Kinetics of Thermal Polymerization of Shellac. Part IV.   Evolution of Water During Curing

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Synopsis

The course of curing was followed by estimating the amount of water evolved at different intervals of time at 150°C. (using compressed air as a carrier gas) in an effort to support the previously proposed mechanism of inter- and intramolecular reactions. Moreover, the effects of various flow rates, gases, and temperatures on the evolution of water were also studied.

INTRODUCTION

It was reported in a previous communication[1] that when shellac is cured thermally, the reaction proceeds through two distinct stages, viz., a pregelation phase and a post-gelation phase.   In the pregelation phase, the linear hemiacetal polymer is formed as a consequence of intermolecular reaction through elimination of water, but near the gel point, intramolecular reactions take place simultaneously with the intermolecular reaction and culminate in the post-gelation phase.   The intramolecular reactions involve the formation of ester and ether links by loss of water molecules leading finally to a thermoset product.   Moreover, throughout the entire curing process there is gradual increase of unsaturation[2] due to reaction between a hydroxyl group and the hydrogen atom attached to the adjacent carbon atom poorer in hydrogen with removal of water.

This water is a continuous by-product of the polymerization process. Therefore, an assay of the amount of water thus chemically formed would furnish a measure of the extent of reaction as well as give support to the mechanism proposed for polymeric reaction.

However, in this connection it will be well to mention that Nagel and Körnchen[3] also observed that the reaction is accompanied by a gradual evolution of water vapor and that no other volatile substance is lost. They estimated the amount of water evolved at different temperatures from the weight loss and the absorption in $CaCl_2$ U-tube in the presence of gases like nitrogen and carbon dioxide.   According to them, the amount of water evolved, after heating at 200–220°C. for 2 hr., was 5.26% and on further heating the evolution of water continued indefinitely without ever reaching an endpoint.

Thus for an understanding of the mechanism of heat-hardening of shellac, it seemed of particular interest to make a more detailed investigation of this aspect.

The present paper summarizes the investigations carried out and conclusions drawn therefrom.

EXPERIMENTAL

As it was reported by Nagel and Körnchen[3] that the percentages of water evolved calculated from the absorption in a $CaCl_2$ U-tube and from the weight loss were the same, the latter method was adopted for the present investigation.

Apparatus and Adjustments

A stream of compressed air from an air compressor pump was employed to carry away the moisture from the reaction vessel instead of an inert gas. Since the polymerization of shellac is carried out in test tubes open to the atmosphere, the compressed air will exert no influence on the polymerization process.

For dehydration, the compressed air was first bubbled through a gas-washing bottle containing concentrated H_2SO_4 and then through a cotton plug (to absorb the fumes of H_2SO_4) to a flowmeter. After that, it was again passed through another cotton plug (to retain the traces of liquid of the flowmeter) before entering a dry $CaCl_2$ U-tube (dried in an oven at 110°C. for 1 hr.) connected, in turn, to a concentrated H_2SO_4 trap, having an inlet and outlet tube, to indicate the flow as well as the rate of flow of the carrier gas. The flow rate of the compressed air was regulated by means of the flowmeter and measured from the volume displacement of water per unit time contained in a measuring cylinder inverted over a glass trough containing water. The flow rate of the compressed air was kept constant (185–205 ml./min.) in all experiments. For heating, a thermostatically controlled oil bath was used whose temperature was maintained at 150 ± 2°C.

Determination of H_2O Evolved

To determining the water evolved during a given reaction time, about 0.5 g. of dried, dewaxed, and decolorized shellac was weighed into a tared 100-ml. glass-stoppered pyrex round-bottomed flask with a stand. After the adjustment of the flow rate of air and the temperature of the oil bath, the glass-stopper of the reaction flask was replaced by ground-joint inlet and outlet tubes, which were connected to a $CaCl_2$ U-tube and concentrated H_2SO_4 trap, respectively. Immediately afterwards, the reaction flask was dipped into the oil bath and a stopwatch was started simultaneously. After a given interval of time, the flask was taken out from the oil bath and carefully disconnected, the stopper being replaced immediately. The adhering oil was then wiped off and the flask was dried under vacuum.

