Studies on Phenolic Resins. IV. Physical and Chemical Properties of Coating Films of Japanese Lac (Urushi) (Rigidity Modulus-Temperature Relations Measured by Torsional Pendulum Method)

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Japanese lac (*urushi*) has been used as a natural coating material for more than two thousand years in Japan and China. It has been recognized that the coating film prepared from Japanese lac has many excellent properties and utility. The decorative coating film for artificial and wooden articles has a beautiful color tone and as the protective coating film, it is known by experience to have outstanding physical and chemical properties, compared with the films of the usual paints or varnishes. Traditional wooden crafts coated with *urushi* are very famous and used with appreciation all over the world, but our country imports a large quantity of raw Japanese lac from other Asian countries, because it produces only five per cent of the demand. Therefore, it has been hoped to make up industrial processes to synthesize some substance that can be used in place of natural Japanese lac, or some kind of compounding component or filler for it. There were two ways of attempting this aim.

One attempt was to synthesize the compouds chemically identical with the natural substance. The substance which is usually called Japanese lac is a sap of Rhus vernicifera D. C., produced in Japan and China. Chemical identification of urushiol, the principal component and polymerization unit of Japanese lac, was carried out by Majima(1) and Dawson(2) and the latter established that urushiol was composed of four

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(1) R. Majima, "Untersuchungen über den Japanlack", (1924).

(2) S. V. Sunthankar and C. R. Dawson, *J. Am. Chem. Soc.*, 76, 5070 (1954).

derivatives of catechol, substituted at 3-position with paraffinic, olefinic, diolefinic, and triolefinic straight chains of 15 carbons, and the average number of double bonds in the mixture were about two for one molecule. Some of these compounds were synthesized by Dawson[3] and Yukawa[4] but their processes cannot be applied to industrial production. Many chemically analogous compounds were synthesized in the past but they could not be used practically.

Another attempt was made in the industrial field for the purpose of obtaining substitutes or fillers for Japanese lac, and several kinds of coating materials, which formed a film apparently similar to that of Japanese lac, were prepared and commercialized as " synthetic Japanese lac ". But the interesting and important feature of Japanese lac, which must be taken into account, is that it contains an oxidation-reduction enzyme, laccase, and air-drying of Japanese lac proceeds through a characteristic oxidation-polymerization of urushiol with oxygen in the air, catalyzed with laccase[5]; also that the characteristic reaction is thought to be one of the factors that give good properties to the film. Though the molecular structure and reaction mechanism of laccase are not yet known, it was proved to act only on *ortho*- or *para*-polyhydroxy or polyamino aromatic compounds[5]. Therefore commercialized so-called " synthetic Japanese lacs ", which are oil varnishes, are not affected by laccase, and they degrade the mechanical properties of the film when used as fillers for Japanese lac.

In another paper the authors studied the preparative method of compounds capable of polymerizing at room temperature together with urushiol, affected with laccase equally to it, when added to natural Japanese lac as fillers[6].

Evaluation of those compounds should be carried out in respect of the physical and mechanical properties of the coating films formed from the mixtures of them and Japanese lac, as compared with the properties of Japanese lac film.

Although it is well known by experience that the coating films of Japanese lac have ideal physical and mechanical properties, scientific studies have been limited to the subjects of resistance to chemical reagents and electrical insulation, and no data were available about the mechanical properties.

In this paper the authors first studied, by means of the torsional pendulum method, the mechanical properties of coating films, prepared through various processes from Japanese lac. This method had been developed to study the visco-elastic behavior of polymers, and in spite of its being a simple operation, it presented useful data such as rigidity modulus and decrement of oscillation at any temperature, and glass transition temperature of the film.

As the results of the observation of the mechanical properties of the coating films which were the oxidation polymerization products of urushiol under the action of laccase or heat, it was revealed that the Japanese lac films had excellent, characteristic properties, never found in other kinds of coating films.

Then the authors determined the mechanical data of three coating film samples each prepared from the mixtures of 10 parts of Japanese lac and 6 parts of the synthetic compound. These three compounds were chosen from a series of catechol derivatives, which had been synthesized by the authors for the purpose of obtaining a good filler for Japanese lac. It was evidently approved by the properties of the film samples that those compounds were excellent fillers for Japanese lac and able to be used in place of urushiol.

