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The Deterioration of Oxidative Polymerized Films

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The deterioration of oxidative polymerized films, such as films of polymerized oils, alkyd resins, and phenolic varnishes, was studied by means of dynamic-mechanical measurements, in addition to such conventional methods as infrared spectral and elementary analysis. The visco-elastic changes induced by thermo-oxidation were correlated with the network structure of the films. The baked films are more stable than the air-dried films. The aliphatic chains decomposed more easily when a comparison was made among air-dried film and baked film of alkyd resin modified by unsaturated fatty acid; this is because of the existence of more hydroperoxyl and conjugated carbonyl groups and the effect of the drying agent contained in the air-dried film. After thermo-oxidation, the glass-transition temperature and the degree of crosslinking of the film showed an increase, an increase which is considered to be the result of the oxidative decomposition and crosslinking of aliphatic chains. It was also observed that the impact strength of baked film decreased upon thermo-oxidation.

Polymerized oils, alkyd resins, and phenolic varnishes are representative of oxidative polymerizable prepolymers widely employed in the coating industry. The film formation is proceeded by the formation of hydroperoxide and then its decomposition leading to a network structure. The autoxidation being complicated, the film structure is much affected by such conditions as the temperature, the catalyst, and the time under which the varnish or film is treated. With this reaction complexity and the easy chemical modification of prepolymers, this is a field of study which correlates the physical properties and the structure of the crosslinking polymer. Not only practical requirements but also the study of the polymer reaction needs such investigation, but the reaction complexity and the difficulty of handling the network structure somewhat affect the carrying-out of this study.

The authors measured the viscoelastic properties, the line-width of the NMR spectra, and the molecular weight between crosslinks, besides such conventional analytical methods as infrared spectral and elementary analysis, in their study. Some information has already been obtained, such as the effect of chemical factors on the glass-transition temperature and the degree of crosslinking of alkyd films,1) the correlation of the glass transition temperature measured by the dynamic-mechanical method and the line-width measurement (NMR) in relation to the chemical structure,2) and the chemical and physical behavior of phenolic resins in films of phenolic varnishes.3)

In this report, the deterioration of oxidative polymerized films induced by thermo-oxidation will be studied by means of dynamic-mechanical

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1) J. Kumanotani, L. W. Chen and T. Kuwata, This Bulletin, **35**, 8, 1341 (1962).

2) L. W. Chen and J. Kumanotani, *J. Appl. Polymer Sci.*, **9**, 3519 (1965).

3) L. W. Chen and J. Kumanotani, ibid., **9**, 2785, (1965).

measurements made in combination with infrared spectral analysis and other methods.

As the deterioration of polymer is of importance in respect to its polymer reactions and its practical requirements, several papers[4-7] regarding the degradation of oxidative polymerized films have been reported. These studies have involved degradation by ultraviolet rays, thermo-oxidative degradation, or aging, and have been carried by means of the analysis of infrared absorption spectra, oxygen absorption, and volatile materials, or by means of the mechanical-property measurement of films, independently or sometimes in combination.

As to the thermo-oxidative degradation of oxidative polymerized films, the films prepared from polymerized oil, alkyd resin, and phenolic varnishes will be studied, and air-dried and baked films will be compared as well.

Their viscoelastic change in correlation with the network structure will also be investigated in this report.

Experimental

Raw Materials.—*Drying Oil (O).*—A mixture of tung oil (iodine value 168, Wijs method) and linseed oil (iodine value 187) (1 : 1) was used.

Phenol Resins. —*p-t*-Butylphenol-formaldehyde resins were prepared by the conventional method; the oil-reactive resin (R) had a molecular weight of 650, as measured by a vapor pressure osmometer (Mechrolab, Inc.) m. p. 65—72°C, while the oil-nonreactive resin (N) had a molecular weight of 375, m. p. 55—62°C.

Linseed Oil Fatty Acid.—Commercially-available: iodine value 187.

Glycerol and Phthalic Anhydride.—They were chemically pure.

The Preparation of Prepolymers.—*Polymerized Oil.* —The drying oil was heated in air at 210°C for 5.5 hr. The heating was stopped near gelation, and the mixture was dissolved in an equal weight of mineral turpentine after it had been cooled to room temperature.

Phenolic Varnishes.—A mixture of oil and resin (6 : 4) was heated in air at 210°C. The heating was stopped near gelation, and the mixture was dissolved in an equal weight of mineral turpentine. The reaction time was 8 hr. for the oil-nonreactive resin (N–O), and 3 hr. for the oil-reactive resin (R–O). Another varnish was prepared by dissolving at room temperature, a mixture of polymerized oil and oil-nonreactive resin (6 : 4) in an equal weight of mineral turpentine containing 2—3% methyl ethyl ketone (N+PO).

Alkyd Resin.—An Equimolar mixture of linseed oil fatty acid, glycerol, and phthalic anhydride was put in a four-necked 500-ml. flask equipped with a sealed glass stirrer, a thermometer, a nitrogen gas inlet tube, and a Stark & Dean trap, and heated in an oil bath at 230°C for 9 hr. The varnish was prepared by dissolving the prepolymer ($\bar{M}_n$, 1710) in an equal weight of xylene.

