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Studies on Confirming the Type of Dried Urushi Film and Its Formation Mechanism (Urushi Hardening Study Report II)

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In a previous report (Ref. 1), the author described the chemical structure of acetone powder (AP, the so-called laccase) of the Japan urushi sap, and dope obtained by the classic Kurome process is interpreted as urushiol orthosilicate. In this paper, the further discussion is given about flake pieces which were accidentally obtained from a broken Al tube containing raw urushi during the summer; also described is dope obtained under a special treatment (three ceramic rolls mill (TR) compounding) and hardening while keeping at room temperature and 80% humidity. Precise studies have shown that both have hexagonally and octahedrally oriented oxygen atoms around the center Si atom of the acetone powder. It has been found that three kinds of urushiol silicate and inorganic bond (peroxide) bridging formation, such as $-H_2C-O-OCaOH$ or $-H_2C-O-OMgOH$, are the true hardening mechanisms, instead of a hitherto considered enzyme action.

This report describes a continued effort to clarify a urushi lacquer hardening film. It is considered that the urushiol orthosilicate, $Si(OUQ)_4$,[1] could be the essence of KU dope, which was obtained by loosing several moles of water from RU by a treatment in the Kurome thickener. Although new cooperative work[2] by Japanese and American urushi research experts was reported, no substantial progress has been realized other than some NMR studies concerning urushiol-quinone (as dimer form compositions). Moreover, two internationally cooperative reports[3,4] in this field recently appeared, which tempted the author to accelerate his work to completion.

It is important to explain the abbreviation symbols for urushi materials, such as UO, UO′, UQ′, RU, KU and AP. First, UO represents the fundamental ingredient of urushi sap, urushiol; and UQ, UO′ mean UO minus OH and a loss of H respectively. Second, people have called the original urushi sap Kiurushi from old times; however, if KU is adopted as this abbreviation, it causes confusion with Kurome urushi dope (next symbol), and thus RU (Raw Urushi) was selected. Third, KU is formed by a blackening pretreatment of raw sap by dehydration and oxidation in air at about 40–45 °C with a special thickener in a flat wooden tub. The last symbol, AP, denotes acetone powder, which is obtained as a white powder by pouring a large quantity of acetone solvent into RU sap and mixing it well in the presence of air. Originally, ethanol was used instead of acetone to obtain a dark- colored pasty substance, the action of which was presumed to be diastase by Yoshida.[5] Bertrant[6] changed the name more direct meaning laccase. Afterward, acetone was found to be a better solvent by Keillin.[7]

Other names, like polysaccharide-protein, which appeared in some report is not considered here, because they differ from the original definition of laccase, which is adapted just to mean acetone powder. Lately, the author could find two new types of urushi hardening materials: one has hexa-coordinated-oxygen atoms, as shown in Fig. 1B and sample B in Fig. 2; the other has octa-coordinated-oxygen atoms, as shown in Fig. 1C, and sample C in Fig. 2.

Experimental

Materials. In this report, the original raw urushi sap (RU) used by the new sample presenters is the same as the Japan urushi reported in the literature.[1] Therefore, the author used the same analytical values of the urushiol and metal components as mentioned in a previous report.[1] Hitherto, it had been impossible for the author to obtain an old dried film sample formed by the routine Kurome procedure and preserved for several years (sample 1). Therefore, he was forced to show only the classic optical IR spectrum measured by H. Oyabu (Fig. 3). However, at this time, K. Toyoshima gave the author his sample (10A1O) after nearly 6 years of preservation in an ordinary room atmosphere. Elemental analyses and FTIR spectra were measured for a comparison with the previous sample. In addition, another new urushi-hardened film sample (sample 3), different from the routine- hardened KU film, was given to the author by Oyabu[8] as a cured flexible film (Fig. 1C). This new kind of dope has a lower viscosity compared to KU dope, and is it possible to obtain a hardening sample under RT and 80% RH on a glass plate, which can be easily peeled off.

Results and Discussion

As can be seen from Table 1, sample 1 was $Si(OUQ)_4$ and the six-year old sample (10A1O) showed almost the same CHN values, though 2 moles of H_2O(water) loss per recurring unit MW was found for this film. For sample 2, an irregular dry flake from RU sap in a broken Al plate tube container shows six oxygen atoms (hexagonally) in a coordinated polymer (Fig. 1B) with a siloxane chain; the empirical formula regarding the C and H contents is $C_{84}H_{122}$, and its MW was calculated to be 1457 ($12.01 \times 84/0.692$).

