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Chemical Modification of Lacquer Tree Paint Using Primary Amines

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An investigation was undertaken on a chemical modification of urushi paint using a small amount of primary amines as additives by taking advantage of their reactivity with urushiol, one of the main components of urushi liquid, at room temperature. The first modification method is related to an accelerated curing reaction of urushi paint, as a result of an enhanced formation of reversed micelles of urushiol. With this method, a large reduction in the curing time and curing at low humidity were achieved, and the light resistance of the cured film was also improved, as evaluated by an accelerated exposure test. The second modification method is based on the functionality of a compound linked to urushiol. Primary amine, having a water-repellent property, was synthesized, added to urushi liquid, and then cured. The resulting film demonstrated a good water-repellent property, and maintained this property even against degradation under accelerated exposure. These primary amines as additives undergo neither bleeding nor elution from urushi film, because they combine with urushiol. In addition, because these methods are based on a homogeneous mixing of additives and urushi liquid, they have advantages that neither large-scale plants nor equipment investment is required for their production.

Urushi liquid, a sap of the lacquer tree named "Rhus vernicifera," contains the enzyme laccase. Generally, this enzyme becomes active at 20 to 30 °C and 70 to 80% RH, and initiates an oxidation-reduction reaction. After this reaction, the polymerization of urushiol, one of the main components of urushi liquid, begins and urushi liquid turns a film.[1]

Under the conditions mentioned above, molecules of urushiol are presumed to be present in the form of reversed micelles. The reversed micelles undergo curing to form a film while developing to a reversed micelle-like cluster, and then to a particle structure, as previously reported.[2,3] Therefore, additives on the enzyme reaction and the reversed micelle structure would have a great influence on the properties of paint film. A urushiol particle model based on the reversed micelle structure is shown in Fig. 1.

The lacquer tree paint film is known to be inferior to light-resistance, and to become thin in proportion to the extent of degradation, which is a phenomenon involving the peeling off of fine particles from the surface of film.[1,4] Therefore, as the remaining degree of film increases, the light-resistance is improved.

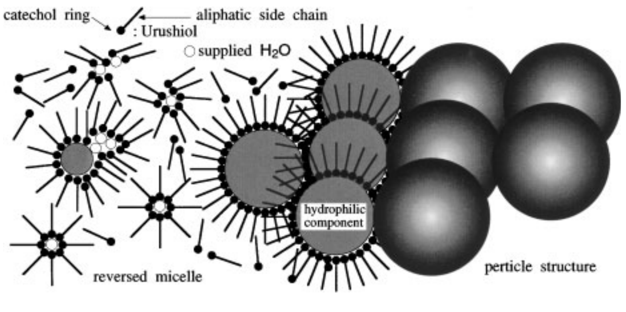


Fig. 1. Particle model of lacquer tree paint film (reversed micelle structure).

We proposed a curing reaction mechanism based on the reversed micelle structure of urushiol, and gave some evidence.[2] Furthermore, experiments on the method of easily proving the curing situation and the degradation state were carried out,[3] and evaluations of the structure of the reagents and their reactions with urushiol were studied.[5] Good reactivity of the primary amines towards urushiol and their potential applications were found.[6] In this study, two modification methods based on this information were demonstrated and the characteristics of the resulting urushi films were evaluated.

Results and Discussion

Urushiol has weak acidity because of catechol derivatives. Since amine is a weak base and has a hydrophilic amino group, a high reactivity of amine with the aromatic diol moiety of urushiol can be expected. Such characteristics have been observed in our attempted experiments.[5,6] Protein molecules having primary amino groups are known to react with urushiol to chemically bind at room temperature.[7–12] This reactivity has also been confirmed in our experiments. The results are given in Table 1. Ionization in our measurements was by the ESI method.

Improvement of Light Resistance and Curing Reaction on Lacquer Tree Paint by Primary Amines. Primary amines would accelerate the formation of reversed micelles through their reaction with urushiol. In this study, the effect of additives was examined using three kinds of amines having more than two primary amino groups in their structures, namely as diamines, dendrimer and polyethylenimine, as shown in Fig. 2 and in Scheme 1.