Conditions of Film Formation.—*Polymerized Oil Film.*—The varnish, containing drying agents, naphthenates of cobalt (0.02%) and manganese (0.02%) was coated on tin plates, the coating and heating at 80°C for 2 hr. were repeated 10 times.

Films of Phenolic Varnishes.—The varnishes, containing drying agents, naphthenates of cobalt (0.02%) and manganese (0.02%), were coated on tin plates. For air drying, the procedure of coating and standing for one day at room temperature was repeated 10 times. For baking, the same procedure was used as with polymerized oil film.

Alkyd Films.—In the case of air drying, the varnish containing drying agents, naphthenates of cobalt (0.04%), manganese (0.04%), and lead (0.2%), was coated on tin plate and left to stand at room temperature two days. This procedure was repeated 4 times. In the case of baking, the varnish, without any drying agent being added, was coated on tin plate and heated at 105°C for 2 hr. in air. This procedure was repeated 4 times. The films were then stripped off by an amalgam method.

The Conditions of Thermal Treatment.—*Polymerized Oil Film.*—After it had stood in air for 3 months, the film was heated in air at 150°C for 3 hr., and then subsequently heated at 200°C for 3 hr.

Films of Phenolic Varnishes.—After they had stood in air for 3 months, the films were submitted to heating, just as in the case of the polymerized oil films.

Alkyd Films.—After it had stood in air for 2.5 months, the air-dried film was heated in air at 105°C for 5 hr., while the baked film, after it had stood in air a week, was submitted to heating just as in the case of the polymerized oil film.

The Dynamic-mechanical Measurement of Films.—The temperature (t) dependence of the shear modulus (G) and the logarithmic decrement (λ) of the film were measured by the torsional pendulum method.[8] The data obtained from the G-t and λ-t curves included the glass transition temperature as measured by the dynamic-mechanical method $(T_g)_d$; the temperature at which λ reaches a maximum (λ_{max}). As the frequency of measurement is in the range of 0.1-1 cycle/sec., the $(T_g)_d$ value is not far from that obtained by the dilatometric method.[9]

Shear modulus at high temperatures G_h; This is the shear modulus obtained from the plateau region at high temperatures. It is a measure of the degree of the crosslinking of film.[10-12] Shear modulus at room temperature G_r; This is the shear modulus at 20°C, noted as a measure of the rigidity of the film at room temperature.

Infrared Spectral Analysis of Films.—The change in the functional group in the process of film degradation was examined by the measurement of the infrared spectra.

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[4] E. B. FitzGerald, *A. S. T. M. Bull.*, **65**, TP 137—48 (1955).

[5] C. D. Miller, *Ind. Eng. Chem.*, **50**, 125 (1958).

[6] A. L. Smith, ibid., **49**, 1903 (1957).

[7] T. Imai, *J. Japan Soc. Colour Material,* (*Shikizai*) **30**, 6, 216 (1957).

[8] Y. Inoue, *J. Soc. Polymer Sci., Japan* (*Kobunshi Kagaku*), **10**, 140 (1953).

[9] L. E. Nielsen, "Mechanical Properties of Polymers", Reinhold, New York (1962), p. 162.

[10] H. F. Drum, C. W. H. Dodge and L. E. Nielsen, *Ind. Eng. Chem.*, **48**, 76 (1956).

[11] K. Ueki, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **65**, 137 (1962).

[12] D. Katz and A. V. Tobolsky, *J. Polymer Sci.*, **A2**, 1587 (1964).

A rock salt was coated with varnish and dried, and then thermo-treated under specified conditions, as mentioned previously, the infrared spectra were then measured. The chemical change in functional groups is reflected in changes in the optical density (D) or the ratio of those of related functional groups.

In infrared spectral analysis, the characteristic absorption bands employed are: ν_{3570} cm^{-1}: hydroxyl, hydroperoxyl, or carbonyl; ν_{2850} cm^{-1}: methyl or methylene of aliphatic chains; ν_{1590} cm^{-1}: the carbon-to-carbon linkages of phthalate; and ν_{980} cm^{-1}, trans ethylenic double bond, while D_{2850}/D_{1590} is expressed as a measure of the ratio of the aliphatic to the phthalate in films.

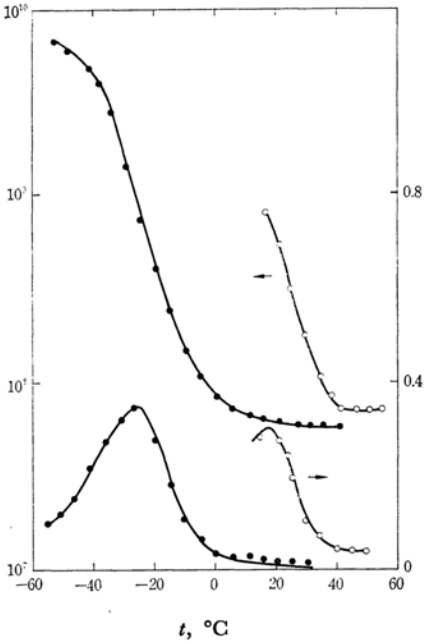

Fig. 1. Thermo-oxidative degradation of polymerized oil film observed in G-t, λ-t curves.
● Original film
○ After heating at 150°C for 3 hr.

