Studies of the Cross-linking and Glass Transition of Fatty Acid-Modified Alkyd Resins

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The air drying of oil paints and varnishes has been considered to proceed by the autoxidative polymerization of the unsaturated part of the acyl groups. Reactions in the process of air-drying have been studied, resulting in some information, but how the unsaturated part of the acyl groups takes part in the cross-linking has scarcely been studied. It is well known that alkyd resin, a thermosetting amorphous polymer, is used as one of the main consituents of synthetic resin varnishes. In this paper, using fatty acid-modified alkyd resins, several factors which might have an influence on the degree of cross-linking and on the glass transition temperature of the films made from the resin have been investigated in order to get further information about the cross-linking reactions of acyl groups and some suggestions for the improvement of synthetic varnishes. The factors studied were:

a) The constitution of alkyd resins, i. e., the ratio of reactants (fatty acid, phthalic anhydride and glycerol).

b) The reaction time (the molecular weight changes with the reaction time).

c) The method of film formation (with or without the addition of a drier, air-drying or baking).

d) The aging of the films.

Experimental

Reagents.—The reagents used, phthalic anhydride, glycerol, lineseed oil fatty acids and soybean oil fatty acids, were chemically pure. The iodine values of the linseed oil fatty acids and soybean oil fatty acids were 183 and 128 respectively (as measured by Wijs' method). Xylene, the thinning solvent, was also chemically pure. Naphthenates of cobalt, lead and manganes were employed as the driers.

Synthesis of Alkyd Resins. — A 300 ml. four-necked flask with a glass stirrer was used, into one neck introducing carbon dioxide gas, into one neck inserting a thermometer, and into another one inserting a 25 ml. Stark & Dean trap for dehydration. The flask was immersed in a silicon oil bath and heated by a gas burner. The reagents were all introduced at once, and the temperature was raised to 230°C within $1^1/_2$ hr. and kept at that temperature for 5 hr.

The Process of Making Films. — The varnishes were prepared in 50% xylene solutions. The varnishes, with or without driers, were brushed on tin plates and dried in air or by baking. The quantity of the drier added to the resin was Mn 0.05%, Co 0.1% and Pb 0.2%. Since film more than 0.1 mm. thick is desirable, the varnishes were brushed 8 times every other day in the case of air drying, and the films were heated 8 times in an electric drier at 105°C for 8 hr. each time in the case of baking.

The Glass Transition Temperature (T_g) and the Degree of Cross-linking.—*The Physical Meaning of T_g and the Degree of Cross-linking.*—The term "glass transition" refers to the characteristic change in polymer properties from those of a relatively hard, brittle, glassy state to those of a softer, more flexible rubbery state as the temperature is raised through the glass transition temperature (T_g). Below the T_g, thermal energy is not available to allow the segments of the chain to move as a whole. The motions of the individual atoms are restricted to small excursions around their equilibrium positions. As the temperature approaches the T_g, the increased thermal energy becomes sufficient to allow larger molecular motions involving the coordinated movement of several atoms. Of course, the rigidity modulus G of a polymer decreases sharply with temperatures near the T_g, until it reaches a definite value enough above the T_g; on further raising of the temperature, the value keeps constant or rises a little. Since the chain segments can move freely at higher temperatures, the rigidity is sustained by the entropy elasticity of the network chains. As predicted by the kinetic theory of rubber elasticity, the rigidity modulus at high temperatures (G_h) is in proportion to the degree of cross-linking.

The Torsional Pendulum Method. — The torsional pendulum method1) developed by Inoue was employed for observing the T_g and G of the dried films. The period and the amplitudes of the damping oscillation of the film were measured; then the rigidity modulus G and logarithmic decrement λ were calculated. The temperature dependences of G and λ were measured in the range of $-70\sim90$°C. When these were plotted on a graph, a kind of characteristic spectrum of the polymer similar to a relaxation spectrum was obtained. As λ is defined as the ratio of the energy consumed by internal friction to the supplied energy, λ is considered to reach its maximum at T_g; reversely, T_g is found from λ_{max} on the garph. The rigidity modulus at high temperatures (G_h) is a direct measure of the degree of cross-linking.

