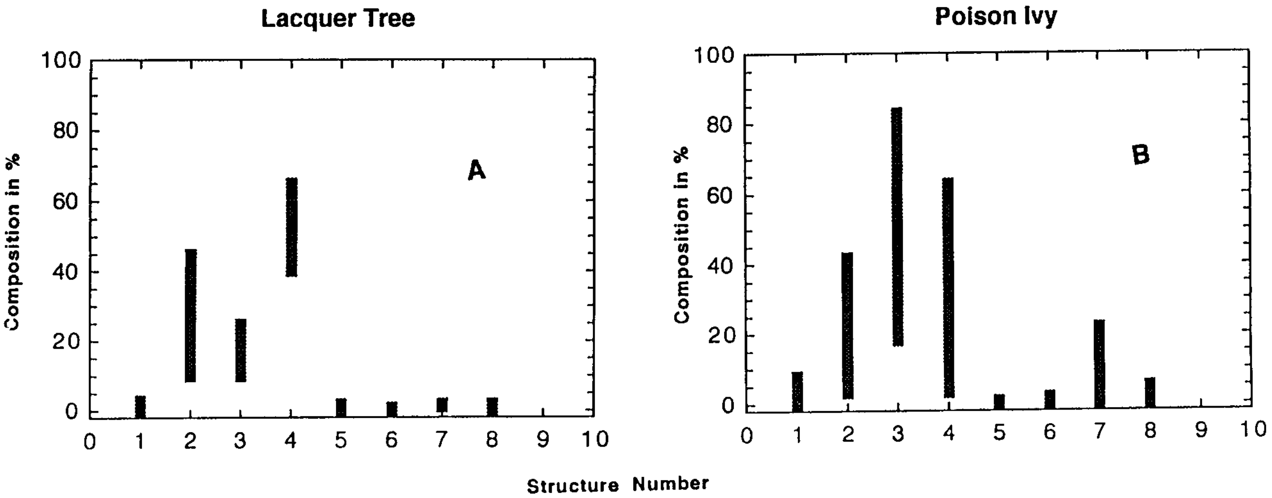


Figure 3. Composition of the 3-alkyl catechols of the lacquer tree and of poison ivy.

decarboxylation of fatty acids and alkylation of phenols, resorcinols, catechols, and salicylic acid (anacardic acid). The attachment of the aliphatic chain is always in the *meta* position to a phenolic group.

The aromatic rings of the catechols of the Thai lacquers, 3-(10-phenyldecanyl) catechols and 3-(12-dodecanyl) catechols, also could have been built starting with the carboxyl group of C_{16} or C_{18} carboxylic acids. Even the formation of decamethylenephenyl or the dodecamethylenephenyl side groups could be rationalized by assuming the addition of terminal methylene radicals formed from the terminal methyl group by selective hydrogen abstraction to the C_{10} of the C_{15} side chain or the addition of a similar terminal radical to the C_{12} double bond of the C_{17} side chain.

PREPARATION AND APPLICATIONS OF URUSHIOL

The sap of the lacquer tree, a water-in-oil emulsion, consists of the "oily," or urushiol, fraction (about 65%) and an aqueous fraction (35%). As has been mentioned, urushiol is a mixture of 3-substituted catechol derivatives with saturated and unsaturated aliphatic side chains. Nitrogen-containing substances (glycoproteins), which are not water soluble but are dispersed or dissolved in urushiol, are stabilizers for the water droplets of the native sap. Some gummy substances and mono-, oligo-, and polysaccharides are in the aqueous portion of the sap. It also contains enzymes, the most important of which is the copper-glycoprotein laccase, which functions as a dimerization catalyst for the 3-substituted catechol derivatives.

To prepare the lacquer from the natural sap, the sap is stirred in an open vessel at room temperature for about 1.5 h and then at a temperature increasing from 20 to 45 °C, where it is kept for 2 to 4 h in specially designed open vessels until the water content is reduced to 2–4% (*sugugome* process). The details of the process are a closely guarded secret and differ from manufacturer to manufacturer. This liquid, known as "raw lacquer," consists of urushiol and oligo–urushiols, dimers (about 5–10%) from the action of laccase on the hydroxyl groups of the catechol portion of the 3-n-alkylcatechols. The raw urushiol then is ready for application. Urushiol is cured by air oxidation; the effectiveness of curing depends very much on the triene components and on the amount and activity of laccase.

