

A Study of
The Baking Process of Oil Varnishes
and Enamels

A disertation presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Master of Science in Chemistry by

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I INTRODUCTION

Before any object which has been given a coat of varnish or enamel is ready for use, the varnish film must be converted to the solid state. This is accomplished either by allowing the film to air dry or by baking it. For a considerable number of purposes air drying is satisfactory. However, in some of our largest industrial applications, as for example in portions of the electrical and automobile industries where the most severe requirements are demanded of a varnish film, baking is extensively used. In certain of these manufacturing operations, as in the manufacture of enameled wire and varnished cambric, the product is almost wholly dependent upon the baking process and the way in which this process is carried out.

Nevertheless, in spite of the extensive industrial use of baking, as one of the two means of converting a varnish film into the solid state, very little is known of what takes place and practically nothing of the fundamental laws that govern the process. It was the desire of improving our knowledge on these points that prompted this investigation. It is interesting to note that this problem corresponds essentially

to No. 90 given in "A List of Research Problems in Chemistry"⁽¹⁾ released by the Division of Chemistry and Chemical Technology of the National Research Council.

II HISTORICAL

For centuries the manufacture of varnishes and enamels was a distinct art. As in the case of the famous French wine and perfume industries, formulae were zealously guarded and often remained in one family for generations. Since about 1850 a constant scientific attack has been maintained on the varnish industry, with the result that today we have a working knowledge of the materials, processes, and reactions that are employed.

Lewkowitsch⁽²⁾, Fahrion⁽³⁾, Friend⁽⁴⁾, Morrell and Waele⁽⁵⁾, Morrell⁽⁶⁾, Morrell and Wood⁽⁷⁾ give an excellent treatment of the composition of the materials used in varnishes. The drying oils which are the basic components of most varnishes, are shown to be mixed glycerides of unsaturated fatty acids of the oleic $C_{18}H_{34}O_2$, linolic $C_{18}H_{32}O_2$, and linolenic $C_{18}H_{30}O_2$ series.

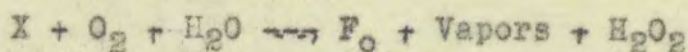
Morrell⁽⁶⁾, "Varnishes and Their Components", 1925, pages 10-14, 42-44 gives a very good summary of the reactions that occur in the conversion of these drying oils to the solid state. As it was not until the establishment of the electrical and automobile industries that baking was used, it is not surprising,

however, that only the reactions occurring during air drying are taken up, and that baking is neglected.

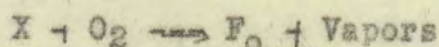
Morrell shows that the setting process of a varnish in air at room temperatures, after evaporation of all or most of the solvent, is principally a reaction with oxygen, whereby the oxygen attaches itself to the double bonds of the unsaturated triglycerides leading to a gradual thickening and ultimate coagulation to the solid state. Morrell⁽⁶⁾, page 42, writes these reactions schematically as follows:

- (1) $X + O_2 \rightsquigarrow XO_2$
- (2) $XO_2 + X \rightsquigarrow 2XO_2$ (no drier present)
- (3) $XO_2 + X \rightsquigarrow 2XO$
- (4) $XO + XO_2$ (Thickening process)
- (5) $XO_2 + H_2O \rightsquigarrow XO + H_2O_2$
- (6) $XO_2 \rightsquigarrow$ Vapors (Decomposition)

where X represents the oil molecule. Combining the above reactions and letting F_o represent the varnish or oil film produced, we obtain for the setting process, in ordinary air, the equation



or, for dry air, the simpler expression



an equation referred to later.

Genthe⁽⁸⁾ seems to have been the first to study the kinetics of the air drying process. He followed the reaction quantitatively by measuring the rate at

which oxygen was absorbed, taking full consideration of such volatile products as were formed. He showed the process to be essentially autocatalytic and, as such, that it obeyed Ostwald's autocatalytic equation, which is:

$$\frac{dx}{dt} = K(m + x)(a - x)$$

where a = total volume of absorbed oxygen,

x = volume absorbed at time t ,

m = a constant proportional to the concentration of the catalyst. In the case where m is negligible Genthe employs the simpler equation:

$$\frac{dx}{dt} = k_1 x(a - x)$$

Fahrion⁽⁹⁾, Fokin⁽¹⁰⁾, Coffey⁽¹¹⁾, Rhodes and VanWirt⁽¹²⁾, Rogers and Taylor⁽¹³⁾ also have investigated the kinetics of the reaction and agree in general with Genthe. Rogers and Taylor include an excellent review of the literature in this field.