Experimental by Torsional Pendulum Method

The torsional pendulum method developed by Inoue[7] to investigate the mechanical characteristics of polymer films is simple in operation, and gives reliable data. Torsional pendulum apparatus has as the main part an inertia bar attached at its center to the lower end of a pending sample film strip, and a mirror is set below the center. The period and the amplitudes of damping oscillation of the bar are measured by the lamp-and-scale system. Rigidity modulus (G) and logarithmic decrement (λ) are calculated from these data.

Procedure.—Torsional pendulum apparatus with sample film was set in a low temperature thermostat, slowly heated up to 40°C and kept at this temperature for 40 min. This duration was necessary for the internal structure of the sample to reach equilibrium at this temperature. Then the temperature was cotinuously dropped at the rate of 1°C/2 min. down to -60°C, while measuring the amplitudes and the period of $3\sim6$ oscillation cycles every 5 or 10°C. The temperature was slowly raised to room temperature, and the apparatus with sample was kept there overnight. Next day it was set in an electric heating thermostat, and the temperature was continuously raised at the rate of 1°C/2 min. to about 150°C and the measurement was carried out every 5 or 10°C.

The rigidity modulus (G) of the sample film was calculated from the period, and the logarithmic

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3) B. Love and C. R. Dawson, ibid., **78**, 4083 (1956).

4) T. Yukawa, Presented at the 13th Annual Meeting of Chem. Soc. Japan, Tokyo, April, 1960.

5) G. Bertrand, *Compt. rend.*, **124**, 1032, 1355 (1897).

6) T. Kuwata, J. Kumanotani and S. Kazama, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **64**, 1629 (1961).

7) Y. Inoue, ibid., **55**, 262 (1952).

decrement (λ) was calculated from the amplitude change.

G and λ were plotted against temperature, and the temperature where λ was maximum was glass transition temperature (T_g) of the sample film.

TABLE I. LIST OF SAMPLES

No.	Sample film
1	Air-dried film of kiurushi
2	Baked film of kiurushi
3	Air-dried film of sugurome urushi
4	Baked film of sugurome urushi
5	Air-dried film of sugurome urushi
6	Tested strip of sample No. 5, heated at 100°C for 2 hr. after measurement up to 110°C
7	Sample No. 5, kept in air for 25 days
8	Sample No. 1, kept in air for 30 months
9	Tested strip of sample No. 8, kept in air overnight after measurement up to 150°C
10	Sample No. 2, kept in air for 30 months
11	Sample No. 3, kept in air for 30 months
12	Tested strip of sample No. 11, kept in air overnight after measurement up to 150°C
13	Sample No. 5, kept in air for 30 months
14	Air-dried film of Thailand-sugurome urushi, kept in air for 30 months
15	Air-dried film of sugurome processed mixture of kiurushi and distilled urushiol (1 : 1 part) kept in air for 7 months
16	Air-dried film of sugurome-processed mixture of kiurushi (10 parts) and linseed oil (3 parts)
17	Air-dried film of sugurome-processed mixture of kiurushi (10 parts) and linseed oil (6 parts)
18	Sample No. 16, kept in air for 30 months
19	Air-dried film of sugurome-processed mixtre of kiurushi (10 parts), linseed oil (2 parts) and ester gum (1 part)
20	Baked film of sugurome-processed mixture of kiurushi (10 parts), linseed oil (2 parts) and ester gum (1 part)
21	Sample No. 20, kept in air for 30 months
22	Air-dried film of sugurome-processed mixture of kiurushi (10 parts) and catechol derivative A (6 parts)
23	Air-dried film of sugurome-processed mixture of kiurushi (10 parts) and catechol derivative B (6 parts)
24	Air-dried film of sugurome-processed mixture of kiurushi (10 parts) and catechol derivative C (6 parts)
25	Air-dried film of oil varnish of reactive *o*-cresol resin
26	Air-dried film of oil varnish of nonreactive *o*-cresol resin

The inertia bar used in the experiment was made of aluminum, the length being 20.64 cm., weight 34.01 g. moment of inertia 1210 g. cm^2. The periods measured were 3∼15 sec. It had been reported that in order to obtain reliable data the periods should lie in the range from 2 to 17 sec.[8]

Sample Films.—The sample films are listed in Table I. The meanings of several terms which are unique to Japanese lac are as follows.

