472 YOSHIDA: CHEMISTRY OF LACQUER (URUSHI).

LXIII.—Chemistry of Lacquer (Urushi) Part I.

Communication from the Chemical Society of Tokio.

Ву Ніковокиво Уозніда.

I have lately, through the kindness of Mr. Magaribuchi, had an opportunity of examining the chemical properties of Urushi in its pure form, as well as of ascertaining the nature and properties of the various substances with which it is decomposed, when it exudes as juice from the tree.

At present much importance attaches to this substance in conse-

YOSHIDA: CHEMISTRY OF LACQUER (URUSHI) Article Office

quence of its many peculiar and excellent qualities, and its increasing application to useful purposes; I have thought therefore that a correct account of its chemical nature would possess some interest.

The specimen I understood had been obtained from Yoshino, in the province of Yamato, and was very nearly in the state in which it came from the tree; it had been altered simply by the formation of a thin crust of hardened urushi on the surface of the juice contained in the bottle. I might also add that, as the juice was originally intended for chemical investigation, and as it was collected in the best place in the empire, and under strict official inspection, it must have been in the purest form obtainable.

When Mr. Magaribuchi gave me the substance and also subsequently, he communicated his observations upon it, which, with others of my own, form the present paper.

I have here to give my sincerest thanks to Mr. O. Korschelt with whose kind counsel I had the pleasure of working the subject in the Chemical Laboratory of the Imperial Geological Survey, and also to Mr. J. Sakurai who helped me in various ways in preparing the present communication.

Urushi is the milky secretion of *Rhus vernicifera*, and is the material for the well-known Japanese lacquer varnish. The tree is cultivated in many parts of the country, throughout almost all latitudes, e.g., at Dewa, Aizu, Hiroshima, and in many places about Tokio; the best urushi, however, is obtained at Yoshino. The tree is very similar in aspect to the ordinary wax-tree, and attains the height of 9—12 feet; trees about fifteen years old yield the largest amount of the juice. Two sorts of the juice are generally obtained from a tree, and by different processes; they are distinguished as ordinary "Ki-urushi" and "Seshime-urushi."

Ki-urushi (or raw lacquer) is the better of the two, and is collected best in June by making shallow cuttings in the stem of the tree, when it exudes as drops from between the outer and inner barks. A single tree yields on an average about $2\frac{1}{2}$ grams of this kind of juice. Branches and twigs of the tree, some of which are usually cut down each year, when steeped in water for some months and afterwards warmed in the fire, give out an inferior kind of juice; this is seshimeurushi, which is used as under varnish after being mixed with some drying oil.

The juice is never sent to market in the form in which it comes from the tree, but is usually mixed with more less of what is called "Mokuyiki" (literally wood-juice), e.g., what is ordinarily called

* Mokuyiki is a substance much resembling ordinary urushi in appearance; it contains about 15 per cent. of the substance insoluble in alcohol, in which gum is present in large quantity. I have not yet been able to make a close examination of

Yoshino. Urushi consists of 60 per cent. of the genuine juice with 40 per cent. of mokuyeki, whilst the inferior quality contains as much as 70 per cent. of the latter substance. Further in the hands of varnish makers, some quantity of linseed oil is generally added to the already mixed juice, which, if excess is avoided, does not much impair the drying power of urushi.

Different colours are imparted to urushi by the addition of body pigments, such as lamp-black, vermillion, indigo, orpiment, &c.; thus red lacquer is prepared with 20 parts of linseed oil, 70 parts of urushi juice, and about 10 parts of vermillion, &c. Such is a rough yet general account of the extraction and preparation of urushi juice for varnish-making, but those who desire to get detailed information on this part of the subject, will find a full and accurate account in the writings of Mr. Quinn, English Consul at Hakodate. The pure and unaltered urushi is a thick greyish fluid of dextrinous consistence, which under the microscope is found to consist of minute globules, some of darker, the others of lighter colour, mixed with small particles of opaque brownish matter, the whole being held mixed in the form of intimate emulsion. It has a characteristic sweetish odour, and sp. gr. 1.0020 (20° C.); some specimens, such as that obtained from Hachiôji, contained a good deal of bark-dust and other impurities which raise it sp. gr. as high as 1.038. If the juice be exposed to moist air in a thin layer at about 20°, it rapidly darkens in colour and dries up to a lustrous transclucent varnish. It contains a small quantity of volatile poison, which acts terribly on some persons, producing very disagreeable itching.