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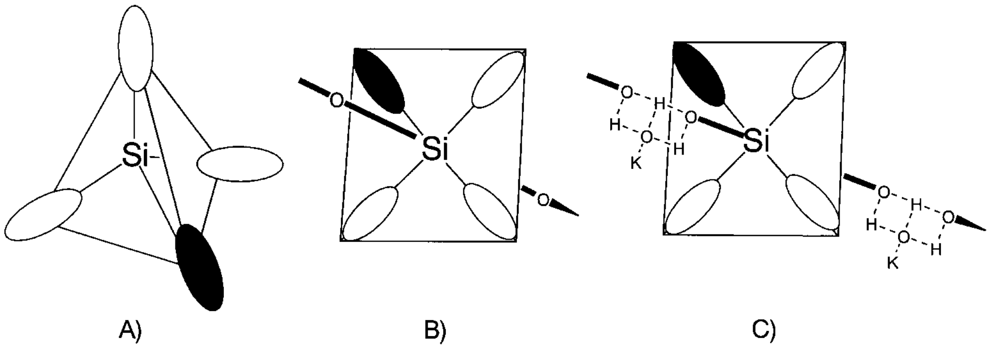


Fig. 1. Three different kinds of urushi dried film. A) KU dried film, Urushiol orthosilicate, Sample 1, Si(O<u>UQ</u>)$_4$. B) Urushiol Si–O–complex black flakes, sample 2, accidentally obtained by RU containing tube broken in summer time. C) Urushiol Si–O–Complex derived from <u>RU</u> by using three roll mill compounding (dope form) and then dried. Sample 3.
⬬– One unit of AP bearing <u>UO</u>, one atom K transfers from -SiOK presented in AP.
⬭– Plain oxidized <u>UO</u>. Exactly <u>UO</u> means with a loss of H.

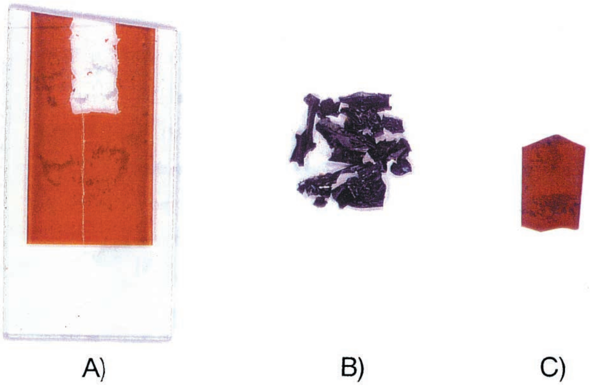


Fig. 2. New three samples' outlookings by color copy. Sample 1: on Glass Plate, Sample 2: Black Flakes. Sample 3: (Treated with Tri-Rohrs) Peeled off Film.

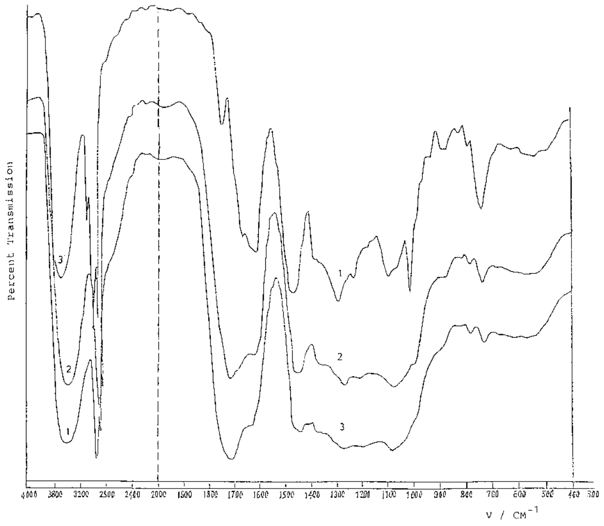


Fig. 3. IR spectra changes with time for Kurome urushi film. 1. 24 h elapsed film. 2. 3 months elapsed film. 3. 6 months elapsed film.