Kiurushi (raw Japanese lac) ; this is the sap of the plant.

Sugurome process ; this is a unique process in the preparation of usual commercial coating material of Japanese lac in Japan. Raw Japanese lac, alone or with other substances, is stirred in a wooden vessel for a time, then heated at about 38°C for about 7 hr. under stirring. During the process dehydration and partial oxidation of the lac take place.

Sugurome urushi ; *sugurome-processed* Japanese lac. The raw Japanese lac of Samples Nos. 1—4, 8—12, 15—24, was taken from a lot produced in Moppo, China. The Samples Nos. 5, 6, 7, 13, were taken from another lot. Sample No. 14 was the film formed from Thailand lac, the main component of which is not urushiol but thithiol.

Sugurome-proscess in the preparation of Sample No. 5, was a little different from that of Sample No. 3, but details were not ascertained.

The torsional pendulum method required the sample film strip, of which the breadth b was about 1 cm. and the thickness h was more than 0.02 cm. because b/h ratio should be 10∼50 in order to obtain reliable data. But the thickness of the uniform film formed by one coating was 0.002∼0.004 cm. The authors prepared the sample coating films by coating the sample lacs on tin plates (25 cm. × 15 cm.), repeating the coating and drying to touch-free state five to ten times until the films formed became thick enough.

Air-drying was carried out in a wet atmosphere in order to activate laccase. In case of baking, every coat was heated by an infrared lamp (40∼60°C) to give a touch-free surface, and finally the film was heated at 100°C for 1 hr. in an electric drier.

The sample film thus formed on the tin plate was cut into strips, about 1 cm. broad, and these strips were torn off after amalgamation of the tin surface. The dimensions of the test strips we used were 13∼15 cm. in length and 30∼60 in b/h.

Samples Nos. 22—24 were the air-dried films of *sugurome-processed* mixtures of *kiurushi* (10 parts) and catechol derivatives (6 parts). Catechol derivative A was the ester of homoprotocatechuic acid and linseed oil alcohol ; B, mixed glyceride of protocatechuic acid and linseed oil fatty acid (1 : 2) ; C, allyl ester of addition product of catechol and linseed oil fatty acid.

Samples Nos. 25 and 26 were the films of varnishes of phenolic resins, observed in comparison with Japanese lac.

All sample films except those of which the duration of exposure to air are noted in Table I were examined within 10 days after preparation.

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[8] J. Furuichi, *J. Appl. Phys., Japan*, **27**, 720 (1958).

TABLE II. PHYSICAL PROPERTIES OF JAPANESE LAC COATING FILMS

Sample No.	T_g°C	G_g, dyn./cm^2	G_r, dyn./cm^2	G_h, dyn./cm^2	λ_{max}
1	70	1.1×10^9	5.2×10^9	4.8×10^8	0.33
2	85	2.2×10^9	7.1×10^9	1.4×10^9	0.19
3	30	7.3×10^8	1.2×10^9	2.4×10^8	0.31
4	45	1.3×10^9	2.7×10^9	3.9×10^8	0.22
5	45	2.4×10^9	5.0×10^9	5.6×10^8	0.21
6	58	4.1×10^9	7.9×10^9	1.3×10^9	0.21
7	63	1.9×10^9	5.8×10^9	6.6×10^8	0.23
8	100	2.1×10^9	7.7×10^9	1.1×10^9	0.27
9	115	2.5×10^9	7.7×10^9	1.3×10^9	0.18
10	130	2.5×10^9	9.7×10^9	1.8×10^9	0.18
11	83	7.9×10^8	5.4×10^9	2.5×10^8	0.49
12	93	1.2×10^9	7.2×10^9	3.5×10^8	0.30
13	95	2.2×10^9	6.8×10^9	7.4×10^8	0.23
14	77	8.4×10^8	3.5×10^9	1.8×10^8	0.29
15	90	2.0×10^9	6.0×10^9	7.9×10^8	0.21
16	10	2.0×10^9	1.4×10^9	3.9×10^8	0.20
17	−45	3.9×10^9	4.5×10^8	2.2×10^8	0.17
18	81	1.3×10^9	6.2×10^9	3.6×10^8	0.28
19	20	1.3×10^9	1.3×10^9	1.4×10^8	0.33
20	35	2.4×10^9	3.6×10^9	7.3×10^8	0.22
21	86	2.4×10^9	8.3×10^9	8.0×10^8	0.27
22	10	1.8×10^9	1.2×10^9	2.6×10^8	0.22
23	0	1.4×10^9	6.4×10^8	2.5×10^8	0.21
24	0	1.7×10^9	8.2×10^8	3.2×10^8	0.20
25	17	1.6×10^9	9.8×10^8	1.8×10^8	0.44
26	8	2.2×10^9	5.2×10^8	—	0.30