Apparatus.—The inner structure of the films was considered to be at mechanical and thermal equilibrium when the films were left at room temperature for a time. The procedure of the measurement was separated into two parts, one part heating up from room temperature and another part cooling drown from room temperature. For the former, as is shown in Fig. 1, an electric drier was devised for hanging down the films and oscillating the pendulum from the outside. The temperature of the cabinet was controlled by a slide regulator and was raised at the rate of 0.5°C/min. For the latter, as is shown in Fig. 2, a core was installed in an ethanol-dry ice bath. The device for oscillating the pendulum, the same as in the electric drier, was set on the upper part of the core. The crushed dry-ice was thrown in the bath for cooling at the rate of 0.5°C/min. The core was equipped with a small fan for keeping the distribution of the temperature homogeneous, and nitrogen gas was suplied to the core continuously to prevent the freezing of moisture on the films.

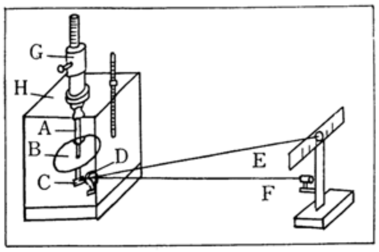

Fig. 1. Heating apparatus for torsional pendulum method.

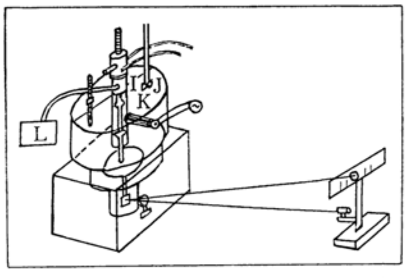

Fig. 2. Cooling apparatus for torsional pendulum method.
A Sample, B Inertia disk, C Mirror, D Lens, E Scale, F Lamp, G Device for twisting, H Electric drier, I Core J Dryice-ethanol bath, K Fan, L Thermocouple

Results and Discussion

The Influence of Oil Length*. — Linseed oil fatty acid-modified alkyd resins of oil lengths 50%, 60% and 70% were prepared. Their acid values were 10.1, 7.5 and 5.1; their molecular weights were 1000, 740 and 690 respectively (as measured by Rast's method). The results are shown in Figs. 3 and 4, and in Table I**.

G_h increased with the oil length; i. e., 2×10^8 dyn./cm² for 50%, 2.7×10^8 dyn./cm² for 60% and 1.5×10^9 dyn./cm² for 70% in the case of baked film without the addition of a drier

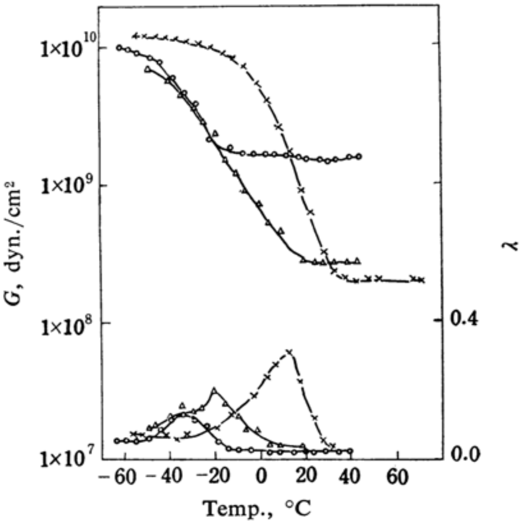

Fig. 3. Influence of oil length. Baking film of linseed oil fatty acid modified alkyd resin without addition of drier, measured at 6 months after preparation.
○ Oil length 70% △ Oil length 60%
× Oil length 50%

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[1] Y. Inoue, *J. Chem. Soc., Japan. Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), 55, 262 (1952).