Genthe, Coffey, Rogers and Taylor consider the effect of temperature but carry their experiments only up to 100°C. All three investigators agree that as the temperature is increased any autocatalytic or catalytic effect that may be present is minimized. Genthe introduces the conception of a side reaction, which he postulates is a combustion process whose rate is directly proportional to the oxygen concentration, and then gives as an equation that better fits his high temperature results:

$$\frac{dx}{dt} = k(a + x) + k_1x(a - x)$$

where k = velocity constant of the side reaction.

The work of Genthe, Coffey, Rogers and Taylor constitute the only investigations that were found, in which baking, as a means of setting varnish films, is discussed to any degree. As true baking is usually carried out^{over 100°C}, it is apparent that our knowledge of the baking process is meager.

Genthe's equation for his results at the higher temperature is interesting and it is quite evident that, as we approach a higher and higher temperature, if we follow Genthe's argument, k_1 gets smaller and smaller compared to k . The second term in the equation will then become negligible and we have

$$\frac{dx}{dt} = k(a - x)$$

the equation for a first order reaction. This is the equation, as will be subsequently shown, which was found to best express the experimental facts that were obtained in the present investigation.

Salway⁽¹⁴⁾, Morrell⁽¹⁵⁾, Leeds⁽¹⁶⁾, Schumann⁽¹⁷⁾, Wolff⁽¹⁸⁾, Long, Knauss and Smull⁽¹⁹⁾, Nagel and Gruss⁽²⁰⁾, Rhodes and Welz⁽²¹⁾ deal with the reactions that occur in the thermal treatment of drying oils prior to and during the manufacture of varnishes. They show that heat causes an inter or intramolecular tieing up of the oil molecules, that is, polymerization. They point out that the polymerization reactions are quite distinct from those which take place with oxygen, and that under certain conditions

both occur simultaneously. They give as the changes that occur on heating: (1) increase in viscosity, (2) increase in density, (3) decrease in hexabromide number, (4) increase in acid value, (5) decrease in iodine value, (6) increase in apparent molecular weight. They show that polymerization is independent of the atmosphere in which it is carried out. As baking fundamentally involves heat, polymerization must be considered in the setting process of a varnish where baking is employed.

III THEORETICAL

Let the symbol V_a refer to any varnish or enamel.

Then if

B represents the varnish base, and

ΣS the solvent or solvents

it is obvious that

$$B + \Sigma S = V_a \quad (1)$$

When a varnish or enamel is exposed in a thin film to any given set of conditions, primarily two things can occur, namely:

- (A) Evaporation of the solvents
- (B) Transition of the base to a useful state which we refer to, practically, as the dry or baked state.

(A) The Evaporation of the Solvents

This process can be represented by equation:

$$V_a - \Sigma S = B$$

or $V_a = B + \Sigma S \quad (2)$

Both expressions are simply equation (1) written in another form. The rate at which this reaction proceeds depends upon several things, namely:

- (a) The temperature and pressure to which the reaction is subjected.
- (b) The evaporation characteristics of ΣS .
- (c) The rate of removal of the gas phase as formed by ΣS .
- (d) The adsorptive (i.e. retaining) power of the base for the ingredients that make up ΣS .

Except for (d) the usual laws of evaporation hold for this reaction. However, with the materials that are generally considered, (d) becomes a very important factor that cannot be neglected. Thus, there is evidence which indicates that in a film made from a 55° naphtha solution of a linseed oil base varnish at a temperature even as high as 200°C, some of the naphtha is retained in the film, particularly in early stages of the baked state, although the temperature here is well above the boiling point of the naphtha and the time sufficient to absolutely volatilize an equivalent film of pure naphtha.

(B) Transition of the Base to the Useful State

I. This transition is primarily the conversion of the base from a sol to a gel state; that is, a process physically, although not chemically, analogous to the conversion of a concentrated solution of gelatine to its jelly (gel) condition.

In the case of the substances that are usually dealt with in varnishes and enamels, the gel state is approached through the building up of molecular aggregates which can be brought about in two ways; namely, through

- (a) Oxygen linkage, i.e. the familiar oxidation process.
- (b) Intermolecular linkage, usually referred to by the general term--polymerization.

(a) Oxygen linkage

This process can be represented by the following chemical reaction:



where B = the varnish base

F_o = the set film, with oxygen only as the contributing factor. Like other chemical reactions, this reaction has a reaction velocity which we will call k_o , and therefore, also a temperature coefficient.