Also, for sample 3, the MW was calculated to be 1598 ($12.01 \times 84/0.634$); in this case, calculated Hn is H115 in order to agree with n 7.2% H.

The MW of the final Si(OUQ)$_4$ was calculated to be as follows: $C_{21}H_{36}O_6Ca_{1.5}K_1 + 3 \times C_{21}H_{36}OK + Si = 467.7 + 961.5 + 28 = 1457$.

The MW increase due to the added oxygen from sample 2 to sample 3, $(1598 - 1457 = 141)/1457$, is 9.6% with no solvent evaporation. This makes the dry urushi film very dense.

As Scheme 5A and the fourth line in the ref. 1 indicate, one atom of Si in one molecule of AP corresponds to $28/633.8 = 0.0441$ (4.41 wt%). Furthermore, because AP has been disclosed as the cyclotrisiloxane type, $n = 3$ (Fig. 4, X-ray diffraction pattern), the Si wt% in this one unit of urushiol should be $4.41/3 = 1.47$ wt%. However, since the actual content was 1.3 wt%, the MW = 633.8 should be amended to be $633.8 \times 1.47/1.30 = 716.68$. This difference between the MW values $(82.88)^{**}$ came from an increase in the metal peroxide content in the final urushi dry film; the total balance is both accurate and reasonable.

The difference of (last line of Table 2) $90.5^{xx} - 82.88^{**} \fallingdotseq 7$ is caused by the H- atom count of the ring and the sesquiterpene chain's Ca (1.5×2) + K $(1.0 \times 2) + 2 = 7$ at the C-1O and C-15 position's –OOH + M(OH)$_n$ (where M(OH)$_n$ means metals' hydroxyl) and dehydration and complex formation by hydrogen bond is appreciable.

The most important information concerning the three types of dried urushi film was obtained mostly by the analytical results for the CHN values given in Table 1. Even Yoshida's old value from 115 years ago is valid. Fig. 3 shows the IR spectral change at different time intervals after coating <u>KU</u> on a glass plate under the condition of RT and 80% RH.[9] Although initial drying film has small distinct absorption peaks at 870 and 802 cm^{-1} (corresponding to –O$_2$Ca, –O$_2$Si respectively),[10] they become very weak in the final drying film.

Among the urushiol components,[1] which have the terminal methyl group adjacent to the double bond, one of the three C–H bonds can easily insert an O$_2$ molecule from the air by the activation of an electron drawing with a neighboring double bond (Chart 1).

Table 1. Three Different Kinds of Urushi Dried Film

Sample formation	CHN analysis			Recurring unit's	
NO.	C	H	N	MW	(Note)
	Calcd for C_{84} H_{119} —				
1. KU dried film, $Si(O\underline{UQ})_4$.	66.3	7.9	0.3	1521	Diff. 36(1521-1548) = 2•H_20,
	Found				dehydration over a long time period
6 years old from Kurome,10AIO	67.9	7.7	0.3	1485	
(urushiol orthosilicate shown in Fig. 1A)					
2. Irregular dry mass from RU	Calcd for C_{84} H_{122} —				
	69.2	8.4	0.3	1457	minimum
(urushiol Si–O–complex shown in Fig. 1B)					
Yoshida's close data on p. 485	70.91	8.55	0.09		
	70.84	7.90	0.09		
3. Dry film of TR Compounded dope	63.1	7.2	0.4	1598	maximum
Yoshida's report close data on p. 483	63.44	7.41	4.01		(using an old N analyser of questionable accuracy)

Note: Yoshida's data were brought from Ref. 5 of this report (II). Given data by SCAS (Sumica Analysis Service) are one order less, such as C; 66.3 H; 7.9, which are practically sufficient.