Mr. S. Ishimatsu, in a paper on urushi, written some years ago at Tokio University, and afterwards communicated to the Manchester Philosophical and Literary Society by Professor Roscoe (Feb. 18th, 1879), has shown that the constituents of urushi are a resin, a gum, water, and a small quantity of residue insoluble in water and in alcohol.

The method of separation of these substances which I pursued was the same as that adopted by Mr. Ishimatsu, thus:—

A resinous acid, together with a small quantity of the volatile poisonous body, is separated from the other substances in the juice by treating it with absolute alcohol, evaporating the solution, and drying the acid at 105—110°.

The residue is boiled for some time with water, and the water extract evaporated on a water-bath till it acquires a constant weight. This gives the quantity of gum.

the substance, but I think that it is in all probability a very impure form of the urushi juice.

YOSHIDA: CHEMISTRY OF LACQUER (URUSHI) Article Online

The final residue, consisting chiefly of a coagulated diastatic matter, with very small quantities of cellulose and insoluble colouring matter, is dried at 100°, and weighed as such.

The difference of the sum of numbers from 100 gives the amount of water and volatile matter. Thus pure Yoshino urushi consisted of—

	Per cent.
Part soluble in alcohol (urushic acid)	85.15
Gum arabic	3.15
Residue (diastatic matter)	2.28
Water and volatile matter	9.42
	100.00

Pure urushi does not, I think, vary much in composition, but as I have already remarked, it is usually mixed with varying quantities of mokuyiki, and it is natural to suppose that such a mixture will rarely show identity in composition. Thus Mr. Ishimatsu gives the following as a mean result of two experiments made on a sample bought at Tokio:—

	Per cent.
Part soluble in alcohol	58.24
Gum	6.32
Residue	2.27
Moisture and other volatile matter	33.17
	100.00

In the Hachiôji sample, which must have contained some quantity of mokuyiki, I have found the amount of gum and diastatic matter very much higher (about 12 per cent.), and the proportion of urushic acid much lower than those indicated in the analysis of a Yoshino specimen.

1. Examination of the Alcoholic Extract:—Urushic Acid and Volatile Poison.

A peculiar acid, which I now call urushic acid, is the main constituent of the original juice, as well as of the portion soluble in alcohol. The juice also contains a very small quantity of a volatile poisonous body, which also passes into alcoholic solution, being almost completely driven out during the drying of the acid at 105—110°. It is a pasty substance of somewhat dark colour, having the characteristic smell of the original juice, readily soluble in benzene, ether, carbon bisulphide, less easily in fusel oil and petroleum of high-boiling point, completely insoluble in water. Its sp. gr. taken at 23° is 0.9851; vol. XLIII.

it remains unchanged at 160°, and above 200 decomposes slowly with carbonisation. Exposed to the air, it neither dries up, nor shows any sign of change as the original juice does, and in other respects it is a very stable body. From the alcoholic solution of the acid many metallic salts can be produced, most of which are slightly soluble in alcohol, but almost insoluble in water.

Silver nitrate gives at first a fine dark precipitate moderately soluble in alcohol; on boiling, silver is reduced, with deposition of a mirror on the sides of a vessel.

Platinic chloride gives a gelatinous black precipitate, somewhat soluble in alcohol; on standing, the precipitate sinks down, and ultimately coheres to a pasty mass.