Results and Discussion

The results of the experiments are shown in Table II and Figs. 1—5. The following abbreviations are used: T, temperature in °C; G, rigidity modulus in dyn./cm^2; λ, logarithmic decrement; T_g, glass transition temperasure; G_g, rigidity modulus at glass transition temperature; G_r, rigidity modulus at 20°C; G_h, high temperature rigidity modulus or the minimum rigidity modulus above T_g; λ_{max}, the maximum logarithmic decrement shown at T_g. (T_g was defined as the temperature at which λ reached the maximum)

Characteristic *G-T* Relations of Coating Films of Japanese Lac.—All kinds of coating films formed from synthetic resins show glass transition phenomena. Not to mention the films of thermoplastic resins[9], those of cross-linked polymers, such as epoxy[10], alkyd[11] and phenolic resin varnish[12] change markedly in physical and mechanical properties as the temperature changes through T_g, over a relatively narrow temperature range. Below T_g they are in the glassy state, being rigid and a little brittle, and values of G are about 10^{10} dyn./cm^2. Above T_g they are in the rubbery state, being soft and flexible, and values of G range between 10^7 and 10^8 dyn./cm^2, so they lack in mechanical strength. The abrupt change in properties depending upon temperature is undesirable for practical use and, therefore, each kind of coating film can be used in a limited range of temperature.

But it is revealed by the authors' experiment that the coating films of Japanese lac were quite different from and superior to those from usual synthetic resins in their properties.

As shown in Fig. 1, in temperature range around T_g, temperature dependence of G of air-dried and baked films of *kiurushi* and *sugurome-urushi* was less than that of Samples Nos. 25 and 26, which were air-dried films of oil varnishes of *o*-cresol resins presented as examples of phenolic resin. G of Japanese lac films changed so mildly with temperature from lower to higher temperature ranges, as T_g could not be determined distinctly from *G-T* curve. T_g was determined from the λ-T relation and the λ-T curve, too, was smooth compared with that of the synthetic resin film.

At room temperature, three coating films, except the baked film of *kiurushi*, had ample flexibility in spite of their great rigidity modulus, compared with synthetic resin films.

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[9] Y. Inoue, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 1427 (1960).

[10] K. Ueki, ibid., **64**, 1425 (1961).

[11] L. W. Chen, unpublished.

[12] J. Kumanotani, unpublished.

Among them the air-dried film of *sugurome-urushi* was the most rigid but as flexible as samples Nos. 25 and 26, which were in the rubbery state and had smaller values of G_r. Values of G_h of Japanese lac films were, generally, larger than those of synthetic resin films, in which case it was reported that films with G_h greater than 10^8 dyn./cm² were insufficient in flexibility$^{13)}$. These data of mechanical properties of Japanese lac films showed that the films had an excellent tolerance to temperature change and good adaptability as protective coating films over a wide temperature range.

By G-T and λ-T relations, G_h and T_g, we are able to know the deformation behavior of a polymer substance when loaded by mechanical force, and assume the internal polymeric structure of the polymers. T_g increases with the increase of intermolecular forces caused by the polar group, and of the density of the cross-link of polymer molecules. This is because T_g shows the temperature at which thermal energy becomes sufficient to allow segments of polymers to move beyond energy barriers of environments. G_h increases with increase of density of cross-link, the deformation of polymer substance being restricted only by cross-links of molecules at the temperatures enough above T_g.