The temperature cycle must be carefully controlled to retain the activity of the enzymes. The sap is now clear, has become darker, and has increased in viscosity. The components of the aqueous phase, which are intimately suspended in the organic phase, seem to play a role in the quality of the final product. Sometimes small amounts of iron salts or other chemicals are added as catalysts for the production of the oriental lacquer.

Curing of the lacquer is a result of enzymatic oxidation and the radical curing of the highly unsaturated systems initiated by the hydroperoxides that are formed on the 10-methylene groups between the double bonds. Painting is done in a multilayer process of many very thin layers. High-quality products have as many as 30–40 layers. Painting and curing must be done in an environment of high humidity (65–80%). Curing of the lacquer does not work well in a dry atmosphere. The detailed nature of the curing mechanism is not known. However, it is known that, even after a month, the curing is not complete. The lacquered sample is still slightly soft and some postcuring still continues. The process from beginning to the end can take 2 months for complete curing.

For painting with oriental lacquer, a base coat is applied to the substrate, often cedar wood. It frequently is regular sap, without processing or with little processing.

A coat of about 5–10 μm in thickness is applied every 1 to 2 days. During the curing, several steps occur simultaneously: water evaporates, polysaccharides are deposited from the water droplets, and fine particles are dispersed into urushiol. Urushi is attached to the glycoprotein and finally, and most importantly, urushi polymerizes. The drying of the lacquer at high humidity is initiated by the oxidation enzyme laccase and is affected by the diffusion rate of the oxygen.

CURING

The curing mechanism of the oriental lacquer consists of two parts: (1) the laccase-catalyzed dimerization of the catechol rings of the 3-n-alkylcatechols; and (2) the oxidative curing of the unsaturated aliphatic side chains.[35]

The laccase-catalyzed curing is an oxidative dimerization involving the catechol rings that ultimately provides the crosslinker of the curing reaction. The urushiol consists of a mixture of 3-n-pentadecylcatechols: the saturated compound in small amounts, smaller amounts of the 3-(8-*cis*-pentadecenyl) catechol, 3-(8-*cis*-11-*cis*-pentadecadienyl) catechols, and mostly the 3-(pentadecatrienyl) catechols. Oxidative dimerization of the catechol mixtures gives dimers of a molecular weight (MW) of 626 to 636 or $[M]K^+$ of 665 to 673. The most important dimer is formed by dimerization of two molecules of the most abundant catechols, 3-(pentadecatriene)s, MW = 626. The dimer from the triene and the diene also may play a role as a crosslinker. The formation of the dimer and the role of the dimer is specific for the 3-n-alkylcatechols.

In addition to the type of process used for the preparation of urushi (we have mentioned only the common *surugome* process), the activity of the enzyme laccase plays a role for the amount of dimers and other condensation products formed during the preparation of the lacquer.

The next step of the oxidative curing reaction involves the structure of the unsaturated aliphatic side chain, commonly used in the drying of oils and, with some modifications, in the curing of butadiene-based rubbers. The mechanism of the curing consists of a number of interconnected steps involving radicals, that is, radical reactions, and radical additions and radical terminations.

It should be pointed out that these reactions proceed in continuously changing environments of viscosity. At the initial application, the lacquer is in a fluid environment. As the curing proceeds, the viscosity of the lacquer increases, which makes the reactive sites less and less available and the individual processes increasingly diffusion controlled. At the same time, the diffusion of oxygen for the oxidative curing to the reaction sites also decreases. As mentioned earlier, it takes almost 2 months until the lacquer is judged cured.

The curing of oriental lacquers seems to proceed according to traditional schemes of oxidative polyene polymerizations that have been established for polydiene curing: (1) creation of the first radical; (2) formation of oxy radicals; (3) addition of low-molecular-weight and polymer radicals to double bonds; and (4) termination of the radical process by radical recombination.

The initial formation of radicals consists of the abstraction of an undefined radical from the activated methylene group in the 10-position of the urushiol components. This radical can (a) add oxygen to form a peroxy radical or (b) recombine with an already existing radical.

Should interaction with oxygen be the path, molecular oxygen can be added to give a peroxy radical, which will abstract hydrogen from an appropriate carbon hydrogen bond and lead to a hydroperoxide. Hydroperoxides can dissociate directly to give a (polymer)oxy radical and hydroxyl radical. This dissociation may occur directly (for example by photo induction) or by thermal induction. A carbon radical or oxy radical can and will add to double bonds, especially sterically available and/or activated double bonds, to form new radicals. Ultimately, the polymer radicals will terminate by recombination.