Films formed without and with additives were compared with respect to the curing time and the color change. The curing

Table 1. Results of Reactivity Experiments (Mass Spectrometry)

	Negative ion	Positive ion	
	Original compound	Original compound	Confirmed reactant
Urushiol: U-ol	313.5 (+H: molecular ion of principal component), 331.4	—	—
C6-DAm	—	117.1 (+H: molecular ion)	—
C12-DAm	—	201.3 (+H: molecular ion)	—
U-ol + C6-DAm	—	—	427.4 (mono-DAm-molecule reactant), 445.4, 457.4 739.5 (di-DAm-molecules reactant), 757.4, 767.4, 769.5
U-ol + C12-DAm	—	—	511.5 (mono-DAm-molecule reactant), 523.5, 541.5 823.6 (di-DAm-molecules reactant), 837.7, 855.7

C*n*-DAm stands for $H_2N–(CH_2)_n–NH_2$.

Table 2. Influence of Additives on Lacquer Tree Paint Film

Additive	Curing time /h	Discoloration					Hardness (pencil) after 2 weeks/a.u.
			ΔE	L*	a*	b*	
No addition (only lacquer tree paint film)	9.3	standard	10.45	26.22	15.94	6.63	3H
C2-DAm	8.8	deep	1.86	23.49	9.09	1.93	4H
C4-DAm	6.8	deep	2.43	21.34	5.78	0.41	3-4H
C8-DAm	7.3	deep	3.19	21.53	4.94	0.12	3-4H
C10-DAm	5.4	deep	2.64	21.85	5.40	0.29	3H
C12-DAm	8.6	deep	4.20	19.67	4.88	−0.08	3H
DAB-Am-4	8.3	deep	2.16	27.78	4.49	1.19	3-4H
DAB-Am-4 (Curing condition: 95% RH −20 °C)	1.5	deep	3.80	27.32	3.02	0.55	—
DAB-Am-4 (Curing condition: 85% RH −20 °C)	2.0	deep	1.43	27.95	7.94	2.19	—
DAB-Am-4 (Curing condition: 65% RH −20 °C)	9.6	deep	1.02	27.78	7.53	2.12	—
DAB-Am-4 (Curing condition: 55% RH −20 °C)	12.7	deep	3.53	28.46	9.80	3.08	—
No addition (only lacquer tree paint film)	5.5	standard	4.31	28.58	5.56	1.19	3-4H
Polyethylenimine (MW 600)	96 over	—	—	—	—	—	—
Polyethylenimine (MW 1800)	10.0	deep	1.69	27.51	0.06	−0.89	3H
Polyethylenimine (MW 10000)	6.9	deep	1.04	28.10	0.64	−0.82	3-4H
Polyethylenimine (MW 75000)	2.5	deep	1.65	28.05	0.04	−0.98	3-4H

C*n*-DAm stands for $H_2N–(CH_2)_n–NH_2$, DAB-Am-4: dendrimer.

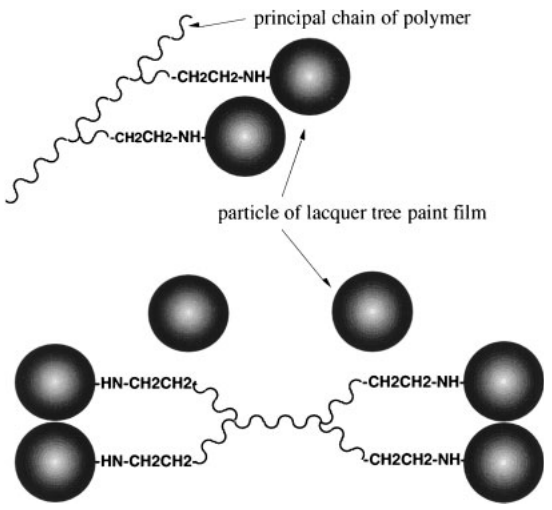
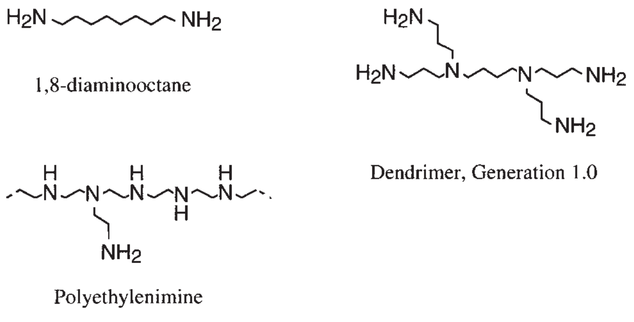


Fig. 2. Aggregation model of lacquer tree paint film by primary amines.