Japanese lac films are cross linked polymers formed by oxidation-polymerization of urushiol, activated with laccase or heat. The cross-linking points are catechol nucleus and double bonds of side chains of urushiol molecules. Therefore the films are considered to have some complicated three dimensional structure. In case of air-drying, the action of laccase contributes to the formation of this characteristic structure. The films are in transitional state, some parts being in the glassy state and the others in the rubbery state over a wide range of temperature and they do not show sharp glass transition. Also the rubber parts increase with the rise of temperature, G and λ changing smoothly.

The ideal combination of rigidity and flexibility of the films is also considered to be owing to the characteristic polymer structure of polymerized urushiol with rigid benzene ring and flexible long side chain.

The large values of G_h of Japanese lac films suggested high density of cross-link, but it must be noted that the density of cross-link at high temperature was higher than that at room temperature, because thermal cross-linking reaction took place during the measurement up to the temperature at which G_h was given. This fact was pointed out from comparison of T_g and G_h between Samples No. 8 and No. 9, and between No. 11 and No. 12. And it may be mentioned that the increase of G with temperature above the temperature at which G_h was given was due to both entropy elasticity effect and the increasing density of cross-link.

The above mentioned two characteristics in physical properties of Japanese lac films (1. They do not show sharp glass transition phenomenon. 2. They have ideally combined flexibility and rigidity.) are unique to them.

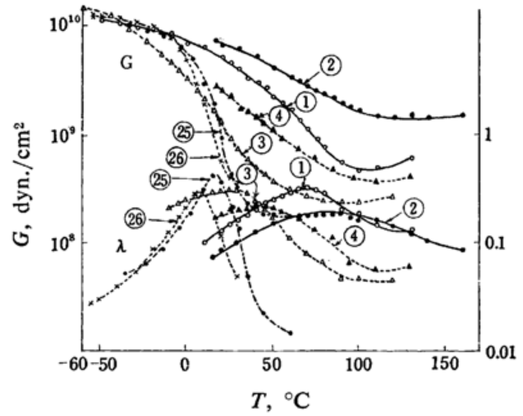

Fig. 1. Rigidity modulus-temperature relations.

① Air-dried film of kiurushi
② Baked film of kiurushi
③ Air-dried film of sugurome urushi
④ Baked film of sugurome urushi
㉕ Air-dried film of oil varnish of reactive *o*-cresol resin
㉖ Air-dried film of oil varnish of nonreactive *o*-cresol resin

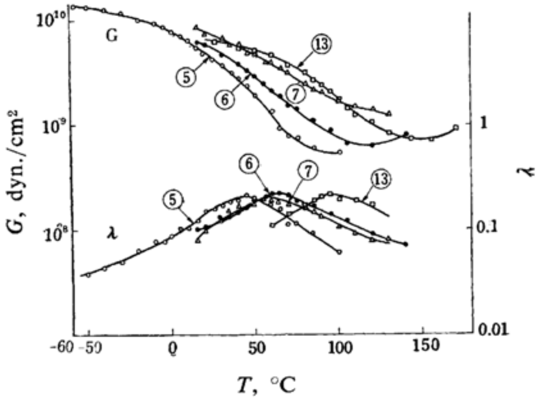

Fig. 2. Rigidity modulus-temperature relations.

⑤ Air-dried film of sugurome urushi
⑥ Tested strip of ⑤, heated at 100°C for 2 hr. after measurement
⑦ Sample ⑤, kept in air for 25 days
⑬ Sample ⑤, kept in air for 30 months

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13) Y. Inoue, "Kōgyōkagaku Zensho", Vol. 30, Nikkan Kogyo Shimbunsha, Tokyo (1960), p. 120.

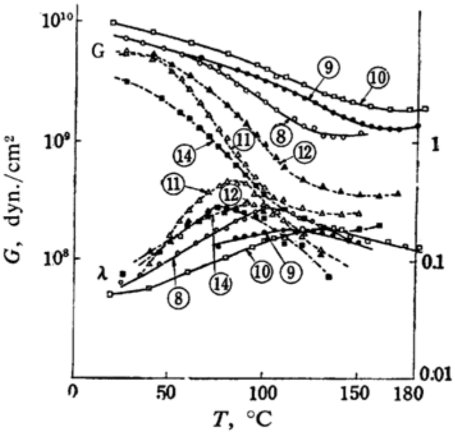

Fig. 3 Rigidity modulus-temperature relations.