* $\text{Oil length}=\dfrac{\text{oil}}{\left(\begin{array}{c}\text{oil+glycerol+phthalic}\\ \text{anhydride−water(calcd.)}\end{array}\right)}\times100$

** Sample films were exposed to the air for 6 months.

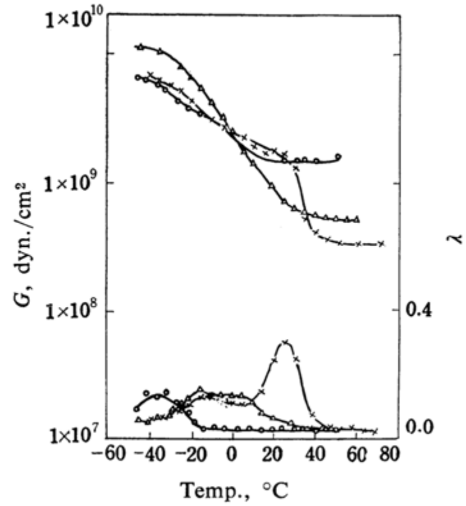

Fig. 4. Influence of oil length. Baking film of linseed oil fatty acid modified alkyd resin with addition of drier, measured at 6 months after preparation.
○ Oil length 70% △ Oil length 60%
× Oil length 50%

and 3.2×10^8 dyn./cm² for 50%, 5.0×10^8 dyn./cm² for 60% and 1.5×10^9 dyn./cm² for 70% in the case of baked film with the addition of a drier. Therefore, the degree of cross-linking increased with the oil length. Since the double bond is considered to be the source of cross-linking and the number of double bonds to increase with the increase in oil length, it is reasonable to assume that the degree of cross-linking increased with the increase in oil length. On the contrary, the T_g decreased with the increase in oil length; i. e., 12°C for 50%, −20°C for 60% and −33°C for 70% in the case of baked film without the addition of a drier, and 25°C for 50%, 0°C for 60%, and −35°C for 70% in the case of baked film with the addition of a drier. The benzene ring plays an important role in preventing molecular movements, resulting in the elevation of the T_g. It is reasonable to assume that the T_g decreased with the increase in oil length, as the concentration of the benzene ring increased with the decrease in oil length. It is also known that the T_g rises as the degree of cross-linking increases. The authors conclude that, in raising the T_g, the steric hindrance of the benzene ring plays a more important role than the degree of cross-linking. The λ_{max} increased with the decrease in oil length as a result of the internal friction of the benzene ring, the cohesive energy of which is relatively large.

The Effect of the Molecular Weight. — Fifty per cent oil length linseed oil fatty acid-modified resin was prepared under the conditions mentioned above. In the course of preparation, the samples of prepolymers of different molecular weights, 430, 570, 1000 and 1400, were taken, and air dried as well as baked film (heated for 16 hr. each time) was prepared from each prepolymer. The results are shown in Figs. 5 and 6 and in Table II. In the case of baked films without

TABLE I. INFLUENCE OF OIL LENGTH*

Oil length %	T_g °C	G_h dyn./cm²	λ_{max}	Prepolymer A. V.	Prepolymer Mol. wt.	Remarks
50	12	2.0×10^8	0.32	10.0	1000	Baking without addition of drier
60	−20	2.7×10^8	0.20	7.5	740	
70	−33	$15\ \times10^8$	0.14	5.1	690	
50	25	3.2×10^8	0.30	10.0	1000	Baking with addition of drier
60	0	5.0×10^8	0.13	7.5	740	
70	−35	$15\ \times10^8$	0.14	5.1	690	

* Measured at 6 months after preparation of the films

TABLE II. EFFECT OF MOLECULAR WEIGHT

Oil length %	T_g °C	G_h dyn./cm²	λ_{max}	Mol. wt. of prepolymer	Remarks
50[a]	− 1	—	0.58	430	Baking without addition of drier
50[a]	18	$0.6\ \times10^8$	0.75	1000	
50[a]	28	0.75×10^8	0.98	1400	
50[b]	5	—	0.67	570	Air drying with addition of drier
50[b]	20	0.28×10^8	1.24	1000	
50[b]	20	0.40×10^8	1.4	1400	

a Measured at 2 weeks after preparation of the films
b Measured at 2 months after preparation of the films

the addition of a drier, the T_g and G_h values were: 28°C, 0.75×10^8 dyn./cm^2 for mol. wt. 1400, 18°C; 0.6×10^8 dyn./cm^2 for mol. wt. 1000, and −1°C for mol. wt. 430*, and in the case of air-dried films with the addition of a drier, those values were: 20°C, 0.4×10^8 dyn./cm^2 for mol. wt. 1400, 20°C, 0.28×10^8 dyn./cm^2 for mol. wt. 1000, and −5°C for mol. wt. 570*. The results show that both the T_g and the G_h increase with the increase in the molecular weight of the prepolymer. The results may be considered as follows:

a) The configuration of the prepolymers of a high molecular weight may favor cross-linking.

b) The prepolymers of a low molecular weight contain more unreactant, which act as plasticizers for the polymer.