Table 2. Material Balance of Metals and Their Peroxides Content in the Urushi Dried Film

Metals	mol or wt%	wt/g	Oxygen wt/g	Note
Ca	0.5	20.06	32	The oxygen wt. is
K	1.0	Already	16	calculated as follows:
(apart from Si)		counted		
	wt%			O/Si
Mg	3.2 × (39/28)	4.46	3.6	← 2 × 3.2 × 16/28
Na	1.9 × (23/28)	1.56	1.1	← 1.9 × 16/28
P	0.67	2.34	—	neglect
	choose Fe			
Fe,Ni,Cu	ca. 3 % × (55.8/28)	5.98	3.4	← 5.98 × 16/28
Total Sum	90.5** ⟵	34.40 +	56.1	

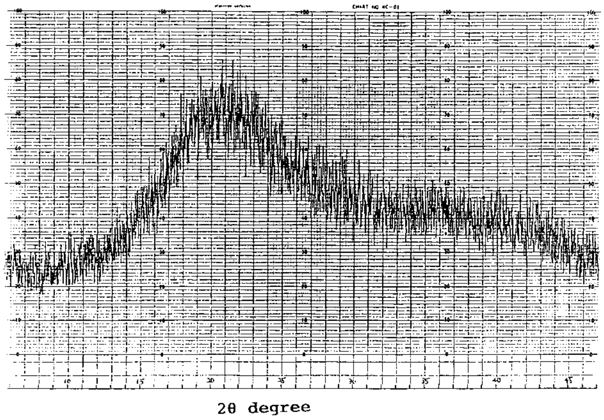


Fig. 4. X-ray diffraction pattern of acetone powder. X-ray test conditions. target Cu, filter monochrome. Volt 10 kV, curr. 15 mA, div.slit 1.00, time const. 0.2 s., rec slit 0.15, min, scan speed 2/min, full scale 400 cps.

Contrary to above, the absorption peaks due to hydrogen bonding (and complex formation) become larger and broader at 3410 cm^{-1} in Fig. 3.

Urushi film coated on a glass plate by the orthodox Kurome procedure adheres firmly, and can't be peeled off. If force is applied using a knife, the film breaks into flakes. Compared to this, sample 3 has a unique characteristic of peeling off as a flexible film, and can be used for special future applications. The reason for this different behavior is due to its different chemical composition. Namely, with this three ceramic bar rolls treatment (TR), a large shear force is applied; this condition (even at the room temperature) accelerates the formation of the hydroperoxide complex at C-10 or C-15 on the sesquiterpene side chain of urushiol with alkaline $Ca(OH)_2$ or KOH. These can cause a temporary crosslinking of this dope within several seconds compared with several hours in the case of the Kurome procedure; afterwards by keeping this dope at RT and 80% RH, it dries as a flexible film.

In Table 3, the author proposes a material balance calculation of metals and their hydroperoxy content in three types of dried urushi film (or flake) using the chemical structure of AP presented by him five years ago.[1] It can explain very well the actual phenomenon of three types of urushi polymerized film or flakes.

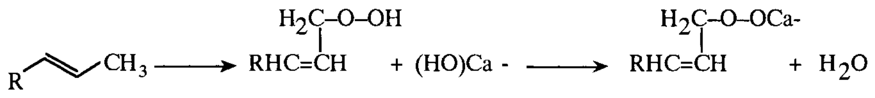
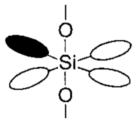


Chart 1.

Table 3. Material Balance Calculations of Metal Oxides and Their Hydroperoxy Content in Three Types of Urushi Dried Film

I) Metal oxides balances calculated from the analytical data.

MO_n	wt%	M wt%		Atoms counted as $Ca(OH)_2$ + KOH	Note
Silica	2.68	Si	1.25		Anal. data, see p.3131 of Ref. 1
Lime	44.36	Ca	24.6	0.615	$+0.709^{\#}$ $0.709/0.9^{*} = 0.787$
Magnesia	5.30	Mg	2.29	0.094	$0.787 \times 0.571^{**} = 0.45^{***}$ (0.9^{*} and 0.57^{**}, see below)
Potash	22.52	K	15.7	0.401	$+0.483^{\#\#}$ $0.483/0.45^{***} = 1.0$
Sodium-carbonate	3.30	Na	1.89	0.082	Namely, M^{+2}/M^{+1}, meets the same conc.
Phosphorous	2.11	P	0.667	0.021	penta oxide



These symbols are explained in Fig. 1 Caption.

II) For all samples' calculation (including sample 2).