Scheme 1. Molecular structure of primary amines.

reaction was conducted using dendrimer, DAB-Am-4, under different conditions of humidity. The results are shown in Table 2. When the curing time becomes longer and the color of film becomes lighter, compared with those of systems without an additive, the curing reaction is considered to be inhibited.[3]

The primary amines with low molecular weight, such as diamines and dendrimer, had a tendency to shorten the curing time

Table 3. Change of Hardness of Lacquer Tree Paint Film Containing Additives

Additive	Hardness (pencil)/a.u.						
	after 3 days	7 days	14 days	21 days	30 days	60 days	90 days
No addition (only lacquer tree paint film)	HB	H	3H	4H	4H	5H	6-7H
C2-DAm	—	3H	4H	4-5H	5H	5-6H	7H
C4-DAm	—	3H	3-4H	5H	5H	6H	6-7H
C8-DAm	—	3H	3-4H	4H	4H	5-6H	6-7H
C10-DAm	—	3H	3H	4H	4-5H	6H	6-7H
C12-DAm	—	3H	3H	4H	4H	5-6H	7H
DAB-Am-4	F	H	3H	4H	5H	5-6H	7H
No addition (only lacquer tree paint film)	H-2H	3H	3-4H	3-4H	3-4H	5H	5H
Polyethyleneimine (MW 600)	—	—	—	—	—	—	—
Polyethyleneimine (MW 1800)	F-H	H	3H	3H	3-4H	4-5H	5H
Polyethyleneimine (MW 10000)	H	3H	3-4H	3-4H	3-4H	4-5H	5H
Polyethyleneimine (MW 75000)	H	3H	3-4H	3-4H	3-4H	4-5H	5H

Cn-DAm stands for $H_2N–(CH_2)_n–NH_2$, DAB-Am-4: dendrimer.

in all cases, and cured the urushi liquid at low humidity, though the enzyme is usually inactive. In addition, the color of film became deeper in all cases. On the other hand, for a system using polyethylenimine as the additive, there was a tendency of the curing time to become longer with a decrease in the molecular weight, though the color of the film turned deeper.

Furthermore, the hardness change of cured films formed with additives was examined. The results are given in Table 3. The measurement of the hardness provides not only an estimation of the film property, but also some information about the inhibition against the curing reaction indirectly.[13]

From the hardness change of films after the same curing time, the hardness at early stages was found to show slightly higher values for those films with additives, except for the system using polyethylenimine, than that for the films without additives. There seems to be no significant difference of the hardness in all of the paint films at later stages. On the other hand, the hardness of the film obtained using polyethylenimine is nearly equal to that of the film without an additive. These phenomena could be interpreted as follows. For those systems using primary amines with low molecular weight, such as diamines and dendrimers, the molecules of urushiol can become close to each other and make reversed micelle formation easier. Therefore, the curing reaction is accelerated, resulting in a reduction at the curing time and the progress of the curing reaction at low humidity. A deep color indicates an accelerated reaction, and a film with high hardness results from to fine particle structure in the film.

Polyethylenimine has a reactivity with urushiol because the color turns deeper. However, it is ineffective for the formation of reversed micelles, and appears to inhibit to form them. In the case of polyethylenimine, the curing reaction becomes less inhibited as the molecular weight increases. This could be because the molecular size does not fit the size of the reversed micelles, and that the high molecular weight polyethylenimine might be unable to penetrate into the reversed micelles. When lower molecular weight polyethylenimine was used as the additive, no curing reaction occurred, and the film hardness was low. On the other hand, films obtained with higher molecular weight polyethylenimine showed properties comparable to those for films without an additive. These results would be compatible with the above considerations.