The Degree of Swelling and the Soluble Portion of the Film.—The degree of swelling and the soluble portion of film were measured as follows:

The film (W_0) was dipped in chloroform at room temperature for more than a week; then the swollen film was weighed in another covered weighing bottle filled with chroloform until the weight was constant (W_s). The degree of swelling is expressed by $(W_s/W_0) \times 100$.

The swollen film was then dried in a vacuum (W_d), and the soluble portion of film was expressed by $(W_0-W_d)/W_0 \times 100$.

Other measurements of the properties of the film, such as elementary analysis, thermograms*[1] and impact strength*[2] were also carried out.

Results and Discussion

The Thermo-oxidative Degradation of Polymerized Oil Film.—The G-t and λ-t curves of polymerized oil film are shown in Fig. 1, while the infrared spectra are shown in Fig. 2. The results are summarized in Table I.

It was observed when the baked polymerized oil film was thermo-treated in air that:

1) The $(T_g)_d$, G_r, and G_h of the film increased; namely, the hardness of film and the degree of the crosslinking of the film increased:

2) D_{2850}, D_{3570}, and D_{980} decreased; and

3) The weight loss amounted to 8.7% when the film was treated at 150°C for 3 hr. in air.

The Thermo-oxidative Degradation of Films of Phenolic Varnishes.—The G-t and λ-t curves of films of phenolic varnishes are shown in Fig. 3 and Fig. 4. The results are summarized in Table II.

It was observed when the films of phenolic varnishes were thermo-treated in air that:

1) The $(T_g)_d$, G_r, and G_h values of the films increased, and

2) The weight loss amounted to 10% or more

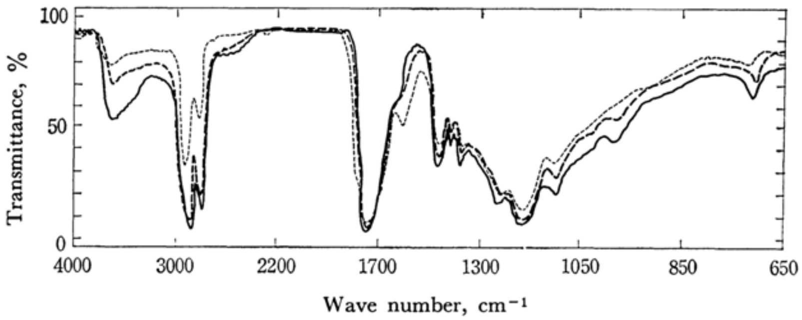

Fig. 2. Thermo-oxidative degradation of polymerized oil film observed in infrared spectra.
—— Original film ---- After heating at 150°C for 3 hr.
······ After heating at 200°C for 3 hr.

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*[1] Measured by a DTA apparatus Shimadzu Type 1A, in air.

*[2] Measured by a du Pont Impact Tester.

TABLE I. THERMO-OXIDATIVE DEGRADATION OF BAKED FILM OF POLYMERIZED OIL

Film	$(T_g)_d$ °C	G_r dyn./cm²	G_h dyn./cm²	D_{2850}	D_{3570}	D_{980}	Weight loss %
Baked film (exposed in air for 33 months)	−27	6.0×10^7	5.8×10^7	0.847	0.213	0.062	
Above film heated at 150°C for 3 hr.	15	6.0×10^8	7.2×10^7	0.662	0.104	0.031	8.7
Above film heated at 200°C for 3 hr.				0.227	0.063	0.06	

TABLE II. THERMO-OXIDATIVE DEGRADATION OF AIR-DRIED FILM OF PHENOLIC VARNISHES

Film	$(T_g)_d$ °C	G_r dyn./cm²	G_h dyn./cm²	Weight loss %
Air-dried film of oil reactive phenolic varnish	32	3.4×10^9	3.0×10^7	
Above film heated at 150°C for 3 hr.	67	3.8×10^9	4.3×10^7	10.4
Air-dried film of nonreactive phenolic varnish (cold blend)	20	2.4×10^9	3.5×10^7	
Above film heated at 150°C for 3 hr.	75	5.5×10^9	4.5×10^7	12.3

TABLE III. THERMO-OXIDATIVE DEGRADATION OF AIR-DRIED FILM OF PHENOLIC VARNISHES
(Infrared spectra)

Film	Thermal treating condition	D_{2850}	D_{3570}	D_{980}
Air-dried film of oil reactive phenolic varnish	(dried for 2 days)	0.296	0.089	0.032
	Heated at 80°C for 10 hr.	0.264	0.069	0.022
	Heated at 150°C for 3 hr.	0.179	0.043	0.017
	Heated at 200°C for 3 hr.	0.148	0.02	0.007
Air-dried film of oil nonreactive phenolic varnish (cold blend)	(dried for 2 days)	0.460	0.140	0.077
	Heated at 80°C for 10 hr.	0.394	0.108	0.040
	Heated at 150°C for 3 hr.	0.390	0.08	0.021
	Heated at 200°C for 3 hr.	0.153	0.03	0