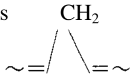
$C_{21}H_{36}O_5Ca_{1.5}$, K + 3 × $C_{21}H_{36}O_2$ + Si = 467.7 + 961.5 + 28 = 1457

(by Ca and K, showed the sum of alkali earth and alkali metals)

III) For sample 3 calculation effective UO analytical values obtained by Kumanotani of the present report Ref. 1 were applied.

Total sum (wt%) of octahed-O–Si–complex, which has group is as follows;

15.0+1.5+4.4+6.5+55.4+7.4 = 90.2 %*



Total sum (wt%) octahed–O–Si–complex, which has ∼=–Me terminal is counted,

1.7 + 55.4 = 57.1 %**

Total Calculation.

				Note
C	12.O1 × 84	= 1008.84		84 = 21 × (1 + 3)
H	1.008 × 144	= 145.15		144 = 36 × (1 + 3)
O	16 × 15	= 240.00		15 = (3 × 3) + (3 × 2)
Ca	1.5 × 40.08 × 0.9*	= 54.11		xxxx ****
K	1 × 39.19 × 0.57**	= 22.33		
		1470.43		
+ O	16 × 8	= 128	4 pairs of 2 hydroxy groups in urushiol group.	
		1598.43	Calculation meets just the same.	

0.615−0.094. ## 0.401−0.082.

Especially in the case of sample 3, the following mechanism can be given reasonably. Namely, in this octahed-O-Si-complex system, Ca and K atoms are brought with 1.5 and 2 atoms from one unit of AP. Because Ca is divalent and K is monovalent, only the former is capable of forming a bridge with this inorganic polymer, and the latter forms a temporary terminal KOH complex. The 2 × KOH stoichiometry (the counterpart –=–Me amount is just enough, 0.57 × 4 = 2.28) is replaced by –OCaOH and Chart 2.

The regenerated 2 moles of KOH can be utilized for other bridging, such as –SiOH or PhOH, as shown in Fig. 5.

$$R_1\text{-OK} + HOCaOR_2 \longrightarrow R_1\text{-OCaO-}R_2 + KOH$$

Chart 2.

Finally, among the three polymers presented by the author, sample 3 is the most interesting and fruitful. The three-dimensionally bridged polymer structure of sample 3 is proposed like that shown in Fig. 5, which is most favorably induced from its preparation and characteristics. The bases of this structure conclusion are shown in Schemes 1 to 3.

Summary and Conclusion

By a combined calculation basad on the analytical results for acetone, powder chemical structure and urushiols' composition results by Kumanotani, which were obtained by independent work, all phenomena comcerning urushi dope were clarified. It is lucky to successfully finish this work just at the