Oriental lacquer is used almost entirely for objects designed for indoor use. In part it is the high cost that limits the use of oriental lacquer for decorative objects, and in part it is based on the fact that further reactions continue in the solid state. After the curing is “complete,” many reactive groups still are available for further curing.

Especially under the influence of the outdoor environment and solar radiation, the oriental lacquer undergoes a photochemical crosslinking reaction that increases the crosslink density and stress on the film. The result is the formation of blisters and cracks.

We have developed polymerizable ultraviolet stabilizers that can be copolymerized with oriental lacquers and drying oils, and for cured oriental lacquer it seems to increase the durability of the coating by a factor of three. The UV stabilizers are linolenic or linoleic esters of 2(2-hydroxy-*tert*-butyl[-5(3’-hydroxypropyl)phenyl]2H-benzotriazole.[37]

ORIENTAL LACQUERWARE

Oriental lacquer as a coating material produces exquisite pieces of lacquerware.[1–3] The number of layers determines the quality of the final product. Specially prepared urushi samples are used for the preparation of high-quality Japanese lacquerware. The lacquer used for individual applications contains several ingredients in addition to the urushiol base, depending on what special effects and what coloring are desired.

Several types of pigments have been used to give color to oriental lacquerware. For the yellow color, orpiment is used, for the red vermilion color, cinnabar or hematite, a ferric oxide pigment, and for black, metacinnabar, black iron pigments, and carbon black as well as Indian ink are used. Heavy pigmentation is needed because the processed raw urushi used for painting has a deep bluish/black to black color.

As the final layer, a clear raw lacquer coat is applied. The final product of the oriental lacquer is a crosslinked polymer; it is resistant to water, alcohol, and oils.

For centuries, actually for millennia, oriental lacquer has been used to coat objects in a highly artistic and pleasing manner. The results have been exquisite artifacts and useful objects of long-lasting beauty. Wooden boxes and other articles coated, using various techniques, with oriental lacquer are a central manifestation of art in the Orient and represent beauty and permanence.

A long time ago, well before the Christian era, the technique of producing boxes with oriental lacquer coating was well developed. We know of an almost perfectly preserved box coated with oriental lacquer from the Qin dynasty, about 200 B.C. Oriental lacquerwares continuously have been improved in China and, especially during the Yuan period (14th century), many beautiful objects have been produced. The lacquered boxes and containers are of black and vermilion colors and are elaborately carved, demonstrating the taste of the time.

Even though oriental lacquer art originally was developed in China, in the 6th century A.D. the art was brought to Japan. Different types of lacquer techniques developed in Japan as the Japanese culture became independent and different from China. The art form that produces Japanese lacquer products has gone through several periods of development and was greatly affected by the religious and ideologic foundation of any given time. The initial lacquer art form of Japan, in the Nara and in the following periods, used the traditional Chinese lacquering style.

Japanese lacquer trays from the 14th and 15th centuries show the impact of the simplicity of Zen Buddhism, a very simple design called the *neguro* style. It is a simple vermilion and black painting without decoration. The beauty of the objects—trays, containers, and boxes—relied in the shape of the original wooden object.

In the Muromachi period of Japan (16th century), another method of designing and producing lacquered objects was developed. It used more elaborate techniques, including the use of gold and silver flakes, mother of pearl, and shell for elegant designs. The interior of the temple Kodaiji in Kyoto, built in the early 1600s, exemplifies the *makie* technique, which uses silver flakes in black lacquer on a large scale.

In the Edo period of Japan, in the late 18th and early 19th century, further advances were made in Japanese lacquerware. Sophisticated decorations with silver, and later more and more gold flakes (*hiramakie*), were incorporated in the last few layers of lacquer on boxes, writing equipment, and desks, trays, and even on tables.

In the Meiji period, at the end of the 19th century, Japanese lacquer products became very fashionable worldwide, and the European market demanded considerable amounts of Japanese lacquerware. A new art form and modifications of the traditional way of preparing Japanese lacquerware were developed to satisfy the European market.

Objects coated with Japanese lacquer have not decreased in desirability or in value. High-quality Japanese lacquerware of high artistic value now can be obtained in traditional and also in novel and modern designs and styles.

Lacquerware originating from Okinawa, Korea, and China have used a considerable amount of mother of pearl or shells as inlay materials for their decoration. These latter techniques also have produced many beautiful objects.