TABLE IV. THERMO-OXIDATIVE DEGRADATION OF AIR-DRIED FILM OF ALKYD RESIN

Thermal treating condition	$(T_g)_d$ °C	G_r dyn./cm²	G_h dyn./cm²	λ	Weight loss, %	Elementary analysis		
						C%	H%	O%
2 weeks after drying						63.78	7.46	28.76
2.5 months after drying	5	1.5×10^8	$<5.7\times10^7$	0.62				
Above film heated at 105°C for 2 hr.	41	3.0×10^9	8.6×10^7	0.36	7	63.39	7.19	29.42
Above film heated at 105°C for 5 hr.								

Thermal treating condition	D_{2850}	D_{1590}	D_{2850}/D_{1590}	D_{3570}	D_{3570}/D_{1590}	D_{980}
2 weeks after drying	0.448	0.090	4.99	0.167	1.85	
2.5 months after drying	0.431	0.092	4.62	0.200	2.22	0.085
Above film heated at 105°C for 2 hr.	0.240	0.090	2.67	0.046	0.51	0.034
Above film heated at 105°C for 5 hr.	0.238	0.090	2.64	0.054	0.60	

when the film was treated at 150°C for 3 hr. in air.

The infrared spectra changes involved in the thermal treating are shown in Figs. 5 and 6, and in Table III. The films prior to thermal treatment were a little different from that used for viscoelastic measurement; namely, each of the varnishes was coated on rock salt and dried for two days, followed by heating at 80°C for 10 hr. and subsequent heating at 150°C for 3 hr. and at 200°C for 3 hr. in air.

It was observed that D_{2850}, D_{3570}, and D_{980} decreased in this thermal treating.

The Thermo-oxidative Degradation of Alkyd Films.—The *G-t* and *λ-t* curves, the infrared spectra, and the thermogram of air-dried film are shown in Figs. 7, 8, and 9 respectively. The results are summarized in Table IV.

It was observed when the air-dried film was

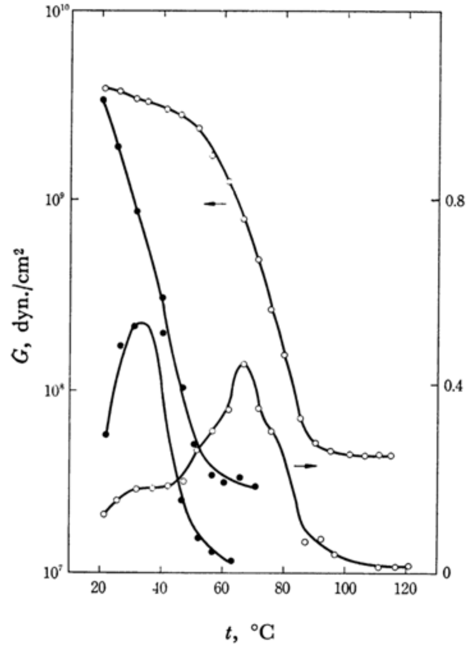

Fig. 3. Thermo-oxidative degradation of air-dried film of phenolic varnish (R-O) observed in *G-t*, *λ-t* curves.

● Original film, R-O

○ After heating at 150°C for 3 hr.

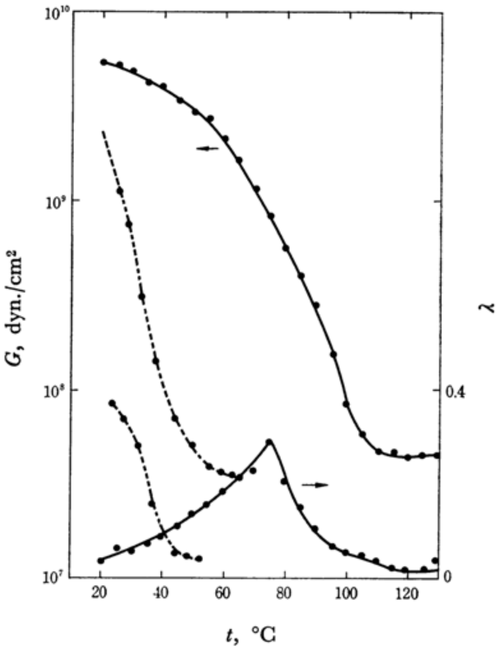

Fig. 4. Thermo-oxidative degradation of air-dried film of phenolic varnish (N+PO) observed in *G-t*, *λ-t* curves.

---- Original film

—— After heating at 150°C for 3 hr.