Gold chloride and acetate of uranium give very fine dark brownish precipitates, behaving like the precipitate obtained with platinic chloride.

Nitrate of copper imparts a black colour to the alcoholic solution of the acid; if it be considerably diluted with water, the copper salt separates out in the most finely divided state.

The acid dried at 110° and analysed gave the following numbers:—

- I. 0.8226 gram substance gave 2.3690 grams CO2 and 0.6871 gram $\rm H_2O$.
- II. 0.4235 gram substance gave 1.1995 gram CO_2 and 0.3334 gram H_2O .

	T.	II.	Theory for $C_{14}H_{19}O_2$.	Theory for $C_{14}H_{18}O_2$.
Carbon	77.09	77.01	76.71	77.06
Hydrogen	9.28	8.75	8.67	8.28
Oxygen	13.63	14.24	14.62	14.66
	100.00	100:00	100.00	100:00

Acetate of lead gives a greyish flocculent precipitate, which is a very characteristic reaction of the acid; a quantity of this compound was prepared, as in Mr. Ishimatsu's experiments, by precipitating an alcoholic solution of the acid with acetate of lead. The precipitate was first washed with alcohol, then with well boiled water, first dried over a water-bath, and finally over sulphuric acid in a desiccator, and analysed.

- I. 0.7236 gram substance gave 1.3818 gram $\rm CO_2$ and 0.3478 gram $\rm H_2O$.
- II. 0.5021 gram substance gave 0.1765 gram PbO. Pb = 32.63 per cent.
- III. 0.6020 gram substance gave 0.2093 gram PbO. Pb = 32.27 per cent.

YOSHIDA: CHEMISTRY OF LACQUER (URUSHI) Article Office

	Per cent.	Theory for $(C_{14}H_{17}O_2)_2Pb$.
Carbon		52.40
Hydrogen	5.34	5 ·30
Oxygen	10.43	10.01
Lead		32.29
	100.00	100.00

This lead compound is a somewhat unstable body; when heated to 100° in an air-bath, it gives out a peculiar odour and turns darker in colour; at 110—115° it melts to a dark brownish mass, and at about 120° it ignites spontaneously in the air, burning with smoky flame, and leaving an oxide of lead.

Another salt of this acid I examined was an iron compound. Ferric chloride gives a deep black voluminous precipitate, very sparingly soluble in alcohol, and almost insoluble in water. A quantity of the alcoholic solution of the acid was precipitated with an insufficient amount of ferric chloride, with the view of seeing whether this fractional precipitation gives a salt of different composition; the compound obtained, however, proved to be a salt of very acid nature, as will be seen below; it was first dried over a water-bath, and then over sulphuric acid, and analysed.

- I. 0.5000 gram substance gave 1.03644 gram CO_2 and 0.3680 gram H_2O .
- II. 0.5000 gram substance gave 1.3640 gram CO_2 and 0.3662 gram H_2O .
- III. 0.7890 gram substance gave 0.0234 gram Fe₂O₃.

		(C ₁₄ H	$H_{17}O_2$) ₃ Fe + 9(C ₁₄ H ₁₈ O ₂) + 2H ₂ O.
	I.	II. `	+ 2H ₂ O.
Carbon	74.42	74.40	74.53
Hydrogen	8.18	8.13	8.03
Iron	2.07	2.07	2.08
Oxygen	15.33	15.40	15:38
	100.00	100.00	100.00

Another preparation of iron salt was made, using a larger quantity of ferric chloride than before; the compound again proved to be another acid salt, but of less complexity than that above indicated; on analysis it gave the following numbers:—

- I. 0·5000 gram substance gave 1·3660 gram $\rm CO_2$ and 0·3670 gram $\rm H_2O$.
- II. 0.6968 gram substance gave 0.0428 gram Fe₂O₃.