Notes from Author. Throughout much of my career in polymer science, I have interacted extensively with the Orient, primarily with polymer science in Japan. I have been in Japan 26 times, having lived there nearly 2 1/2 years when the various periods are added together; and I have had 20 Japanese Postdoctoral Research Associates in my U.S. laboratories, 10 are now Full Professors in Japan. More details are presented in recent articles (J Polym Sci A: Polym Chem 2000, 38, 2293 and 2623).[42]

During this period I became interested also in the art and theater of Japan (Kabuki and Noh). Since I have lived mostly in Kyoto, the old capital and the cultural center of Japan, I have been exposed to many scrolls and screens, in temples and other places, and have become fascinated with the block prints of 19th century Japan (Hokusai, Hiroshige, and Shiganobu) and, most important, with Japanese lacquerware and the interiors and the inner sancta of temples.

When I moved to New York in 1982, I became a member of the Metropolitan Opera and of the Metropolitan Museum, where I became acquainted with people from the Metropolitan Museum in New York responsible for the restoration of old masters. These old oil paintings have a final transparent coating that has to be removed and reapplied from time to time after a few decades because of aging and deterioration. New lighting technology required some new thinking for possible incorporation of UV stabilizers in the coatings. I was involved in the development of polymer-bound UV stabilizers, which was of interest for restorations. Other changes in restoration techniques required improvements in the backings of paintings. As a thesis advisor at the Polytechnic University in Brooklyn, I mentored a joint master's thesis between the University and the Museum.

By 1987 we had founded and created the Pacific Polymer Federation and planned for the first conference in Maui, Hawaii (PPC-1), of which I was chairman. A one-day session on "Polymer Science and the Arts" was included (with the hope it would become a permanent institution). Raoul Hoffman and Hartwig Hoecker organized it, with some input by Seizo Okamura and Riichiro Chujo. Originally it was planned as restoration of art objects by synthetic polymers. For PPC-2, 2 years later in Otsu, Japan, the creation of art using synthetic polymers was added as a new and important aspect of the contribution of polymer science to the field of arts.

After PPC-1 I decided to become more actively involved in the subject of "Polymer Science and the Arts" and selected oriental lacquers as the subject. This selection was influenced by the fact that the main authority in Japan on oriental lacquers, my friend Kumanotani of the University of Tokyo, had just retired and by our having developed and perfected in our research group several techniques that ideally are suited to the complete and rapid identification of all components of samples of urushi, the active component of oriental lacquer. My next trip to Japan brought me to the Kyoto Institute of Technology (KIT), where Takeo Araki, Dean of Technology, and Shinzo Kohjiya were my hosts.

One Saturday I said I would like to see how oriental lacquer is produced, distributed, sold, and used. For many years I had known the Kyoto Handicraft Center as a source of many items of Japan, such as gifts, pearls, and art objects, and where English is spoken. When we went there and asked how to find out about oriental lacquer, we were advised to visit the Zohiko Urushi Art company on Raisen Dori in Kyoto. This company and store are known for their exquisite lacquerware. From there, we were directed to a small company in the heart of old Kyoto. There Araki and I met Mr. Shigero Tsutsumi, the President of the Tsutsumi Asakichi Urushi Company of Kyoto. After a relatively long period of negotiating and explaining the purpose of our visit, we obtained Mr. Tsutsumi's trust, and he explained in detail the growing, harvesting, and preparation of the various kinds of lacquers and the final applications. We purchased three typical samples, received them in sealed tubes, and thereafter we were ready to start our work.

Since it was impossible to work on a problem that involves Japanese culture without a Japanese counterpart, we convinced Professor Koichi Hatada of Osaka University to join us. He was invaluable because his group had high competence in two-dimensional NMR and several separation techniques that were needed to separate the components of urushi. William J. Simonsick, Jr., of DuPont contributed mass spectrometry, especially K^+IDS mass spectrometry of the mixtures and, after separation, of individual components. In Brooklyn, Jan Bartus carried out other analyses, synthesis, and polymerization experiments as well as curing and aging studies.

The work would not have been possible without the input of a competent botanist. Before starting the work, I decided to contact the New York Botanical Garden in the Bronx. I was directed to a certain John D. Mitchell who, I was told, could show me in the herbarium the species of *Toxicodendron vernicifluum*. Not only did he show me the species, collected some time ago in Sichuan, China, but it turned out that he was one of the world's experts on the botanic family of *Anacardiaceae* and especially on the genus *Toxicodendron*. Without his help, cooperation, and his guidance through the botany of these plant species, this work would not have been possible.

In the fall of 1996 when I was a Monbusho Professor at KIT in Kyoto, I reported our work that had been published in eleven articles before a broad audience.

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