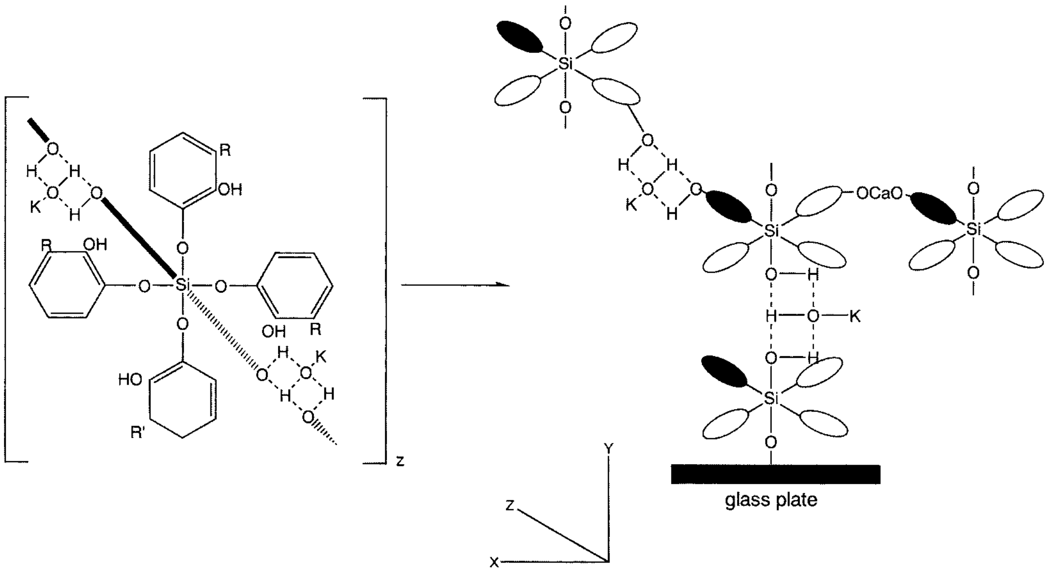
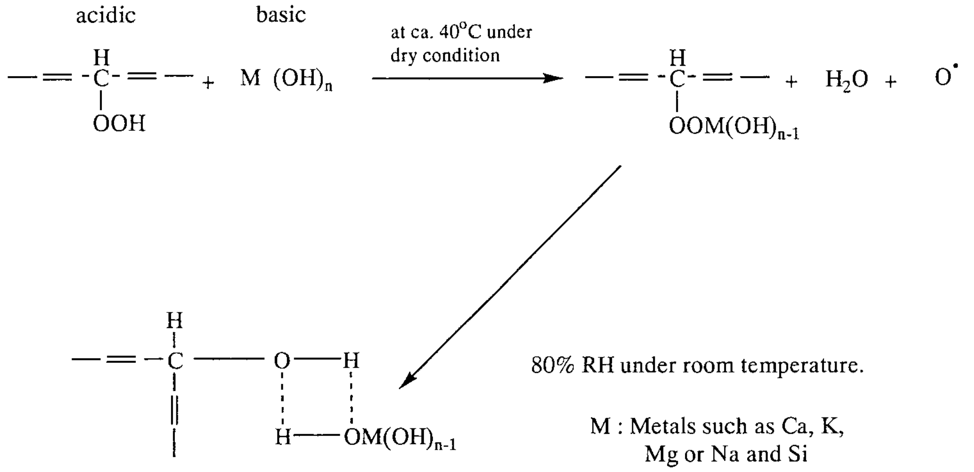
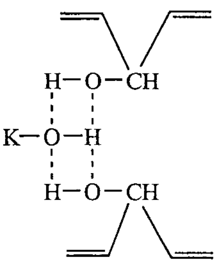


Fig. 5. Three axis directions (X, Y, Z) polymeried precise sketch of sample 3, in Fig. 1C. Z means polymerization number along to Z axis. Left Fig. One unit of urushiol Si–O–complex. R' shows R minus H. Right Fig. Several units of urushiol Si–O–complex.



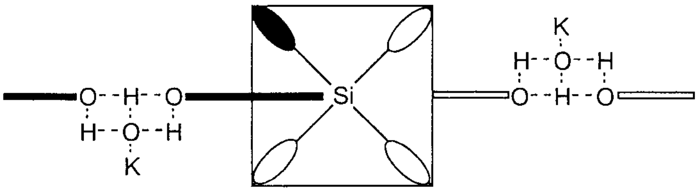
Scheme 1.

Two complexes above mentioned can form a transition state complex with KOH like the following which is substituted further by $Ca(OH)_2$



From Scheme 1 in ref. 1, urushiols which can cause 1 mole -OOH are sumed up,
15.0 + 1.5 + 1.7 = 18.2 wt%, and
2 moles -OOH are
4.4 + 6.5 + 7.4 = 18.3 wt%
both values are equal. As UO MW's are almost same, wt% are proportional to their molecule numbers.

Scheme 2.



It is difficult to understand completely the new type of dried film (sample 3) at this moment, especially the bridging of plain oxidized group with KOH. However, the author proposes the above showing scheme as the most probable. Because, $Ca(OH)_2$ is stronger alkaline reagent than KOH, so KOH is liberated which again may be possible to bridge with two -SiOH groups by one KOH, and can afford the final stable octahed -O-Si- complex.

Scheme 3.

end of the 20th century after being started by Yoshida and Diverse at Tokyo Imperial University 119 years ago.

The author would like to acknowledge H. Oyabu, Kyoto Munucipal Institute of Industrial Research, for making available a TR compounding urushi flexible film, sample 3; K. Toyoshima, former head of SUMIKA CHEMICHAL ANALYSIS SERVICE in Osaka, for supplying preserved urushi KU film to the author; and to Willis T. Schwartz, Occidental Chemical Cooperation Technology Center in USA, an important suggestion concerning the siloxane chemistry and his assistance in preparing this report.

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