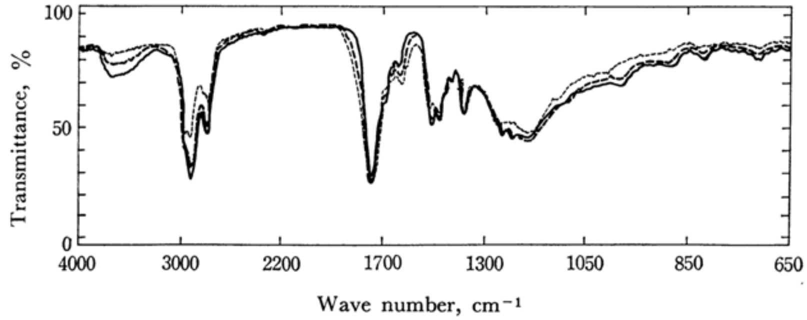

Fig. 5. Thermo-oxidative degradation of air-dried film of phenolic varnish (R-O) observed in infrared spectra.

—— Original film ---- After heating at 150°C for 3 hr.

······ After heating at 200°C for 3 hr.

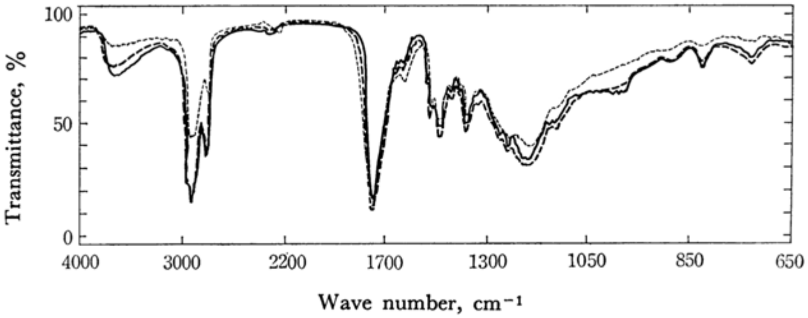

Fig. 6. Thermo-oxidative degradation of air-dried film of phenolic varnish (N+PO) observed in infrared spectra.

—— Original film ---- After heating at 150°C for 3 hr.

······ After heating at 200°C for 3 hr.

TABLE V. THERMO-OXIDATIVE DEGRADATION OF BAKED FILM OF ALKYD RESIN

Thermal treating condition	$(T_g)_d$ °C	G_r dyn./cm^2	G_h dyn./cm^2	λ	Weight loss, %	Elementary analysis C%	H%	O%
Baked film laid in air for one week	4	4.6×10^7	3.7×10^7	0.89		64.29	7.39	28.32
Above film heated at 150°C for 3 hr.	25	8.0×10^8	4.8×10^7	0.99	2.5	65.20	7.33	27.47
Above film heated at 200°C for 3 hr.	55	5.0×10^9	1.1×10^8	0.62	14.0	63.86	6.60	29.54

Thermal treating condition	D_{2850}	D_{1590}	$\frac{D_{2850}}{D_{1590}}$	D_{3570}	$\frac{D_{3570}}{D_{1590}}$	D_{980}	Degree of swelling %	Chloroform soluble portion of film, %	Impact strength (by du Pont Impact Tester)
Baked film laid in air for one week	0.551	0.110	5.02	0.139	1.26	0.081	530	17.3	1/16″×1kg ×50cm.
Above film heated at 150°C for 3 hr.	0.437	0.106	4.12	0.121	1.14	0.058	450	11.9	1/8″×1kg ×50cm.
Above film heated at 200°C for 3 hr.	0.304	0.091	3.34	0.080	0.83	0.037	Disparted	0.4	1/4″×0.5kg ×50cm.

TABLE VI. WEIGHT LOSS OF FILMS OF PHENOLIC VARNISHES DURING THERMO-OXIDATIVE TREATING

	Film of nonreactive phenolic varnish (N-O)	Film of nonreactive phenolic varnish (cold blend) (N+PO)	Film of reactive phenolic varnish (R-O)	Film of reactive phenolic varnish (cold blend) (R+PO)
Air-dried film	9.3[*1]	12.3	10.4	18.0
Baked film	5.6	8.1	5.8	13.3

[*1] Expressed as

$$\left(\frac{\text{film weight prior to thermal treating-film weight after thermal treating}}{\text{film weight prior to thermal treating}}\right)\times 100$$

TABLE VII. ELEMENTARY ANALYSIS OF AIR-DRIED AND BAKED FILMS OF ALKYD RESIN

Film	Elementary analysis C%	H%	O%	C : H : O (in atoms) C	H	O	C : H : O (in atoms) (reduced[*2]) C	H	O	Number of oxygen atoms combined per aliphatic chain[*3]
Air-dried film[*1]	63.78	7.46	28.76	5.31	7.46	1.80	29.0	40.8	9.80	2.80
Baked film	64.29	7.39	28.32	5.35	7.39	1.77	29.0	40.0	9.60	2.60

[*1] Laid in air for weeks after drying.

[*2] The ratio of C, H, and O (in atoms) in prepolymer which contained one aliphatic chain is 29 (C): 41 (H): 7 (O)

[*3] No scission of acyl group taking place during film formation is assumed.