After that, the flask was reweighed along with stopper and stand. From the weight loss, the percentage of water evolved was calculated. Experiments were repeated for different intervals, and the results so obtained are presented in Figure 1.

The effects of various flow rates, gases, and temperatures on the evolution of water were also studied in similar fashion.
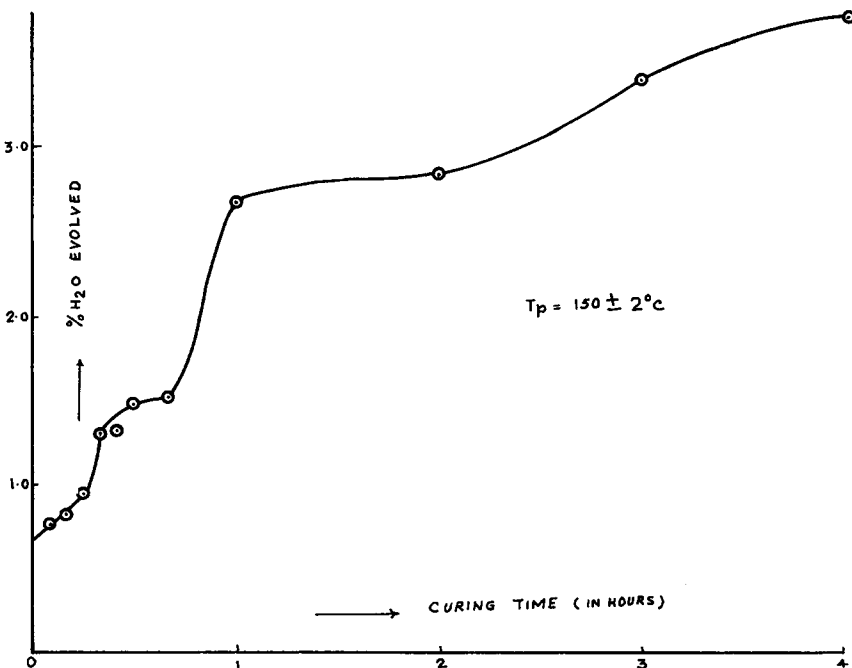

Fig. 1. Variation of per cent H_2O evolved with curing time.

RESULTS AND DISCUSSION

From Figure 1, it is evident that the variation of the percentage of water evolved with curing time remains linear up to the pregelation stage, but near the gel point, there is a sudden rise followed by gradual increase (in somewhat stepwise fashion) leading to an unsmooth curve. Explanations for such behaviors will be offered in the following discussion.

Evolution of Water during the Pregelation Stage

The percentage of water evolved in the pregelation stage at 150°C. is given in Table I. A plot of per cent H_2O evolved versus the curing time is shown in Figure 2. As the time of gelation t_g of the sample under investigation was 19 min. 37 sec. it is quite expected that the percentage of water evolved after 20 min. would be much higher than the values extrapolated from shorter curing times and would depart from linearity. This is so, as is apparent from Figure 2. This supports to the previous finding[1] as well as the general principles of the condensation polymerization.

TABLE I

Evolution of Water during the Pregelation Stage ($T_p = 150 \pm 2°C.$, $t_g = 19$ min. 37 sec.)

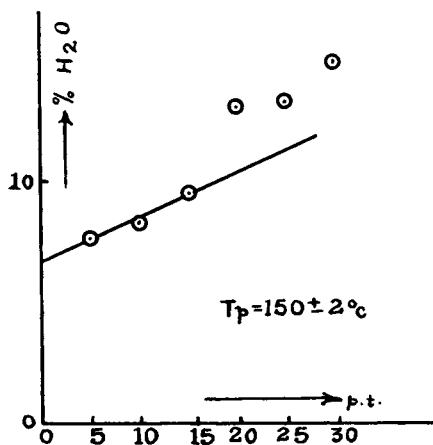| Cure time p.t., min.	Flow rate, ml./min.	H₂O, %		$k \times 10^4$
5		0.76	Pregelation	3.0
10		0.82	stage	2.5
15		0.94		3.0
20	185–205	1.30	Post-gelation	
25		1.32	stage	
30		1.48		
			Avg.	2.83

Fig. 2. Evolution of water in the pregelation stage.