- ⑧ Sample ①, kept in air for 30 months
- ⑨ Tested strip of ⑧, kept in air overnight after measurement
- ⑩ Sample ②, kept in air for 30 months
- ⑪ Sample ③, kept in air for 30 months
- ⑫ Tested strip of ⑪, kept in air overnight after measurement
- ⑭ Air-dried film of thailand-sugurome urushi, kept in air for 30 months

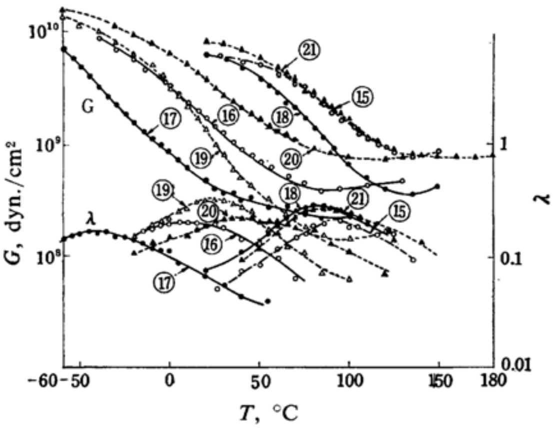

Fig. 4 Rigidity modulus-temperature relations.

- ⑮ Air-dried film of sugurome processed mixture of kiurushi and distilled urushiol (1 : 1 part), kept in air for 7 months
- ⑯ Air-dried film of sugurome processed mixture of kiurushi (10 parts) and linseed oil (3 parts)
- ⑰ Air-dried film of sugurome processed mixture of kiurushi (10 parts) and linseed oil (6 parts)
- ⑱ Sample ⑯, kept in air for 30 months
- ⑲ Air-dried film of sugurome processed mixture of kiurushi (10 parts), linseed oil (2 parts) and ester gum (1 part)
- ⑳ Baked film of sugurome processed mixture of kiurushi (10 parts), linseed oil (2 parts) and ester gum (1 part)
- ㉑ Sample ⑳, kept in air for 30 months

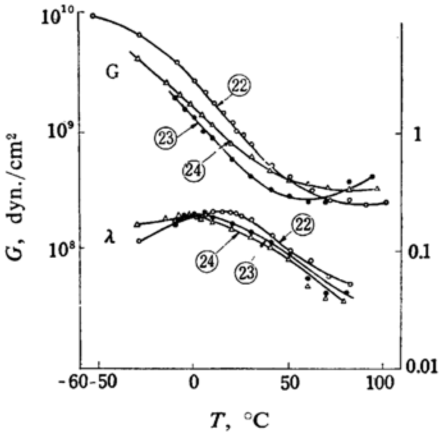

Fig. 5 Rigidity modulus-temperature relations.

- ㉒ Air-dried film of sugurome processed mixture of kiurushi (10 parts) and catechol derivative A (6 parts)
- ㉓ Air-dried film of sugurome processed mixture of kiurushi (10 parts) and catechol derivative B (6 parts)
- ㉔ Air-dried film of sugurome processed mixture of kiurushi (10 parts) and catechol derivative C (6 parts)

The films from synthetic Japanese lac may be necessary to be characterized by these points in order to exceed films from other synthetic resins. These characteristics were retained in Samples Nos. 5—21, which are used in practice as Japanese lac films.

Effect of *Sugurome-process* on Physical and Chemical Properties of Coating Films.— Coating films from *sugurome-urushi* (Samples Nos. 3, 4, 5, 11, 13) were more flexible and had lower values of T_g, G_r and G_h than films from *kiurushi* (Samples Nos. 1, 2, 8 and 10). The differences in those physical properties were remarkable between them either in case of air-dried films (between No. 1 and No. 3) or baked (between No. 2 and No. 4), or after they were kept in air for 30 months (between No. 8 and No. 11). T_g of baked film from *kiurushi* was valued at 85°C and it lacked in flexibility at room temperature. The cause of the difference is not clear but it may be due to the characteristic unit of polymerization induced by laccase-oxygen (air)-polymerization. Further investigation is needed about the chemical change during the *sugurome-process*. But this traditinal process proved to be very advantageous in preparing qualified coating material of Japanese lac to form air-dried film with a large value of G_r and ample flexibility (Sample No. 3).