TABLE VIII. EFFECT OF DRYING AGENT ON DECOMPOSITION OF ALIPHATIC CHAINS

Film	Drying temperature	Heating time	Times of coating	Addition of drying agents	D_{2850}/D_{1590}*	D_{3570}/D_{1590}*	Chloroform soluble portion of film %
1	Room temperature	2 days	6	Co 0.02% Mn 0.02%	3.8	1.29	46
2	105°C	2 hr.	6	none	4.3	1.49	16.5
3	105°C	2 hr.	6	Co 0.02% Mn 0.02%	3.4	1.18	8.4
4	105°C	8 hr.	6	none	4.1	1.41	3.8
5	105°C	8 hr.	6	Co 0.02% Mn 0.02%	2.9	1.03	

* IR spectra were measured by KBr disk method.

thermo-treated in air that:

1) The $(T_g)_d$, G_r, and G_h values of the film increased, and the λ-t curve was broadened:

2) The weight loss amounted to 7% when the film was treated at 150°C for 3 hr. in air, and

3) D_{2850}/D_{1590} and D_{3570}/D_{1590} decreased intensively, whereas D_{1590} unchanged.

The G-t and λ-t curves, the infrared spectra, and the thermogram of baked film are shown in Figs. 10, 11, and 9 respectively. The results are summarized in Table V. The results concerning the degree of swelling and the soluble portion of film, and impact strength of films are also tabulated in Table V.

It was observed when the baked film was heated in air that:

1) The $(T_g)_d$, G_r, and G_h values of the film increased:

2) D_{2850}/D_{1590} and D_{3570}/D_{1590} decreased less than in the case of air-dried film, and D_{1590} decreased also, and

3) The D_{980} decreased also.

It was generally observed when the oxidative polymerized films were thermo-treated that the glass transition temperature and the degree of the crosslinking of the film increased accompanying a decrease in the aliphatic chains and the trans ethylenic double bonds.

The increase in $(T_g)_d$ is considered to be the result of the oxidative decomposition and crosslinking of aliphatic chains. In relation to the network structure, the free aliphatic chains functioned as internal plasticizers; such a function was decreased by the oxidative decomposition of the aliphatic chain induced by thermal treating. Moreover, it may be suggested that such oxidative decomposition induces the decrease in the impact strength of the film.

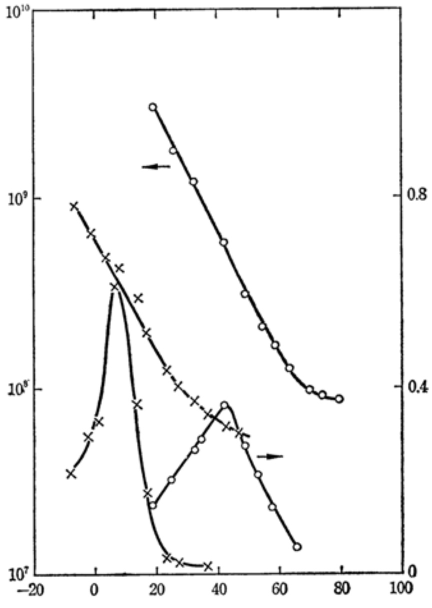

Fig. 7. Thermo-oxidative degradation of air-dried film of unsaturated fatty acid modified alkyd resin observed in G-t, λ-t curves.
× Original film
○ After heating at 105°C for 2 hr.

A Comparison of Thermo-oxidative Degradation of Air-dried and Baked Films.—Smith[6)] reported that the baked film alkyd resin (175°C-1 hr.) decomposed and dissipated completely after being heated at 200°C for 5 days. Miller[5)] reported that the phthalate also suffered decomposition after the baked film of alkyd resin had been exposed (120°C; 1 hr. without the addition of any drying agent) to ultraviolet rays, they described the conjugated carbonyl as especially unstable, as had been recognized by others. FitzGerald[4)] reported that the phthalates decomposed when the baked film of alkyd resin (175°C; 20 min., with the

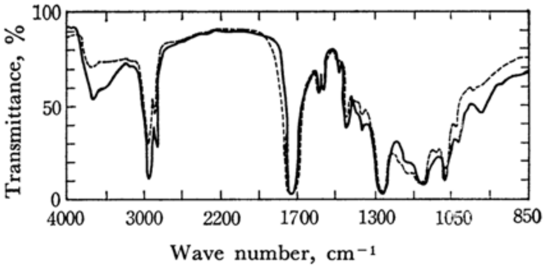

Fig. 8. Thermo-oxidative degradation of air-dried film of unsaturated fatty acid modified alkyd resin observed in infrared spectra.
—— Original film
---- After heating at 105°C for 2 hr.