This equation is identical with the composite equation derived from Morrell's⁽⁶⁾ schematic representation of the oxidation process previously discussed. Genthe's⁽⁸⁾ work shows that the process is autocatalytic at room temperatures, with a first order side reaction beginning to be in evidence as the temperature reaches 100°C. The experimental work given later indicates that when the temperature is increased still higher the process obeys quite well the laws of a true first order reaction.

(b) Intermolecular linkage

This process is more difficult to deal with as it depends considerably upon the chemical nature of the substances present in the base and upon the various types of intermolecular reactions possible between these various substances.

Every base is initially composed of a number of substances $x_1, x_2, x_3 \dots \dots x_m$. As expressed by the equation

$$B_0 = a_1x_1 + a_2x_2 + a_3x_3 \dots \dots a_mx_m \tag{4}$$

where B_0 represents the base in its initial state,

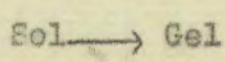
$x_1, x_2, x_3 \dots \dots x_m$ the respective components, and

$a_1, a_2, a_3 \dots \dots a_m$ the respective amounts of each component present.

In the preparation of the base intermolecular reactions, decomposition reactions, and intermixing, usually of a heterogeneous nature occur. The preparation process in its most general form is given by

$$a_1x_1 + a_2x_2 + a_3x_3 + \dots \dots a_mx_m = B + u_0 \tag{5}$$

where u_0 represents such condensation, decomposition, inter-reaction products, and such gases or vapors as may be formed or evolved. The base in this condition is, of course, still in the sol state. Carrying the base into the gel state these reactions continue although gelation itself is, of course, but



Setting a varnish film under conditions that involve only polymerization can, therefore, be expressed as

$$B = F_p - u \tag{6}$$

where F_p = the set film due to these intermolecular linkages only.

u = any further condensation or intermolecular products necessary to produce F_p .

As in the case of the F_o reaction this equation also has a reaction velocity which we will call k_p , and a temperature coefficient.

In the case of our common drying oil base varnishes baked under the usual conditions, i.e. over 135°C in air, it will be shown that $k_o > k_p$; in other words that the oxidation reaction velocity is greater than the intermolecular reaction velocity. Hence reaction (3) predominates and oxidation controls the setting process.

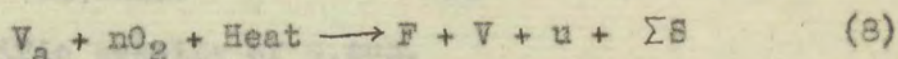
II While this conversion from sol to gel state takes place with every varnish base, in practically no case does this conversion bring the base into the useful state. Something further than merely producing a gel condition has to occur in order that the varnish film may exist in the condition which the non-technical man calls the "dry" or "baked" state (which will be termed the useful state).

Realization of this is why F_o and F_p are referred to above as the set films rather than the final films.

the reaction, expressed by equation (7) above, is applicable.

It must be remembered that although these several reactions involved in the transition of the base to the useful state have been treated as separate and distinct steps, actually the whole process is not quite so simple, one reaction being superimposed upon the other. However, the general order and tendency of occurrence of the reactions is as outlined.

Combining the various reactions that can occur when a varnish film is set, by baking, the general equation



is obtained as representing the baking process. In form this equation is similar to equation (3), the general expression for the air drying process, except that it contains the term u , to take care of the volatile products formed in the polymerization reaction; and that F may vary in composition, i.e. in the amounts of F_o and F_p present, depending upon the conditions under which the baking takes place.

The experimental work shows that the baking reaction obeys the laws of a first order reaction as a first approximation and follows Arrhenius's⁽³²⁾ rule in the relationship between reaction velocity and temperature.

IV MATERIALS

Unless otherwise mentioned, the Varnish used was made up according to the following formula:

Raw Chinawood Oil	363	pts. by wg.
Raw Linseed Oil	110	" " "
Rosin #192	127.5	" " "

all the other materials being of such purity as to pass G.E. Co. purchasing specifications.

The varnish was prepared by heating the above ingredients at 270°C for 1 1/4 hours, cooled to 160°C, then cut with a mixture of

Coal Tar Oil	720	pts. by wg.
Kerosene	30	" " "

to a specific gravity of 0.890.

The above varnish was chosen as it is representative of the type used industrially where the baking process is employed.

The aluminum test strips on which the varnish films were made came from .008" thick pure sheet aluminum. The dimensions of the strips were 1" x 2 1/2", care being taken that all strips used were the same size.