		Theory for $(C_{14}H_{17}O_2)_3$ Fe + $3(C_{14}H_{18}O_2)_*$
Carbon	74.56	74:06
Hydrogen	8.16	7.72
Iron	4.29	4.11
Oxygen	13.59	14:11
		100:00

Both these iron salts have very similar characters; they are light substances of a faint peculiar odour. At 105—110° they melt to a black mass with some decomposition, and at a somewhat higher temperature ignite spontaneously, giving out dense smokes of peculiar odour.

It is owing to the formation of some of these iron compounds, I think, that practical lacquermen carefully avoid the use of iron instruments in dealing with urushi; I have found experimentally that a small quantity of iron rust rubbed with urushic acid at once imparts a dull black colour to the substance.

Free alkalis impart a very dark colour to the solution of this acid, which looks purplish-blue by transmitted light, and very dark brown by reflected light. If exposed to the air, this viscid compound rapidly blackens and dries up; it is a compound of an alkali-metal with the acid, the normal salts of which will probably be represented by the formula $C_{14}H_{17}MO_2$; the substance, however, was not quite fit for analysis, as it was very difficult to purify. It is soluble in a rather large quantity of ether or benzene, and less easily in water and alcohol.

Sulphuric acid apparently produces no change in this black compound, but if boiled with very strong hydrochloric acid, it is converted into an elastic gummy substance, which I shall describe more particularly when I come to speak about the action of hydrochloric acid upon urushic acid. The solution of this alkali compound in light petroleum oil gives an excellent lustrous varnish, which dries up very easily.

Soluble salts of mercury, zinc, nickel, cobalt, manganese, and those of earthy metals do not give any distinctive reaction with urushic acid.

Bromine acts powerfully upon urushic acid, evolving fumes of hydrobromic acid.

To a solution of the acid in carbon bisulphide bromine was gradually added till it was in some excess; the whole was evaporated to dryness over water-bath; the mass exhausted with strong alcohol; and the extract again evaporated, whereupon it yielded a dark semisolid mass. This was examined for bromine by ignition with pure lime: 0.7060 gram substance gave 1.1510 gram AgBr or Br = 69.37

YOSHIDA: CHEMISTRY OF LACQUER (URUSHI), Article of life

per cent., agreeing nearly with a hexbromo-derivative of the acid, viz., $C_{14}H_{12}Br_6O_2$, which requires 69.36 per cent. bromine.

At ordinary temperatures it is almost a solid body, of a brownish colour, and soluble in most solvents of urushic acid; by using regulated quantities of bromine, its lower substitution products might perhaps be obtained. Chlorine also gives a series of substitution products, but the compounds have not yet been fully examined; they will be described in a later communication.

The distillation of urushic acid with lime did not yield any definite results. The decomposition appears to be very complicated, and some oxygenated bodies are still present amongst the products, contrary to the expectation that a hydrocarbon would be obtained corresponding to the original acid. It should be observed, however, that these lower fractions, which are free or nearly so from oxygenated bodies, approach the composition C₁₄H₂₄, probably one of the higher hydrocarbons of the terpene series. They are nearly colourless light oils of a peculiar odour, somewhat recalling that of borneene; they absorb oxygen from the air and resinise; they unite readily with bromine, and are blackened by concentrated sulphuric acid in the cold.

Long-continued action of strong hydrochloric acid upon urushic acid produces a peculiar change in the latter, the resulting body having exactly the same composition as the original acid, but very different properties. A quantity of urushic acid was heated with a very large excess of strong hydrochloric acid for about three days, the acid lost by evaporation being replaced. Urushic acid under this treatment first swells up to a soft sponge, gradually assumes a caoutchouc-like state, and finally hardens to a dark nonadhesive mass. The substance was cut up into small pieces, boiled with water, filtered,* and dried over a water-bath till the last trace of hydrochloric acid retained in the pores of the substance had been On cohobation with alcohol, a small quantity of the substance dissolved, which on examination showed the usual characters of unchanged urushic acid. The residue dried at 105°, and analysed, gave the following numbers. No chlorine was found in the substance :--

0.4022 gram substance gave 1.1360 gram $\mathrm{CO_2}$ and 0.3356 gram $\mathrm{H_2O}.$

	Found.	Mean number obtained for urushic acid.
Carbon	77.07	77.05
Hydrogen		9.01
Oxygen	14.16	13.94
•	100.00	100.00

^{*} The filtrate left no residue on evaporation.