As shown in the earlier investigations,[1,2] the intermolecular reaction of the pregelation stage is of zero order. Hence, the rate of reaction would be equal to the rate constant. In the present case, the rate or the rate constant of the intermolecular reaction[1] was found by (1):

$$R_p = d(\% \ H_2O)/ \ dt = k \qquad (1)$$

Values, so obtained, are given in Table I. The average value for k is thus 2.83×10^{-4}. The value for k obtained from viscosity measurements[1] is 2.93×10^{-4}. The close agreement between these two values supports the previous results.

Elucidation of the Mechanism of Intermolecular Reaction

In preceding papers[1,2] it was shown that at the gel point, only tetramers are formed. Moreover, on the basis of chemical investigations an attempt was also made to represent the chemical formula of the tetramer.[2] In accordance with the proposed formula, the percentage of water evolved at

the gel point should be equal to $3 \times 18 \times 100/4000$ or 1.35 (with the assumption that the molecular weight of shellac is 1000).   Since the t_g for the sample under investigation was 19 min. 37 sec., the percentage of water evolved after 20 min. should be about 1.35%.   The results of the experiment give a value of 1.30–1.32%, and thus affords further evidence for validity of the proposed mechanism of intermolecular reaction of the pregelation stage.

It may be mentioned at this point that the linear shellac polymer formed in the pregelation stage, can be compared with the cellulose chain comprised of β-D-glucose units linked together by 1,4-glycosidic bonds having one hemiacetal and three hydroxyl groups in each glucose unit.

Since the cellulose can be acetylated only to a triester,[4] it is evident that neither the hemiacetal nor the glycosidic linkage is broken by treatment with the acetylation mixture.   Similarly, it is expected that during acetylation of shellac polymer, no cleavage of such bonds would take place and consequently, acetylation would provide a measure of only free hydroxyl groups present in the polymer.   However, interference due to aldehydic group can not be neglected.   Moreover, the hemiacetal and glycosidic bonds are very stable and can be decomposed only by oxidation with periodic acid, Br_2, etc., which invariably leads to the formation of free carboxyl groups.   As the mode of decomposition is solely dependent on the type of the oxidizing agent used, a more exact idea of the structure of linear polymers can be gathered from such oxidative methods.

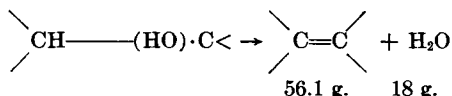## Evolution of Water during the Post-Gelation Phase

The percentage of water evolved in the post-gelation stage is shown in Table II.   In the post-gelation stage, the evolution of water first rises slowly and then, suddenly (at the end of 1 hr.) increases sharply; thereafter it increases steadily and indefinitely as stated above.   Despite the complexity of the reaction an effort will be made here to understand the nature of evolution of water during the post-gelation phase on the basis of the reaction scheme proposed for the gelation process.   In the preceding paper,[2] it was stated that there is no decrease in hydroxyl value due to the acetal formation reaction.   However, hydroxyl groups are consumed by three types of interactions: (1) between the carboxyl and hydroxyl groups, (2) between the hydroxyl group and the hydrogen atom attached to the adjacent carbon atom, and (3) between two hydroxyl groups, all leading to the elimination of water.   These facts may enable us to compute the amount of water evolved after a given interval of time at a particular temperature.   For this computation, let us consider all possible reactions one by one.   Main reactions responsible for the evolution of water are (1) esterification, (2) formation of double bonds, and (3) etherification.

Esterification.   The reaction between a carboxyl and a hydroxyl group leading to the formation of an ester can be represented as:
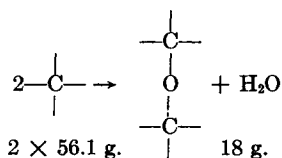
$$RCOOH + HOR \rightarrow RCOOR + H_2O$$
$$\text{56.1 g.} \qquad\qquad\qquad\qquad \text{18 g.}$$
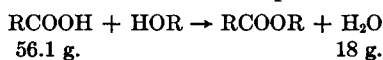
It is evident that if the decrease in acid value is 56100 units, the amount of water evolved would be equal to 18 g. Now if Δ A.V. represents the decrease in acid value after a given reaction time at a particular temperature, then the amount of water split off would be equal to 18 Δ A.V./56100. This would correspond to the curing of 1 g. of the substance. Therefore, the percentage of water given off would be 18 Δ A.V./561.