The gases used were of standard laboratory purity and were dried by passing through sulphuric acid and over phosphorous pentoxide.

V APPARATUS

1. The Baking Oven

The baking oven employed was of special design and is illustrated in Fig. 1. It consisted of two concentric hard glass cylinders, the inner one acting as

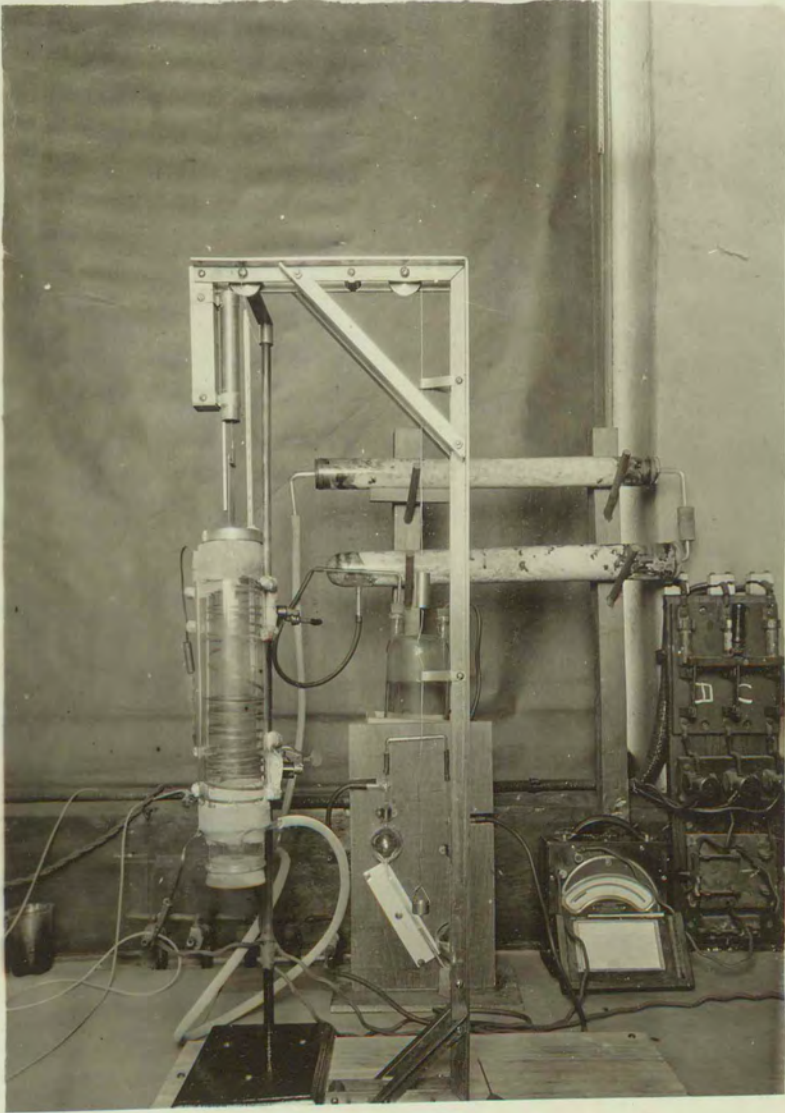


Figure I

the baking chamber, the outer one as insulation.

The inner cylinder was 2 1/4" in diameter and 15" long. It was wound with twenty turns of .125" x .018" nicrome wire and provided at its base with a sidearm to allow for conditioning of the baking chamber.

The outer cylinder was 3" x 12". It was slipped over the inner cylinder and fastened thereto with asbestos waterglass cement.

The bottom of the baking oven was closed with a rubber stopper, wrapped with asbestos paper for insulation, through which was inserted a calibrated copper-constantine thermocouple.

The top of the oven was closed with a chrome steel cap containing a 2" x 1/4" rectangular slit for introduction of the samples and removal of the vapors.

The baking oven, as shown in Fig. 1, was mounted in a vertical position under a counter weight device to allow for rapid insertion and removal of the test strips.

The conditioning of the baking oven was controlled by a flow meter separately calibrated for each of the several gases used.

The temperature was controlled by resistance in the heating circuit.