It appears from this that urushic acid suffers molecular transformation (polymerisation) under the influence of strong hydrochloric acid. β -urushic acid thus formed is a dark brownish solid body, having a faint peculiar odour, and is soluble in the usual solvents of urushic acid.

As such was the case, an experiment was tried to ascertain whether urushic acid dries in an atmosphere charged with hydrogen chloride. A glass plate very thickly coated with pure urushic acid placed upon a basin containing fuming hydrochloric acid under a bell-jar, dried after standing for about two days. The urushic acid darkened in colour on drying, and looked somewhat similar to the naturally dried lacquer. Strong nitric acid has no action upon β -urushic acid, even on boiling, though it acts very powerfully upon urushic acid; when the β -acid is heated to 100° it merely softens a little, and even at 130° it shows no sign of decomposition. It appears that the substance obtained by the decomposition of an alkali salt of urushic acid with hydrochloric acid is the same body as β -urushic acid.

The action of strong nitric acid upon urushic acid gives rise first to a series of nitro-substitution products, which appear to change afterwards into another acid containing a larger number of oxygen-atoms. The reaction is very energetic, the urushic acid first swelling up to about thirty times its original bulk in the form of a yellowish sponge, which disappears gradually with the progress of the reaction. A quantity of this porous body was collected after about half a day's heating, treated with a larger quantity of water, and then dissolved in alcohol, and an iron compound precipitated from it with ferric chloride. The substance, after the usual purification and drying, was analysed, and the following numbers were obtained:—

- I. 0.5031 gram substance gave 0.9498 gram CO_2 and 0.2183 gram H_2O .
- II. 0·3802 gram substance gave 27·5 c.c. nitrogen at 23° and 784 mm. P.
- III. 0.4139 gram substance gave 0.0578 gram Fe₂O₃.

		Theory for $(C_{14}H_{15}(NO_2)_2O_2)_3Fe$.
		$(C_{14}H_{15}(NO_2)_2O_2)_3Fe.$
Carbon	51.49	51.59
Hydrogen	4.82	4.61
NO ₂	28.16	28.25
Iron	9.77	9.81
Oxygen	5.76	5.74
	100.00	100.00

This is the iron salt of dinitrourushic acid.

YOSHIDA: CHEMISTRY OF LACQUER (URUSHI) Article Offine

The original acid is a bright yellowish solid, readily soluble in the usual solvents of urushic acid, and gives characteristic reactions with many metallic salts; those of silver, lead, zinc and manganese are light yellowish precipitates, of copper and iron greenish-yellow, and of soda and potash brownish. The acid itself and its metallic salts are to some extent soluble in water, and more soluble in alcohol.

The higher nitro-substitution products, which are likewise yellowish solid substances, and also their salts, are characterised by their greater solubility in water and alcohol. The other properties of these, as well as those of the product of the final action of nitric acid upon urushic acid, are now being studied.

We are not yet acquainted with the chemical nature of the volatile poisonous substance which passes into alcoholic solution, together with urushic acid from the juice. It comes over with water in the form of a thin oily film when a quantity of the juice is distilled; the distillate reduces solution of mercuric chloride, but does not give any precipitate with acetate of lead; it is almost impossible to do anything with it unless very large quantities of the juice are operated upon.

2. Examination of the Water Extract—the Gum.

Gum is another normal constituent of urushi, and forms 3—8 per cent. of the original juice.