Formation of Double Bonds. Similarly, the reaction between a hydroxyl group and a hydrogen atom attached to the adjacent carbon atom leading to the formation of a double bond can be represented as:

$$\underset{\diagup}{\overset{\diagdown}{}}CH\text{———}(HO)\cdot C< \rightarrow \underset{\diagup}{\overset{\diagdown}{}}C{=}C\underset{\diagdown}{\overset{\diagup}{}} + H_2O$$
$$\qquad\qquad 56.1\text{ g.}\quad 18\text{ g.}$$

Evidently, if Δ U.V. is the change in hydroxyl equivalent of unsaturation value, then, on a similar basis, it can be shown that the percentage of water evolved would be equal to 18 Δ U.V./561.

Etherification. The reaction between two hydroxyl groups leading to the formation of an ether link and water can be represented as:

$$2\text{—}\overset{|}{\underset{|}{C}}\text{—} \rightarrow \begin{matrix} \text{—}\overset{|}{\underset{|}{C}}\text{—} \\ O \\ \text{—}\overset{|}{\underset{|}{C}}\text{—} \end{matrix} + H_2O$$
$$2 \times 56.1\text{ g.}\qquad\qquad 18\text{ g.}$$

If the decrease in hydroxyl value is 2×56100 units, then the amount of water evolved would be equal to 18 g.

Now, if the decrease in the hydroxyl value due to etherification is equal to b, then the percentage of water evolved would be equal to $18b/(561 \times 2)$. Again, if the decrease in hydroxyl units due to its reaction with carboxyl group and the adjacent hydrogen atom is equal to a, then,

$$a = \Delta\text{ A.V.} + \Delta\text{ U.V.} \qquad (2)$$

Therefore,

$$b = \Delta\text{ H.V.} - (\Delta\text{ A.V.} + \Delta\text{ U.V.}) = \Delta\text{ H.V.} - a \qquad (3)$$

where Δ H.V. represents the total decrease in units of hydroxyl value after a given reaction time.

Therefore, the total percentage of water evolved after a given time at a given temperature can be expressed as:

$$\%\text{ H}_2O = (18/561)\,(a + {}^1\!/_2 b). \qquad (4)$$

The percentages of water evolved, computed from the data of the preceding paper[2] by use of eq. (4), are given in Table II; these values compare well with the present data to a great extent, supporting thereby the plausibility of reaction mechanism proposed for the gelation. Some differences

in these values may be ascribed largely to different t_g values of samples used as well as to errors incorporated in evaluation of chemical constants and percentages of H_2O evolved.

Dependence of H_2O Evolved on the Fraction of Reacted Hydroxyl Groups

From the eqs. (2)-(4) it can be shown that

$$\% \ H_2O = (18/561) \ (a + {}^1\!/_2 \ \Delta \ H.V. - {}^1\!/_2 a)$$
$$= (18/2 \times 561) \ (a + \Delta \ H.V.) \tag{5}$$

Now, a must be a function of Δ H.V. To find out the relation, a was plotted against Δ H.V. (Fig. 3). A straight line was obtained which could be represented by eq. (6):
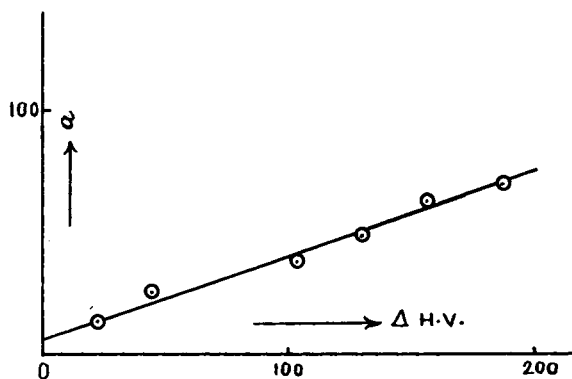
$$a = x \ \Delta \ H.V. + c \tag{6}$$

Fig. 3. Plot of a vs. Δ H.V.

where x and c are constants. Substituting the value of a in eq. (6) we have

$$\% \ H_2O = (9/561) \ (x \ \Delta \ H.V. + c + \Delta \ H.V.)$$
$$= (9/561) \ [(x + 1) \ \Delta \ H.V. + c] \tag{7}$$

Now, let Δ H.V./H.V. $= p$, where, H.V. is the hydroxyl value of the sample.