2. Dip Machine

The dip machine is shown in Fig. 2. It consisted of a 1/200 h.p. type, S D Motor, which was directly connected to a suitable set of gears, allowing for dipping

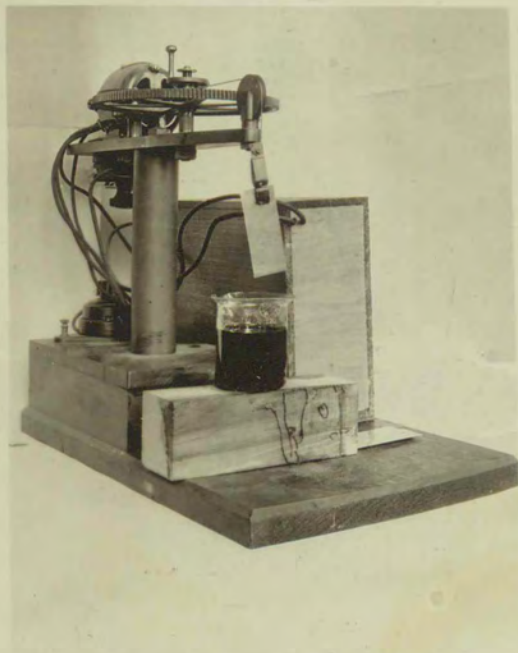


Figure II

of the test strips at a rate of 2 to 4 feet per min.

3. Spectrophotometer

The spectrophotometer used was a Keuffel and Esser Color Analyzer, Model E, No. 51131.

VI EXPERIMENTAL PROCEDURE

The set (V_s), useful (V_u), and deteriorated or useless (V_f) states of a varnish film are usually determined in a very arbitrary manner, the set state being the time when the film is just dry to the touch; the useful state, when the film is non-tacky, both when warm and cold; the useless state, when the film cracks or checks on the slightest abuse. The determination of these points in this fashion is by no means suitable for studying the baking process quantitatively. A method had to be devised whereby the condition of a baked film could be expressed in some units, perhaps relative to be sure, but with some degree of accuracy and reproduceability.

As the baking process is dependent upon more than reaction with oxygen, measuring the rate of oxygen absorption, as was done in studying the air drying process, is not applicable.

As the films produced are insoluble in nearly all solvents, chemical methods, such as determining the change in Iodine number, acid value, apparent molecular weight, etc. are also out of question.

In the preliminary experiments it was noted that as baking progressed at any constant temperature, a very

distinct and definite color change takes place. This color change is quite marked and fairly reproducible, especially on a shiny surface such as copper or aluminum. Qualitative experiments showed that the changes in dielectric strength, power factor and mechanical strength of the films ran parallel to it. Apparently change in color is proportional to degree of bake and can be used as a relative means of measuring and comparing it. This was the criterion adopted.

Color has been used before to follow a reaction. Lapworth⁽²³⁾ used it in a study of the addition of hydrocyanic acid to camphor quinone, Harcourt⁽²⁴⁾ in a study of the reduction of ferric chloride by stannous chloride, Edgar and Wakefield⁽²⁵⁾ in a study of the rate of conversion of creatine to creatinine.

To determine the V_s , V_u , and V_f states by use of this colorimetric method under any given set of conditions, standards for the several states were first prepared. This was done by setting the baking oven at some convenient temperature and carrying out a series of trial bakings, until the times were found that corresponded to the V_s , V_u , and V_f states; that is, until the film was (a) dry to touch, (b) dry both warm and cold, and (c) brittle. The latter state was considered as reached when the film first showed a crack on being bent through an angle of 120° . A fresh set of films were then made by

baking to the several times just determined. These new films constituted the standards. Thereafter in determining when the V_s , V_u , or V_f states were reached, it was simply a question of color matching; that is, it was only necessary to bake until the proper color was attained.

Owing to its dark color and the difficulty of accurately following changes in dark colors, it was found advisable to use as a measure of the useless state, not the true V_f state but rather an intermediate state, in a manner similar to the well known technique adopted in following the decay in radioactivity of a substance. The intermediate state chosen, called the V_d state, was that corresponding to one-third life, as measured in time units. In other words, to get the true values of the useless state from the experimental values recorded, the V_d values must be tripled, i.e.

$$V_f = 3V_d$$

As will be seen from Fig. 3, the use of the V_d state as measuring deterioration makes its determination quite easy and fairly accurate.