As gum is insoluble in alcohol, it is conveniently separated by treating that portion of the original juice insoluble in alcohol with boiling water, filtering, and finally evaporating the aqueous solution of gum over the water-bath till the weight of the substance remains constant. In this way a friable light-coloured substance is obtained, tasteless and inodorous; this is the anhydrous gum. On combustion it gave the following numbers:—

 $0.5267~\rm gram~substance~gave~0.7823~\rm gram~CO_2$ and $0.2834~\rm gram~H_2O$, and $0.0267~\rm gram~ash$.

Analysis of the ash in a separate sample of the substance gave the following:—

	Per cent.
Silica	0.48
Alumina	7.85
Lime	44.77
Magnesia	5.79
Potash	13.68
Soda	1.33
Carbonic acid	26.10 (by difference)
	<u> </u>

100.00

If the metals in the ash be replaced by the equivalent amount of hydrogen, and the result calculated for carbon, hydrogen, and oxygen, the above numbers will give—

		Arabic acid, (C ₁₂ H ₂₂ O ₁₁).
Carbon	$42 \cdot 47$	42.11
Hydrogen	6.40	6.43
Oxygen		51.46
	100.00	100.00

Mr. Ishimatsu's analysis of the gum is as follows. In it, however, no mention is made of the quantity and nature of the ash:—

	Per cent.
Carbon	41.37
Hydrogen	6.55
Oxygen	52.08
	100.00

The gum when inverted has the power of reducing Fehling's solution.

0.4747 gram substance (ash deducted) after inversion with 10 per cent. hydrochloric acid and precipitated gave 0.8114 gram CuO.

If we suppose that after the hydration, 1 mol. of arabic acid ($C_{12}H_{22}O_{11}$) changes into 2 mols. of $C_6H_{12}O_6$, the molecular ratio which the product of inversion, be it glucose or arabinose, bears to cupric oxide will be 1:5, exactly the same as that of dextrose to CuO, and consequently its cupric oxide reducing power, or K, will be 100. These facts leave no doubt as to the identity of the gum in urushi with the essential constituent of gum arabic; it is present in urushi in the form of acid salts of arabic acid, chiefly of potash, lime, alumina, and magnesia, and the only point of difference which is probably of interest is the presence of an alumina salt, which has not hitherto been observed in other gums.

A mixture of gum and urushic acid (and with water) in the proportion in which they exist in the juice, does not undergo any change whatever, even when exposed to the condition most favourable for the drying of the lacquer. Moreover part of the gum can be extracted in an unchanged state from the once perfectly dried lacquer; and since it exists in the original juice in the form of aqueous solution, it probably serves to keep the constituents of the juice in a state of uniform distribution and intimate emulsion. It may also act as a binding material, and assist the adhering power of the lacquer when laid upon any surface.

3. The Diastatic Matter and its Action upon Urushic Acid.

That portion of the juice which remains insoluble in alcohol and boiling water, consists chiefly of a nitrogenous substance, the action of which upon urushic acid has been ascertained to be the cause It forms 3-8 per cent. of the original of the drying of the lacquer. juice, that which contains it in larger proportion having the property of drying more quickly, while such a lacquer gives a varnish with inferior lustre.

The substance, as separated from the gum by the usual method of boiling with water, has no action upon urushic acid, but the residue itself (after the separation of urushic acid), or its extract with cold water, shows that peculiar diastatic activity in an unimpaired degree; when such a solution is boiled, the albuminoud coagulates in the form of a white precipitate.

The substance dried first over water-bath and then over sulphuric acid, and analysed, gave the following numbers:

- I. 0.5008 gram substance gave 1.1610 gram CO_2 , 0.3336 gram H_2O , and 0.0060 gram ash.
- II. 1.0000 gram substance gave 0.6360 gram (NH₄)₂PtCl₆.