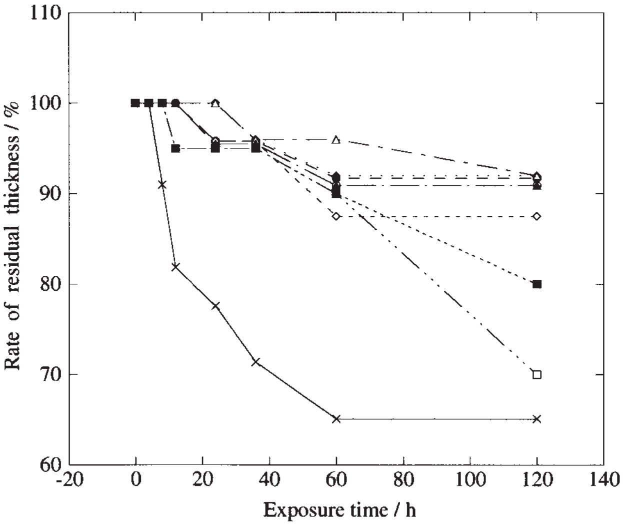


Fig. 3. Extent of residual films for the lacquer tree paint films with additives as a function of exposure time.
×: No addition, ○: 1,2-diaminoethane, ●: 1,4-diaminobutane, ◇: 1,8-diaminooctane, ◆: 1,10-diaminodecane, △: 1,12-diaminododecane, ▲: dendrimer, generation 1.0/ N,N,N',N'-tetrakis(3-aminopropyl)-1,4-butanediamine, □: polyethylenimine (average molecular weight = 1800), ■: polyethylenimine (average molecular weight = 75000).

Figure 3 shows the results of the residual proportion of film cured with additives under the conditions of accelerated exposure.

At the initial stage of exposure, for all films with additives, the residual proportions were larger than those for films without additives. Diamine- and dendrimer-added films also showed higher residual proportions with the progress of exposure, though the residual proportion became lower for some films with polyethylenimine. Thus, an excellent improvement in the light-resistance was achieved using small amounts of primary amines as additives.

When the curing reaction proceeds through the formation of reversed micelles, even for films formed with additives, the degradation should follow the normal mechanism, in which the

Table 4. Comparison of Characteristics

Kind of films	Curing time/h	Discoloration	Gloss (60°)/a.u.	Contact angle/°	Hardness (pencil) after 2 months/a.u.
No addition	7.9	standerd	56.1	83.3	5H
CF-OH added	9.5	same	56.8	85.3	—
CF-NH_2 added	14.6 (53.7)	light–same	79.5	107.6	3-4H
TEFLON AF	—	—	—	115.9	—

CF-OH: 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluoro-1-nonanol. CF-NH_2: 10-(4-Aminobutoxyl-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluorodecane. ( ): State of remaining dent-line by steel needle drawing.

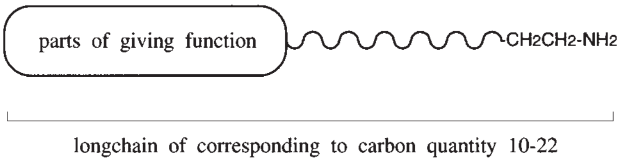
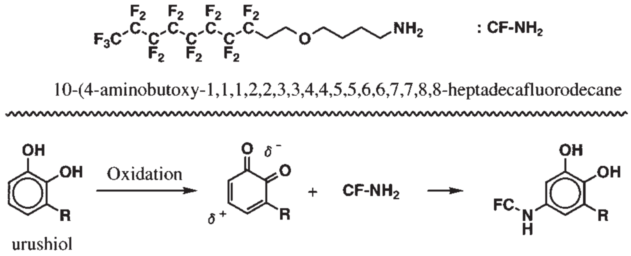


Fig. 4. Molecular design for chemical modification.



Scheme 2. Reaction mechanism of urushiol with amine fluoride.

particles peel off from the film surfaces. In the case of the films in this experiments, if the additives accelerate the formation of reversed micelles of urushiol, the formation of the particles should also be accelerated, resulting in an increased formation of particles with smaller size. Thus, the particles become smaller and strongly entangle with each other, and hence the residual proportion of films could be enhanced. Such an effect was observed for films formed with diamines and with dendrimer.

On the other hand, in the case of some films formed with polyethyeneimine, the residual proportion of film was high at the initial stage of exposure, but became low at the final stage. This is probably because the particles linked by the polyethylenimine chain peel off from the film. The film thickness can be kept at the initial stage of exposure because particles are linked by the polyethylenimine chain. However, particles, which are not linked by the polyethylenimine, peel off at the final stage because of a weak interparticle interaction. In addition, low molecular weight polyethylenimine inhibited the curing reaction, which made the film very fragile.