Therefore,

$$\Delta \ H.V. = p \ H.V. \tag{8}$$

and

$$\% \ H_2O = (9/561) \ [p(x + 1) \ H.V. + c] \tag{9}$$

Now, x, H.V., and c are constants. Hence, a plot of H_2O against p should be linear. The values of p and H_2O, calculated with the help of the above equations on the basis of data of the preceding paper,[2] are given in Table II.

TABLE II
Evolution of Water during Post-Gelation Stage ($T_p = 150 \pm 2°C.$)

Cure time p.t., hr.	Flow rate (air), ml./min.	H_2O, %	H_2O, %[a]	p[a]
$^1/_3$	205	1.30	0.58	0.085
$^2/_3$	185–190	1.52	1.14	0.171
1.0	190	2.68	2.33	0.413
2.0	195	2.84	2.88	0.499
3.0	210	3.42	3.53	0.622
4.0	200	3.81	4.15	0.762

[a] Calculated on the basis of data of the preceding paper.[2]

A plot of p vs. per cent H_2O is shown in Figure 4. This plot is linear, which implies that the percentage of water evolved is a linear function of the ratio of reacted and total hydroxyl groups present at time t (i.e., p). Therefore, the value of per cent H_2O corresponding to $p = 1$ would represent the total amount of water given off during the entire process of curing. From Figure 4, this amounts to about 5.65%. This fact can be easily verified either by increasing the time or the temperature of curing.
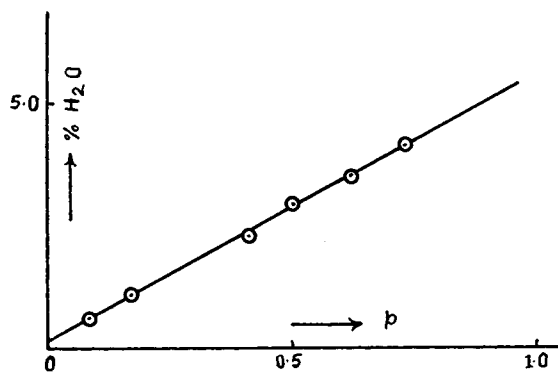

Fig. 4. Plot of p vs. per cent H_2O.

Effects of Flow Rates and Carrier Gases on the Evolution of Water

The results showing the effects of various flow rates and carrier gases on the evolution of water are shown in Table III.

A critical review of the data reveals the fact that, as expected, air has no catalytic influence on curing. Moreover, it may be also inferred that the percentage of water evolved after a given reaction time at a particular temperature is independent of the flow rate as well as of the nature of the gas.

TABLE III
Effects of Flow Rate and Carrier Gas on the Evolution of Water ($T_p = 150 \pm 2°C.$, p.t. = $^2/_3$ hr.)

Gas	Flow rate, ml./min.	H_2O, %
Air	185.0	1.52
''	300.0	1.52
N_2	205.0	1.62

Effects of Temperature on the Evolution of Water

The effects of temperature on the percentage of water evolved during a given reaction time are presented in Table IV. It is apparent that the

TABLE IV
Effects of Temperature on the Evolution of Water

Temperature T		Cure time p.t., hr.	Flow rate, ml./min.	H_2O, %	log (% H_2O)
°C.	°K.				
125	398	3	205.0	1.28	0.11
150	423	''	''	3.42	0.53
175	448	''	''	5.44	0.74

higher the temperature of curing, the greater is the percentage of water evolved.   Moreover, it has been established that[5]

$$P = A \exp (BT) \tag{10}$$

where P is the percentage of the product formed after time t, T is the temperature of reaction (in absolute units), and A and B are constants.   Since eq. (10) is a general equation, we may write:

$$\log (\% \ H_2O) = \log A + (B.T./2.303) \tag{11}$$

Evidently, a plot of log (% H_2O) against T should be a straight line.   Such a plot is shown in Figure 5.   Still further evidence for the applicability of the above relationship was provided by the data of Nagel and Körnchen[3] presented in Figure 6.