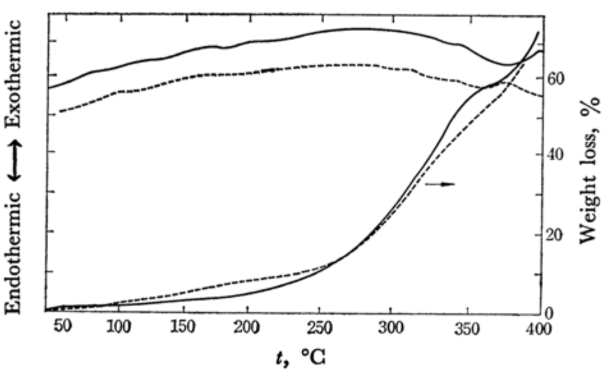

Fig. 9. Thermograms of films of unsaturated fatty acid modified alkyd resin.
---- Air-dried film, —— Baked film

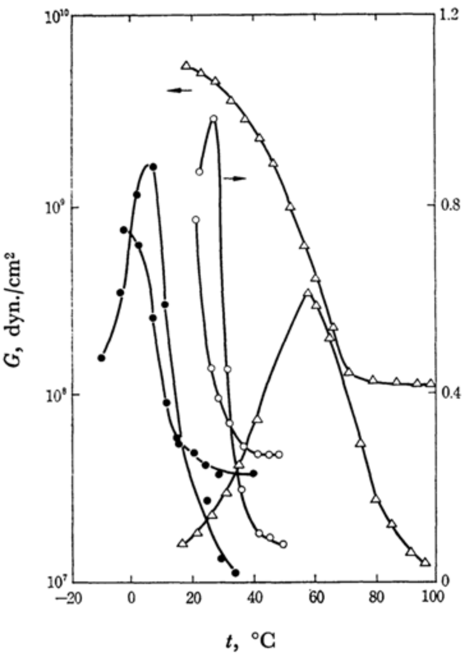

Fig. 10. Thermo-oxidative degradation of baked film of unsaturated fatty acid modified alkyd resin observed in G-t, λ-t curves.

- ● Original film
- ○ After heating at 150°C for 3 hr.
- △ After heating at 200°C for 3 hr.

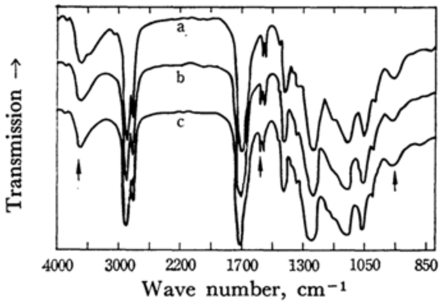

Fig. 11. Thermo-oxidative degradation of baked film of unsaturated fatty acid modified alkyd resin observed in infrared spectra.

- a Original film
- b After heating at 150°C for 3 hr.
- c After heating at 200°C for 3 hr.

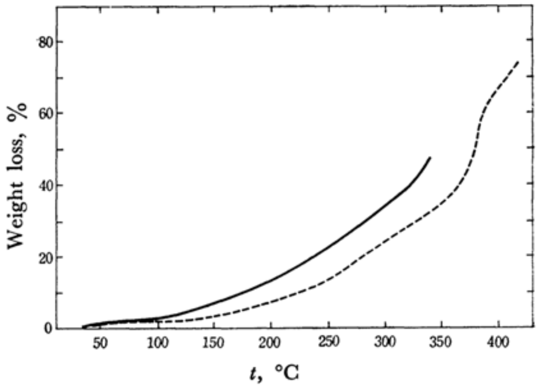

Fig. 12. Thermograms of polymerized oil films (PO).
—— Air-dried film, ---- Baked film

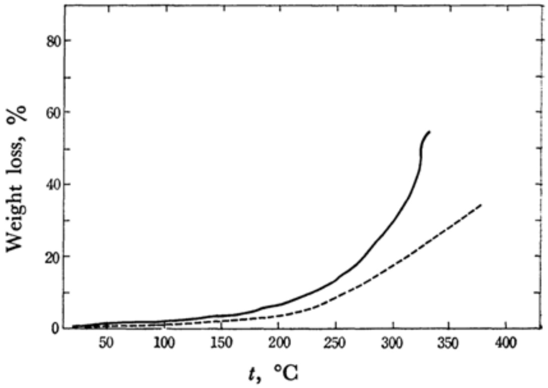

Fig. 13. Thermograms of films of phenolic varnish (R-O).
—— Air-dried film, ---- Baked film

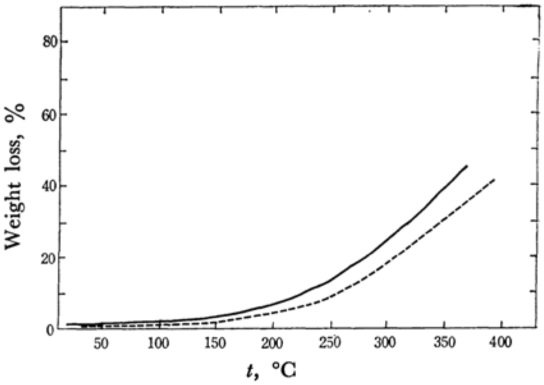

Fig. 14. Thermograms of films of phenolic varnish (N+PO).
—— Air-dried film, ---- Baked film

addition of a drying agent: stored in air for one month) was thermo-treated (120°C-72 hr.), or exposed to ultraviolet rays. Such a decomposition was initiated at the unsaturated part of aliphatic chains and propagated to the glyceride part and the phthalate part; as a result, the alkyd molecules decomposed and dissipated.

When the thermo-oxidative degradations of air-dried and baked alkyd films were compared, it was found the aliphatic chain decomposed more in the case of air drying; nevertheless, it was treated mildly, and the phthalate was unchanged.