The method used to study the reaction velocity of the baking process followed a slightly different procedure. It consisted in making a series of films, all baked at successively increasing intervals of time, starting with the raw state and going into the V_f state. The type of results obtained for a typical run is shown

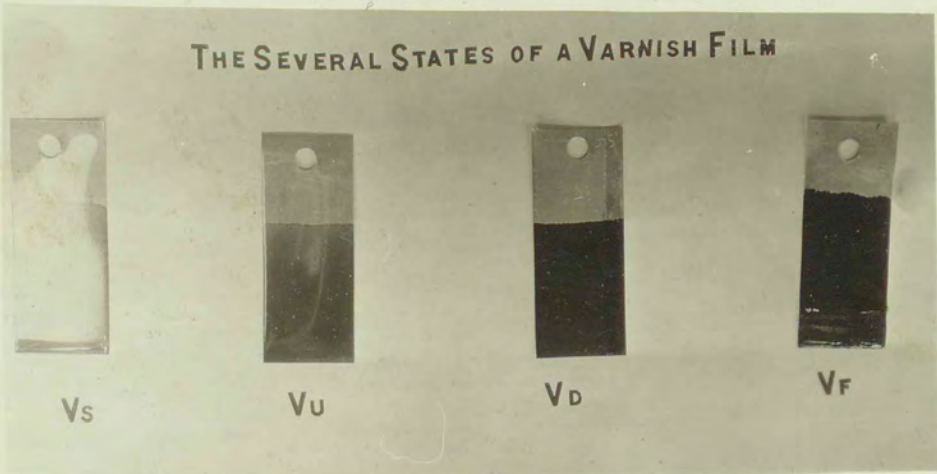


Figure III

in Fig. 4. Each film was then examined with a spectrophotometer to determine the percentage of light of wave length 6600 \AA reflected, the change of which was used as a relative measure, at any instant of time, of the degree of bake. Fundamentally this is the same as the colorimetric comparison just discussed, except that the second method is quantitative and measures differences in films at the same temperature.

The reason for the adoption of the wave length, 6600 \AA , for the spectrophotometer measurements was that the examination of films covering the entire baking range on aluminum by reflected light and on glass by transmitted light, showed that the predominating wave length, although shifting slightly, was in the red of the visible spectrum. The wave length 6600 \AA was a good average value. Table No. 1 and Curve Sheet No. 1 will serve to illustrate this conclusion.

TABLE NO. I

Color Analysis Varnish Films

Temp. Preparation of Films 275°C .

<u>Wave Length</u> Millimicrons	<u>% Reflected Light</u>		<u>% Transmitted Light</u>	
	V_s	V_f	V_s	V_d
450	8.2	8	9	--
470	14.5	8	13	--
500	20.	8	25	--
530	29.	8	40	2

G.E. 199 Enamel
T = 295°C

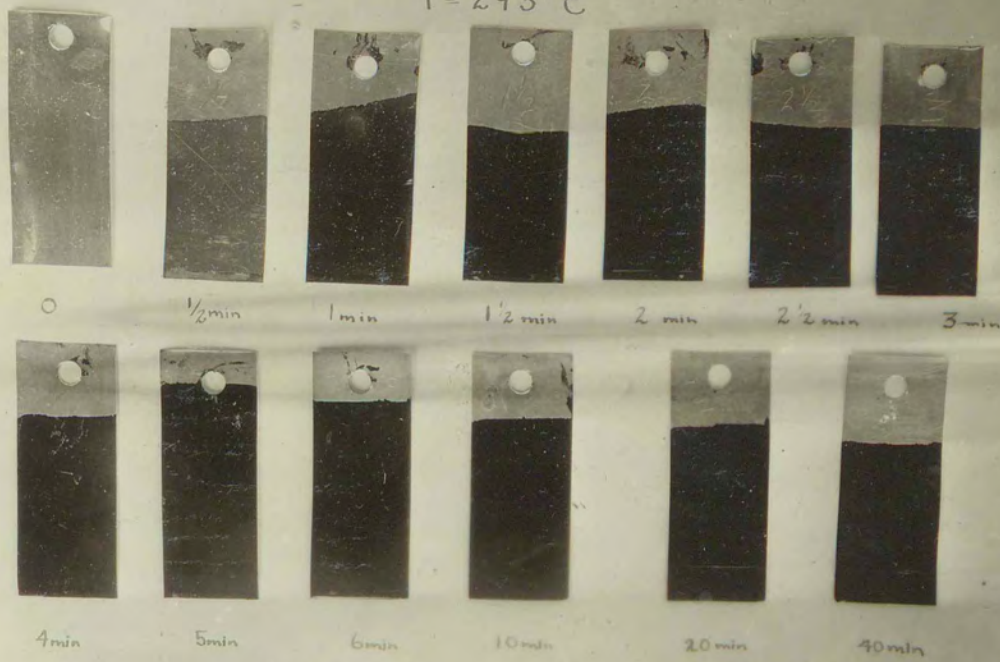


Figure IV

Table I (con't)

<u>Wave Length</u> Millimicrons	<u>% Reflected Light</u>		<u>% Transmitted Light</u>	
	V_s	V_f	V_s	V_d
560	41	8	53	5
590	45	9	67	12
620	50	12	74	21
660	56	16	85	38
690	61	20	91	50

Reflected Light films made on aluminum.