From these results, it can be concluded that primary amines, such as diamines and dendrimer, had large effects on the acceleration of curing reaction and the improvement of light-resistance of the urushi film.

Water Repellent Modification of Lacquer Tree Paint by Primary Amines. The second method concerns a surface modification of urushi paint by connecting functional primary amine with urushiol. The functional compound should have a long hydrocarbon chain with a primary amino group at the end, and be active enough to react with urushiol.[5] The compound having a carbon number of 10 to 20 is suitable for being incorporated into reversed micelles. Moreover, it must not interfere the enzyme reaction of laccase by a steric hindrance.[6] The molecular design of primary amine based on these considerations is shown in Fig. 4.

A water-repellent property was selected as a function in this study. Fluoroalkylamine was synthesized and added to urushi liquid. A commercial fluoroalkyl alcohol with an analogous structure was used in a control experiment and treated in the same way. First of all, the films formed with each additive were compared with those without an additive with respect to the curing time, color change, gloss, contact angle and pencil hardness. The results are given in Table 4. The reaction mechanism of urushiol and fluoroalkylamine is shown in Scheme 2, and water drops on the urushi films formed with fluoroalkylamine and without additive are depicted in Fig. 5.

A longer curing time, compared with that for film without an additive, indicates that the curing reaction is inhibited.[3] Furthermore, when the color becomes lighter and the gloss becomes higher, the reaction is also considered to be inihibited.[3] From these points of view, there is a tendency of the fluoroalkylamine to inhibit the curing reaction. The molecular structure well satisfies with requirements from our molecular design, and hence the existence of fluorine atoms in the additive could be responsible for the inhibition. In other words, the amino group of fluoroalkylamine normally functions as the primary amine, but a long fluoroalkyl chain could be incompatible with the long alkyl chain of urushiol, resulting in an inhibition of reversed micelle formation. Moreover, a decrease in the humidity, indispensable for the curing reaction, may take place on account of the orientation of fluoroalkyl chains at the surface of urushi paint during the reaction. The reactivity of the amino group of fluoroalkylamine is not inhibited. This can be understood from a comparison with the case of using flluoroalkyl alcohol with an analog structure as the additive. Fluoroalkyl alcohol is not compatible with urushi liquid, probably because of the higher proportion of fluorine atoms in the molecule. Therefore, it seems to be difficult to dissolve into urushi liquid and to be incorporated into reversed micelles. Furthermore, fluoroalkyl alcohol is not able to link to urushiol on account of no reactivity of the hydroxy group. Consequently, the curing reaction would be similar to that with a non-reactive additive. On the contrary, fluoroalkylamine well dissolved in urushi liquid, and was smoothly incorporated into reversed micelles in spite of the presence of a fluoroalkyl chain. The formation of reversed micelles appeared to be somewhat inhibited, probably because of the presence of fluorine