As to baked film, the phthalate dissipated after this thermal treating; this result accorded with those obtained by others.

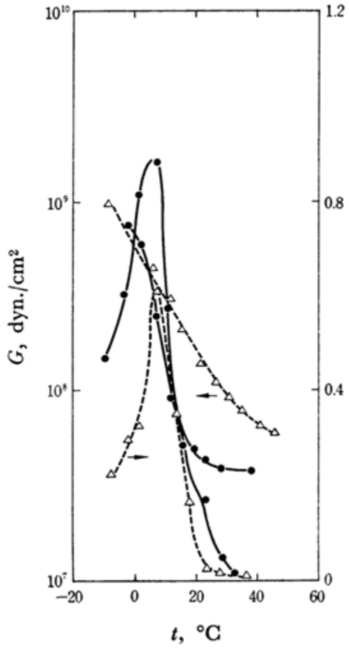

Fig. 15. Comparison of G-t, λ-t curves of air-dried and baked film of unsaturated fatty acid modified alkyd resin prior to thermo-oxidative degradation.
--△-- Air dried film, —●— Baked film

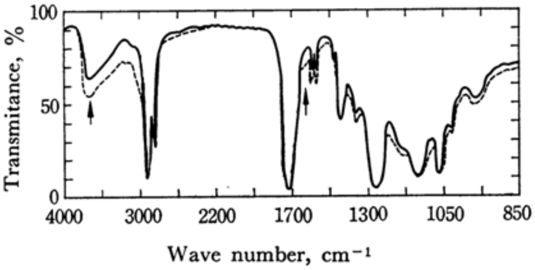

Fig. 16. Comparison of infrared spectra of air-dried and baked film of unsaturated fatty acid modified alkyd resin prior to thermo-oxidative degradation.
---- Air-dried film, —— Baked film

The easy decmoposition of air-dried film is also observed in films of phenolic varnishes and polymerized oil films (see Figs. 12, 13, and 14 and Table VI). Table VI is a comparison of the weight loss during thermal treatment, and Figs. 12—14 are thermograms of air-dried and baked films of phenolic varnishes or polymerized oil exposed in air for the same time and thermal treated under the same conditions.

The infrared spectra, G-t and λ-t curves, and elementary analysis of alkyd films prior to thermal treatment were compared. It was found that:

1) The absorptions near 3500 cm^{-1} and near 1600 cm^{-1}, which are due to conjugated carbonyl, of air-dried film were more intensive (see Fig. 16):

2) The $(T_g)_d$ values are the same, and the shear modulus of plateau region was not observed in air-dried film. The degree of crosslinking of air-dried film is small, suggesting a less crosslinked network structure (see Fig. 15), and

3) The oxygen combined per acyl group in film is nearly the same (see the last column of Table VII).

In combination with these results and the application of the mechanism of autoxidation, it may be suggested that the amount of hydroperoxyl group in air-dried film is more than that in baked film.

Another factor which should be taken account of in connection with easy decomposition of aliphatic chains in the network structure is the effect of drying agents. In this connection, the following five were prepared from a varnish of a composition similar to that of the varnish used in the above experiment.

Film 1.—The varnish, with drying agents (Co 0.02%, Mn 0.02%) added, was coated every other day (6 times) at room temperature.

Film 2.—The varnish, without any drying agents added, was coated and heated at 105°C for 2 hr.; this procedure was also repeated 6 times.

Film 3.—As with Film 2, except that drying agents were added (Co. 0.02%, Mn 0.02%).

Film 4.—The varnish, without any drying agents added, was coated and heated at 105°C for 8 hr.; this procedure was repeated 6 times.

Film 5.—As with Film 4 except that drying agents were added (Co 0.02%, Mn 0.02%).

And their D_{2850}/D_{1590} and D_{3570}/D_{1590} values are compared in Table VIII.

There is an effect of drying agents on the decomposition of aliphatic chains, but the decrease in D_{2850}/D_{1590} is less than that in the thermal treatment of air-dried film.

Therefore, it may be concluded that the easy decomposition of the aliphatic chain, without an accompanying dissipation of the phthalate in air-dried film, is due to the networks containing more hydroperoxyl and conjugated carbonyl groups and their consequent instability, as well as to the presence of drying agents.

From the above results, the extent to which autoxidation is induced by air-drying and baking, and how the structure of the network affects the thermo-oxidative degradation of oxidative polymerized films, have been established.

Summary

1) The aliphatic chains decomposed more easily, and the phthalate was rather more stable in oxidative thermal treatment in air-dried film than in baked film of unsaturated fatty acid-modified alkyd resin.

2) This is a result of the presence of more hydroperoxy and conjugated carbonyl groups, and of the drying agent in air-dried film.

3) After the thermo-oxidation of oxidative polymerized films, the glass transition temperature, the hardness of film, and the degree of crosslinking of film showed an increase: this is considered to be the result of the oxidative decomposition and crosslinking of aliphatic chains. It has been observed also that the impact strength of baked film decreased upon thermo-oxidation.

4) The drying agents contained in film accelerated the decomposition of aliphatic chains during thermal treatment.