In the glass transition state, both the G-T and λ-T curves were sharp compared with the curves found in the samples of the same oil length used above, because the cross-linking was not fully completed, and the λ_{max} increased with the increase in the molecular weight of the prepolymer. This suggests that the λ-T curve's tendency to be flat is not a mere result of the progress of the cross-linking.

The Effect of Excess Glycerol. — In connection with reducing the acid value of resins less than 10, which is important practically, two 50% soybean oil fatty acid-modified resins were prepared: (A) with an equivalent weight of glycerol and (B) with a 20% excess (by weight) of glycerol. The acid values were

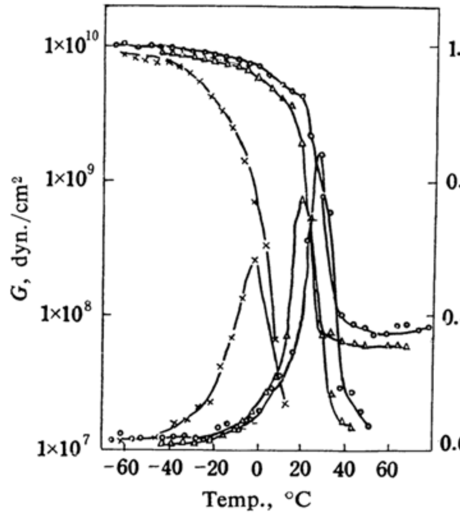

Fig. 5. Effect of molecular weight. Baking film of 50% oil length linseed oil fatty acid modified alkyd resin without addition of drier, measured at 2 weeks after preparation.
○ Mol. wt. 1400 △ Mol. wt. 1000
× Mol. wt. 430

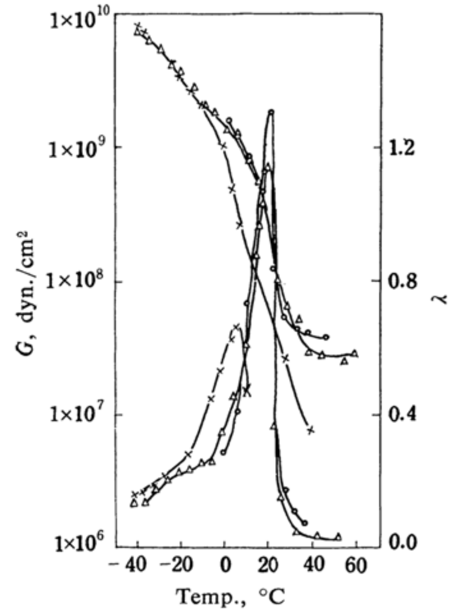

Fig. 6. Effect of molecular weight. Air drying film of 50% oil length linseed oil fatty acid modified alkyd resin, measured at 2 months after preparation.
○ Mol. wt. 1400 without drier
△ Mol. wt. 1000 with drier
× Mol. wt. 570 with drier

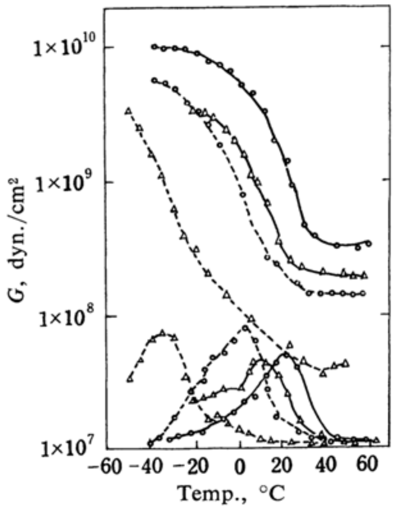

Fig. 7. Effect of excess glycerol. 50% oil length soybean oil fatty acid modified alkyd resin, measured at 6 months after preparation.
○ 20% excess glycerol
△ Equilibrium weight of glycerol
—— Baking film, with drier
---- Air drying film, with drier

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* No G_h values of the sample were observed, since the films elongated and broke off at high temperatures.