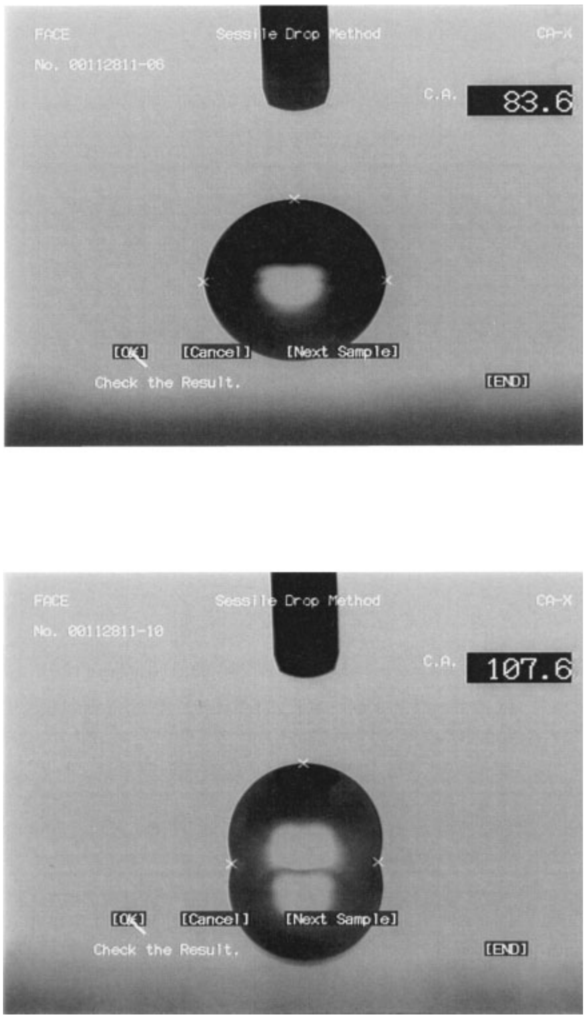


Fig. 5. Water globe on the lacquer tree paint films with amine fluoride additive (lower photograph) and no addition (upper photograph).

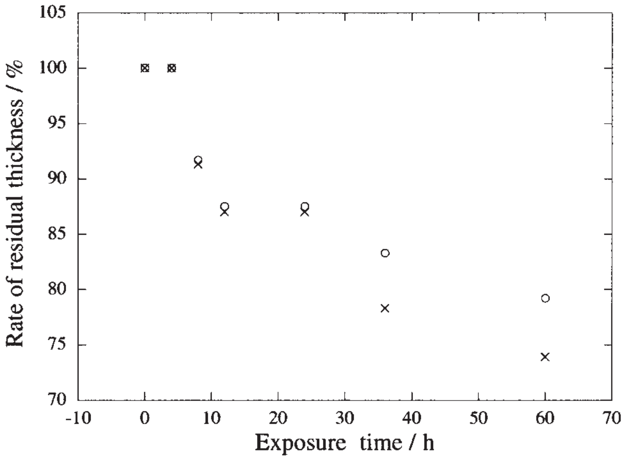


Fig. 6. Extent of residual films for the lacquer tree paint films with amine fluoride additive as a function of exposure time. Additive ×: no addition, ○: amine fluoride.

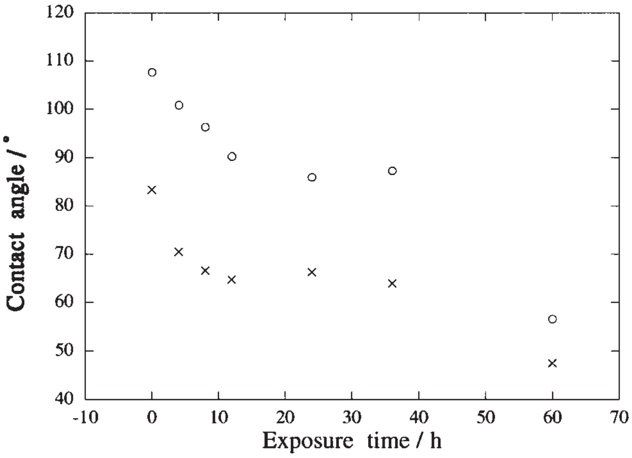


Fig. 7. Contact angle of lacquer tree paint film as a function of exposure time. Additive ×: no addition, ○: amine fluoride.

atoms in the additive. The film exhibited the contact angle of water expected from the orientation of fluoroalkyl chains at the reversed micelles. The results evaluated by an accelerated exposure test support this interpretation, as mentioned later. Urushi film cures in the presence of fluoroalkylamine, whereas the curing reaction does not proceed completely, resulting in a lower hardness of the films. Such a consideration is supported by the results given in Table 4.

Next, the results concerning the residual proportion and contact angle of urushi films obtained with fluoroalkylamine under accelerated exposure are shown in Figs. 6 and 7.

As the exposure progresses, the residual proportions of film with fluoroalkylamine become somewhat larger than that of film without an additive. However, the difference would not be considered to be very large. This means that there is not a large difference in the fine structure of the particles of urushiol and, furthermore, the interparticle interaction. Films formed with fluoroalkylamine always show high values by a certain value, compared with that of films without an additive, though the film thickness decreases. The exposure causes a decrease in the contact angle, which could be attributed to a change in the film roughness and a deterioration of the film surface. Such a change should occur for all paint films exposed. Films with fluoroalkylamine exhibit a high contact angle, even after exposure by a certain value, being due to the contribution of the fluoroalkyl chain. Thus, film surfaces keep a water-repellent property, even if fine particles peel off from the surfaces, and new particles appear at the surfaces. These results suggest that fluoroalkylamine molecules are incorporated not only at the film surfaces, but also in the particles.