Sample No. 5 was also air-dried film of *sugurome-urushi*, but it differed from Sample

No. 3 in physical properties, because the lot of *kiurushi* and conditions of *sugurome-process* and drying process were respective for each. The properties of Sample No. 5 lay between those of Sample No. 1 (from *kiurushi*) and No. 3, and this relationship was retained after time elapsed (Samples Nos. 8, 11 and 13). The quality of Japanese lac may be modified to various extents by changing the condition of the *sugurome-process*.

Effect of Fillers.—Linseed oil is used today commonly as a filler for Japanese lac. A mixture of *kiurushi* and linseed oil is *sugurome-processed* and commercialized. Sample No. 16 which was air-dried film of *sugurome-processed* mixture of *kiurushi* (10 parts) and linseed oil (3 parts), had a lower value of T_g, about the same value of G_r and a higher value of G_h than Sample No. 3 (from *sugurome-urushi*). No considerable difference was found between *G-T* curves of the two (Figs. 1 and 4), and they were almost identical in mechanical properties. The decrease of T_g was due to the decrease of intermolecular force caused by the addition of the drying oil, and the increase of G_h was due to the increase of cross-link density induced by the reaction of the double bonds.

But in the case of Sample No. 17 (*kiurushi* 10 parts, linseed oil 6 parts), T_g was much depressed to -45°C and values of G_r and G_h also depressed. At high temperatures the oil oozed out of the film. The small values of λ_{max} of these samples were due to their plasticity. Those facts indicate that if a large amount of linseed oil is added to Japanese lac, its plasticizing effect deteriorates the physical properties of the film.

Sugurome-processed mixture of *kiurushi*, linseed oil and ester gum is called "*shuai-urushi*" and is of general use. Owing to the polar group and polycondensed ring of ester gum, the T_g of air-dried film of *shuai-urushi* (sample No. 19) was rather high but the small value of G_h indicated the small density of cross-link. In baked film (Sample No. 20) values of G_r and G_h were greater than those of baked film from *sugurome-urushi*.

Sample No. 15 was air-dried film from *sugurome processed* mixture of 10 parts of *kiurushi* and 10 parts of urushiol isolated by molecular distillation of alcohol extract from kiurushi, and kept in air for 7 months. The content of laccase of the mixture equalled a half of that of No. 3 (*sugurome-urushi*). The film had a strong esthetic appeal and excellent flexibility, and what is more, values of T_g, G_r and G_h were higher than those of Sample No. 11 (Sample No. 3, kept in air for 30 months). Contrary to the case of linseed oil, laccase acted on urushiol very effectively, and it is concluded that if any compound similar to urushiol is obtained, a great amount can be added to Japanese lac.

The principal component of Thailand lac is not urushiol but thithiol, a mixture of 4-heptadecenylcatechols with 1.5~2 double bonds in average. It contains laccase but the content is less than in Japanese lac, and 4-substituted catechol seems to be inferior to 3-substituted catechol in chemical reactivity. Therefore its film formation takes a long time and it is used as a filler for Japanese lac. Sample No. 14 was air-dried film of *sugurome-processed* Thailand lac, kept in air for 30 months. The film was bad in its physical properties and color. Compared with No. 11 (*sugurome-urushi* of Japanese lac), values of T_g, G_r and G_h were lower, showing low density of cross-link.

Effect of Heat and Exposure to Air.—There are two ways of drying, namely, air-drying and baking. In most cases *sugurome-urushi* is air-dried on articles. Samples Nos. 2, 4 and 20 were baked films of *kiurushi*, *sugurome-urushi* and *shuai-urushi* respectively. Compared with Samples Nos. 1, 3 and 19 (air-dried films), baked films had higher values of T_g, G_r and G_h, lower value of λ_{max} and were less flexible and less glossy than the corresponding air-dried films. These differences in properties between them were also found in the case of No. 8 and No. 10 (after 30 months). The reaction mechanism in film formation is considered to be respective for each drying process.