Transmitted Light films made on glass.

In the analysis of the reaction velocity data a value representing the initial film and one representing the film at infinite time were required. The former, a_o , was directly determined from a film of unbaked varnish and found to be 94; the latter, a_{oo} , was extrapolated as 8 from curve sheet No. I, which shows that this is the limiting value eventually reached by films on aluminum for all wave lengths.

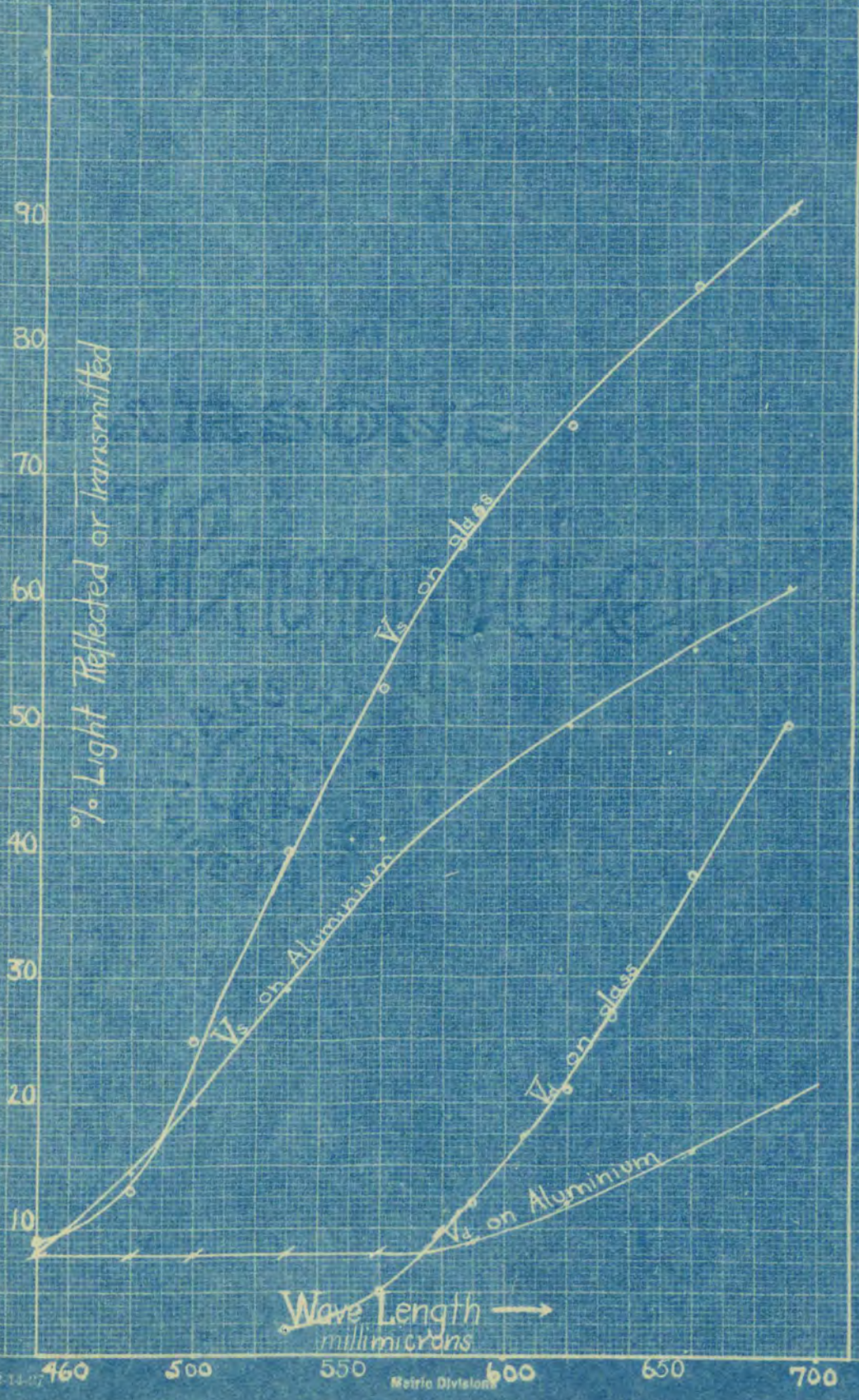
To be assured that all films were as near alike as possible, every film was prepared in the same manner. The procedure adopted was to submerge the aluminum three quarters of its length in the varnish, remove it with the dip machine at a rate of two feet per minute, and allow to drain three minutes before using.