Carbon	$63 \cdot 44$	
Hydrogen	7.41	In the ash small quantities
Nitrogen	4.01	of sulphur and phosphorus
Oxygen	22.94	were detected.
Ash	1.20	
		
	100.00	

It differs from other vegetable albuminoïds in containing a notably smaller amount of nitrogen; the latter, as well as the active principles of the diastase (malt), koji, and saliva, do not possess the same property of exerting the peculiar action above-mentioned upon urushic acid.

Two series of experiments were instituted to test the activity of the diastatic matter upon urushic acid, first at different temperatures in the air, and secondly under different gaseous media.

For this purpose, a small quantity of the original juice was put into a covered breaker and subjected to the regulated heat of a waterbath, a small quantity of water lost by evaporation from the juice being afterwards replaced by approximately the same amount.

The heated juice was next very thinly coated on a glass plate and left to dry in a box, the air of which was kept constantly moist by the falling in of the drops of water. The time of heating the juice was, in each experiment, $3\frac{1}{2}$ —4 hours, and the temperature of the drying box was 20° .

- 1. At ordinary temperature (20°) the sample dried after $3\frac{1}{2}$ hours in air, and the same under a bell-jar containing moist oxygen dried after less than 2 hours.
 - 2. Heated at 30°, the sample dried after 4 hours.
 - 3. Heated at 40—43°, the sample dried after $4\frac{1}{2}$ hours.
 - 4. Heated at 50°, dried, time not known.
 - 5. Heated at 55—59°, almost dried after 24 hours; the surface of the lacquer had a dull appearance.
 - 6. Heated at 60-63°, did not dry.
 - 7. Heated at 80°, did not dry.
 - 8. Heated at 100°, did not dry.

Next, a glass plate similarly coated with urushic juice was put under a bell-jar containing an experimental gas, and left to dry at the temperature of the surrounding air, which at this time ranged between 13—15°.

- 1. In dry air, the sample did not dry.
- 2. In moist air, the sample dried after 4 hours.
- 3. In dry oxygen, the sample did not dry.
- 4. In moist oxygen, the sample dried after $2\frac{1}{2}$ hours.
- 5. In dry hydrogen, the sample did not dry.
- 6. In wet hydrogen, the sample dried after $1\frac{1}{2}$ days.
- 7. In dry carbonic acid gas, the sample did not dry.
- 8. In wet carbonic acid gas, the sample dried very slowly after 2 days.
- 9. In dry nitrogen, the sample did not dry.
- 10. In wet nitrogen, the sample dried after $1\frac{1}{2}$ days.

The most legitimate inference to be drawn from all these experiments, is that the combination of oxygen and moisture at the temperature of 20°, or thereabouts, is an essential condition for the display of the fullest activity of the diastase, and consequently most favourable for the drying of the lacquer; with increase of temperature the drying power diminishes, until at 63—63° the substance entirely loses its activity; this is then the point at which the coagulation of the albuminoid takes place, or, in other words, the diastatic matter dies. With other gases, however, I am inclined to think that a small quantity of atmospheric air, which may have been present in them, might have favoured the condition for drying, which otherwise could not have been possible.

These conclusions bear out the practical experience of our lacquer men, viz., that lacquer dries best in the rainy reason; it dries better

YOSHIDA: CHEMISTRY OF LACQUER (URUSHI) Article Offin

in summer than in winter—a damp atmosphere of about 20—30° being just the state of air during the rainy season of a year.

The question still remains to be asked, How does the diastase act upon urushic acid, or what is the change which the urushi juice undergoes on drying? To solve this question, the states of the lacquer, before and after the drying, have been examined and compared.