From the results of the two experiments mentioned above, the methods using primary amines as the additives were found to be effective for the chemical modification of urushiol. These methods can be applied under mild conditions and no special apparatus is required. The methods make possible to control the curing reaction according to the conditions of urushi liquid, and to impart new properties to the film, which will permit the use of urushi in wide fields. The present methods could not be applied only to urushi, but are also applicable to analogues of urushiol and compounds bearing catechol, phenol and polyhydric phenol rings. The methods presented in this study have wide potential applications. In fields dealing with natural compounds as raw materials, the chemical modification of phenolic compounds would be a key technology for the utilization of natural materials.

Experimental

The urushi liquid (Rhus vernicifera) used in our experiment is a product of China, and nothing was added to the sap. For diamine- and dendrimer-added urushi liquids, the additives were well-dispersed, and then a water reduction treatment ("ROIRO" treatment) was made by stirring. The composition was 82.3% urushiol, 7.4% nitro-containing ingredients, 7.6% gum-like material and 2.7% water. For polyethylenimine-added urushi liquid, "KIURUSHI" without the above treatments was used. A water-reduction treatment of the urushi liquid was made after the addition of polyethylenimines.

The preparation of the film method was made by painting urushi liquid on a glass plate using an applicator, followed by curing at 75% RH at 20 °C in the temperature and humidity-regulated chamber, except for the cases where the effect of the humidity was examined. The cured paint films were kept in a dark and cool place.

The added amount of diamines or dendrimer was 0.01 molar amount to urushiol (the average molecular weight is 315.6) contained with 82.3% in urushi liquid.[2] Polyethylenimines have primary amino groups in their side group at random, which are reactive groups with urushiol. In the present study, polyethylenimines with different molecular weights were added to urushi liquid. The added amount of these polyethylenimines was 0.01 molar amount, based on the average molecular weight of 600, similarly to other additives.

Fluoroalkyl alcohol used as the additive is a commercial 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluoro-1-nonanol (Aldrich Chemical Co. Inc.). 10-(4-Aminobutoxyl-1,1,1,2,2,3,3,4,4,5,5,6,6,-7,7,8,8-heptadecafluorodecane used as fluoroalkylamine was synthesized in this study. The molecular structure was confirmed by IR, MS, NMR analysis.

10-(4-Aminobutoxyl-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluorodecane: IR 3334, 3290, 2941, 2861, 1365, 1322, 1242, 1207, 1149, 1068 cm^{-1}. MS (ESI) m/z 536 (+H ion), 518, 464. ^{1}H NMR (DMSO, $CDCl_3$) δ 1.46 (quintet, 2H, $J = 6.5$ Hz), 1.63 (quintet, 2H, $J = 8.00$ Hz), 2.28–2.55 (m, 4H), 2.97 (t, 2H, $J = 7.5$ Hz), 3.42 (t, 2H, $J = 6.5$ Hz), 3.91 (m, 2H).

The amount of additives was 0.01 molar amount to urushiol. Mixing was carried out using a blade until a good dispersion was obtained.

The curing time of the paint film was measured by a rotary curing time measuring apparatus set on the urushi liquid painted glass plate in a temperature and humidity-regulated chamber. In this measurement, a circle mark was drawn on the paint film using a steel needle, and the time when the mark disappeared was taken as the curing time. Other properties were measured by the following methods: The color difference was measured with a view of 10° using sun light (D65 light source), where normal reflected light was eliminated (SCE). The color-difference expression (CIE ΔE) was calculated by CIEL*a*b*. Gloss was taken as the average of the values obtained by measuring three times at a standard reflection angle of 60°. The measurement of the contact angle was carried using a water drop of 0.9 mL. The pencil hardness was determined using pencils of 9H, 8H, 7H, 6H, 5H, 4H, 3H, 2H, H, F, HB, B, 2B, 3B, 4B, 5B and 6B, according to the JIS K 5400-1990 testing method. Accelerated exposure test was carried out without a water shower at an emissive illumination of 60 W/m^2 in a chamber at 63 °C and 50% RH. The residual proportion of the film was determined by measuring the thickness of films as a function of the exposure time.

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