TABLE III. EFFECT OF EXCESS GLYCEROL*

	T_g °C	G_h dyn./cm²	λ_{max}	A. V. of prepolymer	Remarks
A	10	2.0×10^8	0.27	32.7	Baking
B	21	3.2×10^8	0.28	9.6	
A	−11	0.4×10^8	0.34	32.7	Air drying
B	2	1.5×10^8	0.36	9.6	

* Measured at 6 months after preparation of the films

TABLE IV. EFFECT OF DRIER AND METHOD OF DRYING

	T_g °C	G_h dyn./cm²	λ_{max}	A. V. of prepolymer	Remarks
A_1	13	1.8×10^8	0.38	26.1	Measured at 6 months after preparation of the films
A_2	13	3.2×10^8	0.30	26.1	
B_1	23	5.4×10^8	0.26	26.1	
B_2	28	$11\ \times10^8$	0.16	26.1	
A_1	22	2.5×10^8	0.50	26.1	Measured at 10 months after preparation of the films
A_2	26	4.0×10^8	0.36	26.1	
B_1	41	7.8×10^8	0.26	26.1	
B_2	52	$11\ \times10^8$	0.18	26.1	

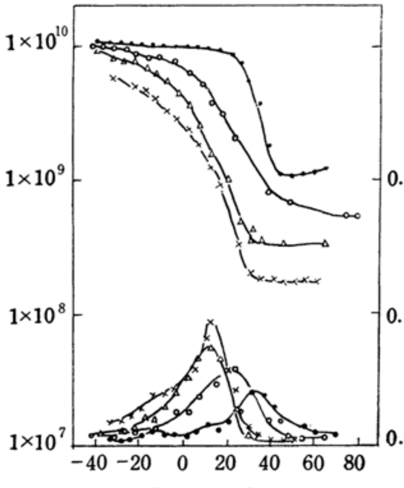

Fig. 8. Effect of drier and method of drying. 40% oil length linseed oil fatty acid modified alkyd resin, measured at 6 months after preparation.
● Baking with drier
○ Baking without drier
△ Air drying with drier
× Air drying without drier

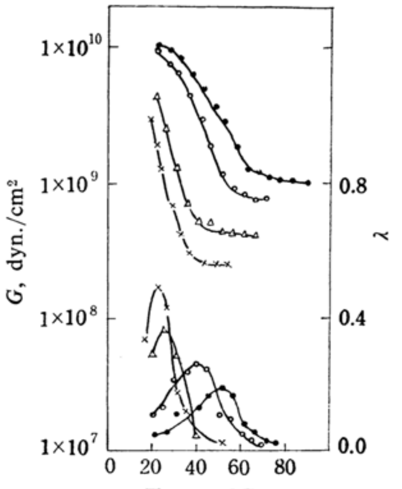

Fig. 9. Effect of drier and method of drying. 40% oil length linseed oil fatty acid modified alkyd resin, measured at 10 months after preparation.
● Baked with drier
○ Baked without drier
△ Air dried with drier
× Air dried without drier

32.7 for A and 9.6 for B. The results are shown in Fig. 7 and Table III. The G_h and T_g values were 3.2×10^8 dyn./cm², 21°C for B, 2.0×10^8 dyn./cm², 10°C for A in the case of baked films and 1.5×10^8 dyn./cm², 20°C for B, 0.4×10^8 dyn./cm², −11°C for A in the case of air-dried films. The results show that both the T_g and the G_h of B were larger than those of A. This may be considered to be result of the effects of the molecular weight and of the plasticizing action of the unreactant for the polymer.

The Effect of the Drier and the Method of Drying.—A 40% oil length, linseed oil fatty acid-modified resin was prepared under the same reaction conditions mentioned above, except

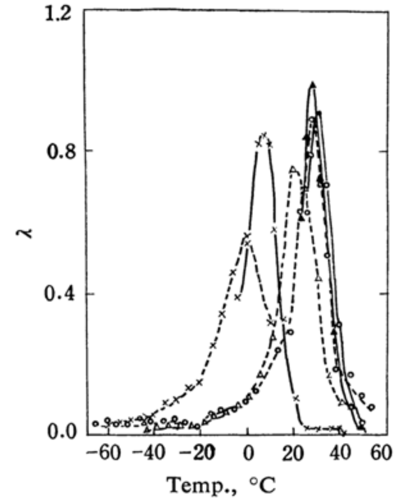

Fig. 10. *λ-T* relation of 50% oil length linseed oil fatty acid modified alkyd resin at early period of drying.