A quantity of the fresh juice was rapidly heated over the waterbath so as to coagulate the albuminoid and put a stop to its further action upon urushic acid. After continuing the heat, so as to expel all the water from the juice, it was analysed and gave the following numbers:

- I. 0·4090 gram substance gave 1·1318 gram CO2 and 0·3290 gram $\rm H_2O.$
- II. 0·4213 gram substance gave 1·1679 gram $\rm CO_2$ and 0·3420 gram $\rm H_2O$.
- 1II. 2.0540 grams substance gave 0.0359 gram (NH₄)₂PtCl₆.
- IV. 2.1564 grams substance gave 0.0046 gram ash.

	I.	II.	Mean.	Numbers calculated from the constituents of the juice.
Carbon	75.47	75.61	75.54	75.54
$\mathbf{Hydrogen}$	8.93	9.01	8.97	9.14
Nitrogen	_		0.11	0.10
$\mathbf{A}\mathbf{s}\mathbf{h}\ \dots\dots$			0.21	0.21
Oxygen \dots			15.17	15.01
			100.00	100.00

The lacquer dried (hardened) in the usual manner, and afterwards heated at 100°, has the following composition:—

- I. 0.5434 gram substance gave 1.4124 gram CO2 and 0.4186 gram $\rm H_2O.$
- II. 0.4608 gram substance gave 1.1970 gram $\rm CO_2$ and 0.3276 gram $\rm H_2O$.
- III. 2:1215 grams substance gave 0:0310 gram $(NH_4)_2 PtCl_6.$
- IV. 1:1717 gram substance gave 0:0043 gram ash.

	Ι.	II.	Mean.
Carbon	70.91	70.84	70.85
Hydrogen	8.55	7 ·90	8.22
Nitrogen			0.092
Ash		_	0.032
Oxygen			20.52
			100.00

The comparison of the results of these two sets of analyses indicates that the lacquer in hardening had taken up oxygen, and we see that, other things remaining the same, the amount of oxygen thus taken up is very nearly accounted for on the supposition that each molecule of urushic acid, $C_{14}H_{18}O_2$, in the juice, has taken up 1 atom of oxygen, and changed into another body of the formula $C_{14}H_{18}O_3$.

Further proof of this theory has been arrived at by the isolation of pure oxy-urushic acid (C14H18O3), which showed all the properties of a dried lacquer.

Urushic acid was subjected to the action of strong chromic acid mixture (which contains some excess of sulphuric acid, so as to prevent the precipitation of chromic hydrate). The product cohobated with absolute alcohol for some time to dissolve away the unacted urushic acid, gave, on drying (at 105°), a brownish powder having the following composition:—

- I. 0.3059 gram substance gave 0.8021 gram CO₂ and 0.2296 gram $\rm H_2O$.
- II. 0.4245 gram substance gave 1.1134 gram CO_2 and 0.3103 gram H_2O .

	I.	II.	Mean.	Theory for $C_{14}H_{18}O_3$.
Carbon	71.55	71.50	71.52	71.79
Hydrogen	8.32	8.13	8.23	7.69
Oxygen			20.25	20.52
			100.00	100.00

This substance is very stable, and resists the action of strong boiling nitric acid; no solvent has yet been found for it.

An attempt was also made to estimate the quantity of carbonic acid evolved during the drying of the lacquer. It was found that this quantity is so small as not to affect the general result in any sensible degree. Thus, 1.5 gram of the juice gave out 0.0036 gram CO₂ (= 0.24 per cent.) during its hardening in an atmosphere of moist oxygen, which was completed at the end of two hours. I am inclined to attribute this phenomenon to the decomposition of a small quantity of gum (= 0.0085 gram in this case) by the diastase, simultaneously with its action upon urushic acid.

The results, so far arrived at, may be summed up in the following statement:--

Urushi juice (lacquer) consists essentially of four substances, viz., urushic acid, gum, water, and a peculiar diastatic matter; and the phenomenon of its drying is due to the oxidation of urushic acid, $C_{14}H_{18}O_2$, into oxy-urushic acid, $C_{14}H_{18}O_3$, which takes place by the aid of diastase in the presence of oxygen and moisture.