Furthermore, eq. (11) permits the calculations to be made for the percentage of water evolved at any temperature after a given reaction time provided the values of constants A and B are known.
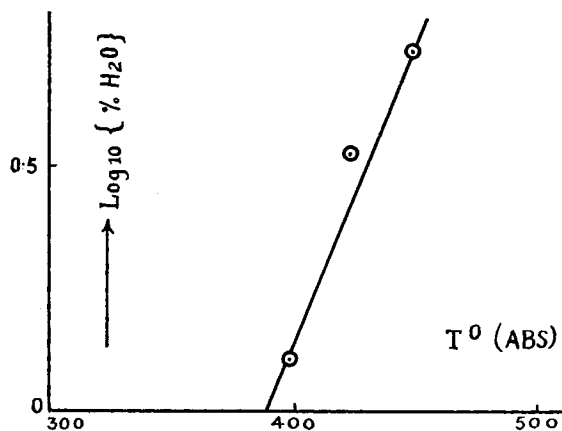
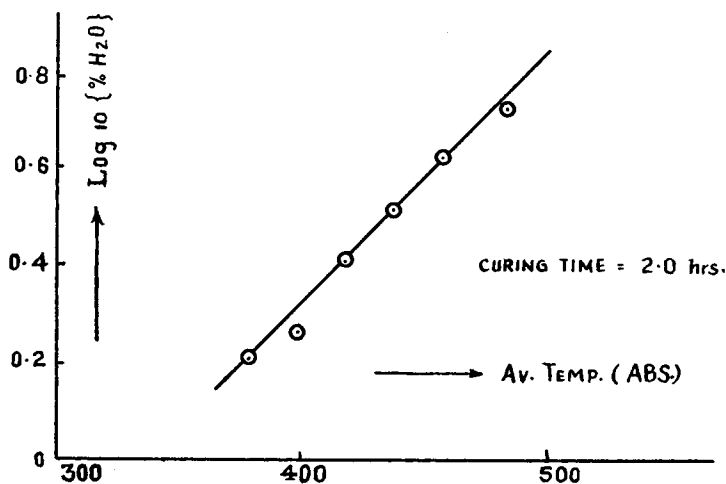Fig. 5. Dependence of per cent H_2O on temperature.   Curing time = 3.0 hr.

Fig. 6. Dependence of per cent H_2O on temperature.   Data of Nagel and Körnchen.[3]

References

1. Kumar, A., *J. Appl. Polymer Sci.*, **8,** 1185 (1964).
2. Kumar, A., *J. Appl. Polymer Sci.*, **9,** 3263 (1965).
3. Nagel, W., and M. Körnchen, *Wiss. Veroef. Simens Konzern.*, **6,** 235 (1927).
4. Malm, J., et al., *Ind. Eng. Chem.*, **38,** 77 (1946); *ibid.*, **47,** 955 (1955).
5. Kumar, A., unpublished work.

Résumé

Antérieurement, on a proposé un mécanisme inter- et intramoléculaire pour le recuit. Pour étayer le mécanisme, on a suivi la réaction en mesurant la quantité d'eau libérée à différents intervalles de temps et à 150°C (en utilisant de l'air comprimé comme gaz porteur).   De plus, on a étudié l'influence des différentes vitesses d'écoulement, de la nature des gaz et de la température sur la libération de l'eau.

Zusammenfassung

In der vorliegenden Mitteilung wurde der Härtungsverlauf durch Bestimmung der zu verschiedenen Zeitintervallen bei 150°C entwickelten Wassermenge (mit komprimierter Luft als Trägergas) verfolgt, um den Mechanismus der früher vorgeschlagenen inter- und intramolekularen Reaktionen zu bestätigen. Weiters wurde der Einfluss einer Änderung der Strömungsgeschwindigkeit, verschiedener Gase und Temperaturen auf die Wasserentwicklung untersucht.