●, ○ Mol. wt. 1400 ▲, △ Mol. wt. 1000
× Mol. wt. 430
—— Baked film without drier measured at 2 months after preparation
---- Baked film without drier measured at 2 weeks after preparation

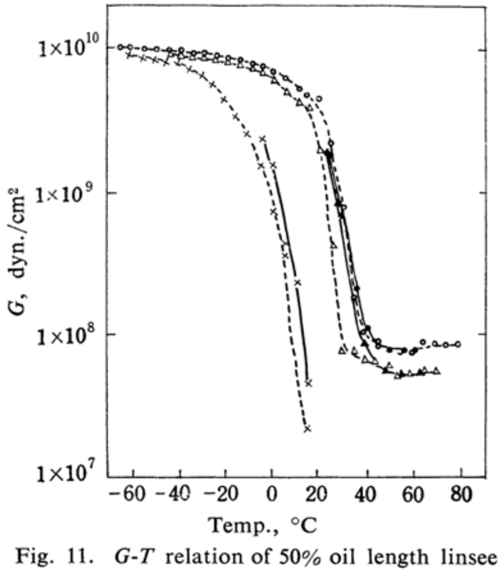

Fig. 11. *G-T* relation of 50% oil length linseed oil fatty acid modified alkyd resin at early period of drying.

●, ○ Mol. wt. 1400 ▲, △ Mol. wt. 1000
× Mol. wt. 430
—— Baked film without drier measured at 2 months after preparation
---- Baked film without drier measured at 2 weeks after preparation

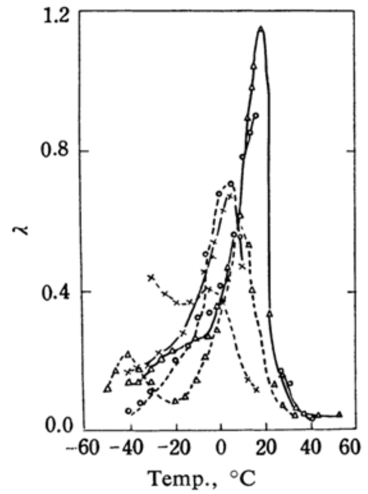

Fig. 12. *λ-T* relation of 50% oil length linseed oil fatty acid modified alkyd resin at early period of drying.

○ Mol. wt. 1400 without drier
△ Mol. wt. 1000 with drier
× Mol. wt. 570 with drier
—— Air dried film measured at 2 months after preparation
---- Air dried film measured at 2 weeks after preparation

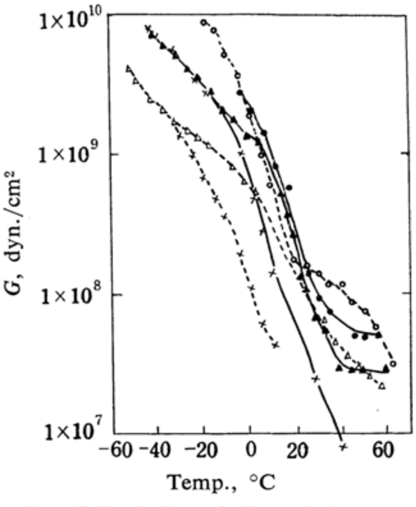

Fig. 13. *G-T* relation of 50% oil length linseed oil fatty acid modified alkyd resin at early period of drying.

●, ○ Mol. wt. 1400 ▲, △ Mol. wt. 1000
× Mol. wt. 570
—— Air dried film measured at 2 months after preparation
---- Air dried film measured at 2 weeks after preparation

that the reaction time was limited to 2 hr. in order to avoid gelation. Because the functionality per mole is larger in this case, it gels at a higher acid value(2). The acid value of the resin in this case was relatively large, i. e., 26.1. Air-dried (A) and baked film (B) with a drier (A_2, B_2) and without a drier (A_1, B_1) were

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2) W. H. Carothers, *Trans. Faraday Soc.*, 32, 39 (1936).