Samples Nos. 1, 2, 3, 5, 16 and 20 were kept in air for 30 months to investigate changes in physical and chemical properties with time. They were Samples Nos. 8, 10, 11, 13, 18 and 21 respectively. As shown in Table II, changes of values of T_g and G_r for each were as follows:

Sample	T_g,°C	$G_r \times 10^{-9}$, dyn./cm^2
Air-dried film of kiurushi	70→100	5.2→7.7
Baked film of kiurushi	85→130	7.1→9.7
Air-dried film of sugurome-urushi (No. 3)	30→ 83	1.2→5.4
Air-dried film of sugurome-urushi (No. 5)	45→ 95	5.0→6.8
Air-dried film of sugurome-processed mixture of kiurushi (10 parts) and linseed oil (3 parts)	10→ 81	1.4→6.2
Air-dried film of shuai-urushi	35→ 86	3.6→8.3

But concerning the values of G_h of these samples, they were almost unchanged except in the case of air-dried film of *kiurushi* whose G_h changed from 4.8×10^8 to 1.1×10^9 dyn./cm^2.

These facts indicated that the films were oxidized in air, polar groups being formed in polymer molecules. On account of the increase of intermolecular forces caused by the polar groups, the films became rigid at room temperature and values of T_g rose. However, cross-liking did not take place during the exposure except in air-dried film of *kiurushi*. This phenomenon may be associated with the effect of heating or sugurome-process when the film was formed.

Even in the films kept in air for 30 months, thermal cross-linking occurred during the measurement up to 150°C, and as shown in Fig, 3, values of T_g, G_r and G_h increaed. (No. 8→No.9, No. 11→No. 12)

Evaluation of Synthetic Catechol Derivatives as Fillers.—As reported in another paper[6], the authors synthesized a series of catechol derivatives for the purpose of obtaining good fillers for Japanese lac. From them the next three compounds were chosen;

A. Ester of homoprotocatechuic acid and linseed oil alcohol
B. Glyceride prepared from 1 mol. of protocatechuic acid, 2 mol. of linseed oil fatty acid and 1 mol. of glycerine.
C. Allyl ester of addition product of catechol and linseed oil fatty acid.

Mixtures of 10 parts of *kiurushi* and 6 parts of catechol derivatives were *sugurome-processed*, and air-dried films shown in Table I were formed, namely, Samples Nos. 22, 23 and 24 respectively. Velocity of the drying was not slow.

Physical data of these samples mesured by the torsional pendulum method are given in Table II and Fig. 5.

Values of T_g of these samples ranged from 0~10°C, closing that of Sample No. 16 (*kiurushi* 10 parts and linseed oil 3 parts) and far above that of No. 17 (*kiurushi* 10 parts and linseed oil 6 parts, T_g; -45°C). Therefore it was evidently approved that these catechol derivatives were much more advantageous than linseed oil as fillers for Japanese lac. Especially the $G-T$ curve of Sample No. 22 was almost identical with that of Sample No. 3 (*sugurome-urushi*). It is considered that catechol derivative A polymerizes together with urushiol under the action of laccase, to form a film almost identical with the film of pure Japanese lac in physical properties.

Summary

As to Japanese lac some reports are found in literature concerning chemical identification of the lac component, or electrical insulation and resistance of the film to chemical reagents, but no physical and chemical properties related to internal polymer structure of the film had ever been investigated. In this paper the authors studied the physical and chemical properties of the film of Japanese lac by means of the torsional pendulum method.

As the results of the experiment, the following characteristics of the films prepared by various processes from Japanese lac were revealed:

1. The films do not show sharp glass transition phenomenon and are durable as a protective coating over a wide range of temperature.
2. The films from *sugurome-processed* Japanese lac have ample flexibility and considerable rigidity, ideally combined.
3. During exposure to air, the films are oxidized with formation of polar group in polymer molecules. But cross-linking does not take place except in air-dried film of raw Japanese lac.

The above mentioned physical and chemical properties of the film account for the characteristic, complicated three dimensional polymer structure caused by action of laccase and chemical structure of urushiol, and such excellent properties can not be found in any other films from synthetic resins. The results obtained are of practical use and they should be taken into consideration in the study of preparation of fillers or substitutes for Japanese lac.

Catechol derivatives synthesized by the authors were confirmed to be fairly good fillers.

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