TABLE V. EARLY PERIOD OF DRYING

Mol. wt. of prepolymer	Exposed time	T_g °C	G_h dyn./cm²	λ_{max}	Remarks
430	2 weeks	0	—	0.57	Baking
430	2 months	6	—	0.9	
1000	2 weeks	20	0.54×10^8	0.75	
1000	2 months	27	0.54×10^8	1.2	
1400	2 weeks	28	0.8×10^8	0.98	
1400	2 months	30	0.8×10^8	1.02	
570	2 weeks	−5	—	0.41	Air drying
570	2 months	5	—	0.67	
1000	2 weeks	9	—	0.59	
1000	2 months	19	0.18×10^8	1.25	
1400	2 weeks	5	—	1.0	
1400	2 months	20	0.4×10^8	1.0	

prepared. The results are shown in Figs. 8 and 9 and in Table IV. The degree of cross-linking was in the order of $A_1<A_2<B_1<B_2$; the T_g was in the same order, and the λ_{max} decreased in this order. The G at a sufficiently low temperature was 10^{10} dyn./cm², and the same G values were observed in other films.

Aging of Films.—*Early Period of Drying.*—A 50% oil length linseed oil fatty acid-modified resin was prepared, from which air-dried and baked films were made. Their properties were measured 2 weeks and 2 months after the preparation. The results are shown in Figs. 10, 11, 12 and 13 and in Table V. For baked films, no distinguishable difference in the T_g and the G_h was observed between the films prepared from the prepolymer of a larger molecular weight. For air-dried films, the elevation of the G-T curve and the T_g (about 10°C) were observed, and the cross links were developed to the extent of sustaining the applied load.

Aging at a Later Period.—A 40% oil length linseed oil fatty acid-modified resin was prepared, from which air-dried and baked films were made. The results of the measurement 6 months and 10 months after the preparation are shown in Fig. 14. In the course of 4 months, the elevation of the G-T curve and the raising of the T_g (10～20°C) were observed. The λ_{max} was larger, and the λ-T curve tended to be sharp. It is notable that, in the case of baked film with the addition of a drier, no change in the G_h was observed, although the T_g was raised more than 10°C. This may be explained by the fact that, in the course of time, the film was gradually air-oxidized with the formation of polar groups, with the result that their cohesive energy became larger and led to a rise in the T_g. Owing to the increase in the energy consumed by the internal friction caused by the increase in the concentration of the polar group, the λ_{max} became larger. Generally the driers accelerate the drying of film in the early period, resulting in the G_h values of the films with a drier being higher than those of the films without a drier (measured 6 months after the preparation of the films); this effect of acceleration still held even 10 months after the preparation of the films. Both the T_g and the G_h were larger in the case of baked films. Comparing the baked to the air-dried films, the authors found that the effect of heating held even 10 months after the preparation of the films. Concerning

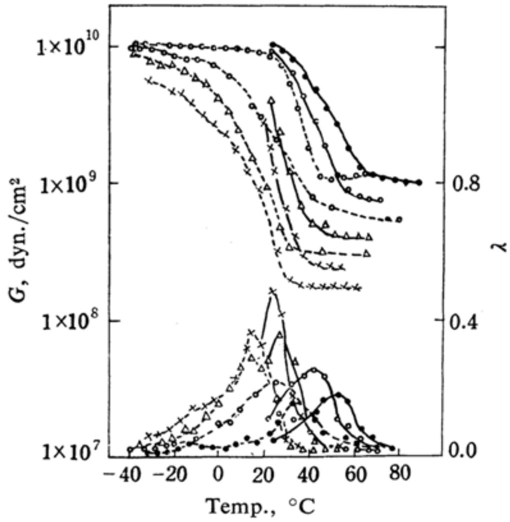

Fig. 14. The aging of the films of 40% oil length linseed oil fatty acid modified alkyd resin.

● Baked with drier
○ Baked without drier
△ Air dried with drier
× Air dried without drier
—— Measured at 10 months after preparation
---- Measured at 6 months after preparation

TABLE VI. AGING AT LATER PERIOD

Exposed time	T_g** °C	λ_{max}**	T_g* °C	λ_{max}*	G_h dyn./cm²	Remarks
6 months	5	0.14	−33	0.32	—	Baking
10 months	3	0.17	−32	0.24	0.75×10^8	
6 months	—	—	−35	0.36	0.4×10^8	Air drying
10 months	11	0.32	−33	0.28	0.84×10^8	

* Values at sub-glass transition
** Values at main glass transition

the acceleration of the cross-linking, heating was found to be more effective than driers. It may be suggested that the mechanism of cross-linking is not the same in the case of baking and of air-drying.

Sub-glass Transition. — In some experiments, two glass transition points were observed; the authors have named the higher one, the main glass transition point, and the lower one, the sub-glass transition point. The sub-glass transition was observed between −30 to −40°C. In the case of air-dried film prepared from the prepolymer of a low molecular weight, the sub-glass transition was found in the early period of drying (Fig. 15). Comparing the films two weeks and two months after preparation, the λ_{max} of the sub-glass transition tended to be small and the λ-T curve at the sub-glass transition state became flat; on the other hand, the λ_{max} of the main glass transition tended to be larger and the λ-T curve at the main glass transition state became sharp. The same glass transition phenomenon was observed in the case of a 50% oil length soybean oil fatty acid-modified resin using an equivalent weight of glycerol even 10 months after the preparation of the films (Fig. 16 and Table VI). Though the reasons are not fully understood, this finding suggests that such a kind of sub-glass transition is due to the unrestrained chain of the acryl groups.

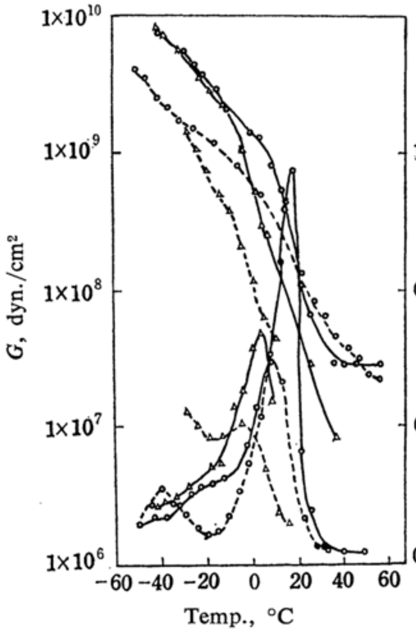

Fig. 15. Sub-glass transition. 50% oil length linseed oil fatty acid modified alkyd resin at early period of drying with addition of drier.
○ Mol. wt. 1000 △ Mol. wt. 570
—— Measured at 2 months after preparation
---- Measured at 2 weeks after preparation

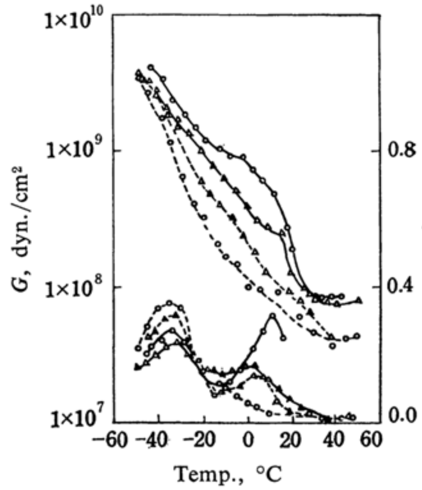

Fig. 16. Sub-glass transition. Air dring films of 50% oil length soybean oil fatty acid modified alkyd resin with equivalent weight of glycerol.
○ With drier △ Without drier
—— Measured at 10 months after preparation
---- Measured at 6 months after preparation

Summary

a) The degree of cross-linking observed in films of fatty acid modified alkyd resins increases with the content of unsaturated acids. Moreover, cross-linking is not so effective in raising the T_g as the benzene ring, which has a larger cohesive energy.

b) Both the T_g and the degree of cross-linking increase with the increase in the molecular weight of the prepolymer.

c) The excess of glycerol employed in fatty acid-modified alkyd resin is effective in raising the T_g and encouraging the progress of the cross-linking.

d) Generally, the cross-linking is not soon completed; as time elapses, the T_g rises, and the cross-linking progresses. No change in the G_h with the elevation of the T_g (baked film with the addition of a drier) is considered to be caused by the formation of polar groups by air-oxidation.

e) In the early period of drying, a sub-glass transition caused by the unrestrained chain of the acyl groups is observed.

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