In order that the baking chamber be as free from any undue disturbing influences it was conditioned at a rate of

Curve Sheet No 1

Color Analysis Varnish Films.

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two liters per minute, this rate previously being determined as optimum for the most efficient results. Air, nitrogen, hydrogen, or oxygen were used as required.

VII. EXPERIMENTAL RESULTS

Qualitative Verification of Reactions

The baking process reactions were verified qualitatively by a series of experiments summarized in Table 2. Experiments 1 to 4 of this series were made by placing a film, prepared on metal as stated above, into a hard glass tube, approximately 12" long, the glass tubes being treated, sealed and heated as recorded. Experiments 5 to 7 were made in the Baking Oven.

TABLE NO. II

Exp.1 Tube filled with air. Sealed cold. Heated 200°C, 5 hrs. Film turned brown, got very streaky. On opening noted pressure developed. Film rubbery, yet soft and tacky.

Exp.2 Tube evacuated cold, using standard lamp vacuum system, then sealed. Heated 200°C, 5 hrs. Film hardly changed, was viscous and still liquid. Heated 200°C 8 1/2 hrs. more. On opening noted slight pressure. Film as above stated. No appreciable setting occurred.

Exp.3 Tube filled with dry CO₂. Sealed cold. Heated 200°C, 13 1/2 hrs. Film

sticky, liquid as in previous experiment with vacuo.

Exp.4 Tube filled with dry CO_2 . sealed cold. Heated 200°C , 24 hrs. On opening film still liquid, darkened a bit but no setting evident.

Exp.5 Film baked in current of dry hydrogen atmosphere. Flow 2 liters per min. Temp. 200°C . Film excellently baked in one hour. Texture rubbery, breaking when pulled with clean cut edge.

Exp.6 Film baked under vacuum in baking oven. Vacuum pump on continually. Temp. 200°C . Film excellently baked in one hour. Texture rubbery, breaking when pulled with clean cut edge.

Exp.7 Film baked in current of air. Flow 2 liters per min. Temp. 200°C . Film excellent in 10 min. Texture granular, breaking when pulled with ragged edge.

The heating in the case of the sealed tube experiments was sufficient to produce setting if any was to take place. A true equilibrium probably was established.

These experiments point out:

- (a) that a varnish film can be set independent of the baking atmosphere simply by heat, Exps. 5,6,
- (b) that when heat alone is used, vapors must be removed

or no setting occurs, Exps. 6, 2,

(c) that the presence of oxygen without removal of vapors causes some setting, Exp. 1,

(d) that in the latter case also, the removal of vapors is requisite, Exps. 1, 7,

(e) that when oxygen is present the reaction is more rapid than in an inert atmosphere, Exps. 5, 7,

(f) that the films produced when oxygen is present have a different texture from those produced by heat alone, Exps. 5, 6, 7.

A varnish film, set by baking is the result therefore of either or both of two types of reactions; namely, oxidation and polymerization. That the reaction may go to completion, removal of vapors is necessary. Equations (3), (6), (8) are apparently representative of what occurs in the baking process.

Nature of Baking Atmosphere

In order to further verify the fact that the baking process in an inert gas is truly the result of thermal changes and therefore independent of the nature of the atmosphere, the quantitative experiments summarized in Table 3 were carried out.

Analysis of the results show that the time required to attain the V_u state is actually constant in the case of inert gas atmosphere, while when oxygen is present, it decreases as the oxygen concentration increases.

TABLE NO. III

Nature of Baking Atmosphere

Gas Flow: 2 li. per min.

All films to V_u state.

Exp. No.	Gas in Baking Oven	Temp. °C.	Time to V_u State	Texture Film
1	Nitrogen	220 - 230	53 min.	Rubbery
2	Hydrogen	"	54 "	"
3	Lab. Vacuum	"	55 "	"
4	Air	"	240 sec.	Granular
5	Oxygen	"	100 "	"

Concentration of Oxygen

In Table 3, it was shown that as oxygen was introduced into the baking atmosphere the time to reach any particular baked state was decreased, due to oxygen reactions that occurred simultaneously with polymerization, and to the greater velocity of the former. In Table 4 are given the results of three runs to the V_d state carried out to particularly show this effect. The results are plotted as Curve Sheet 1-A.

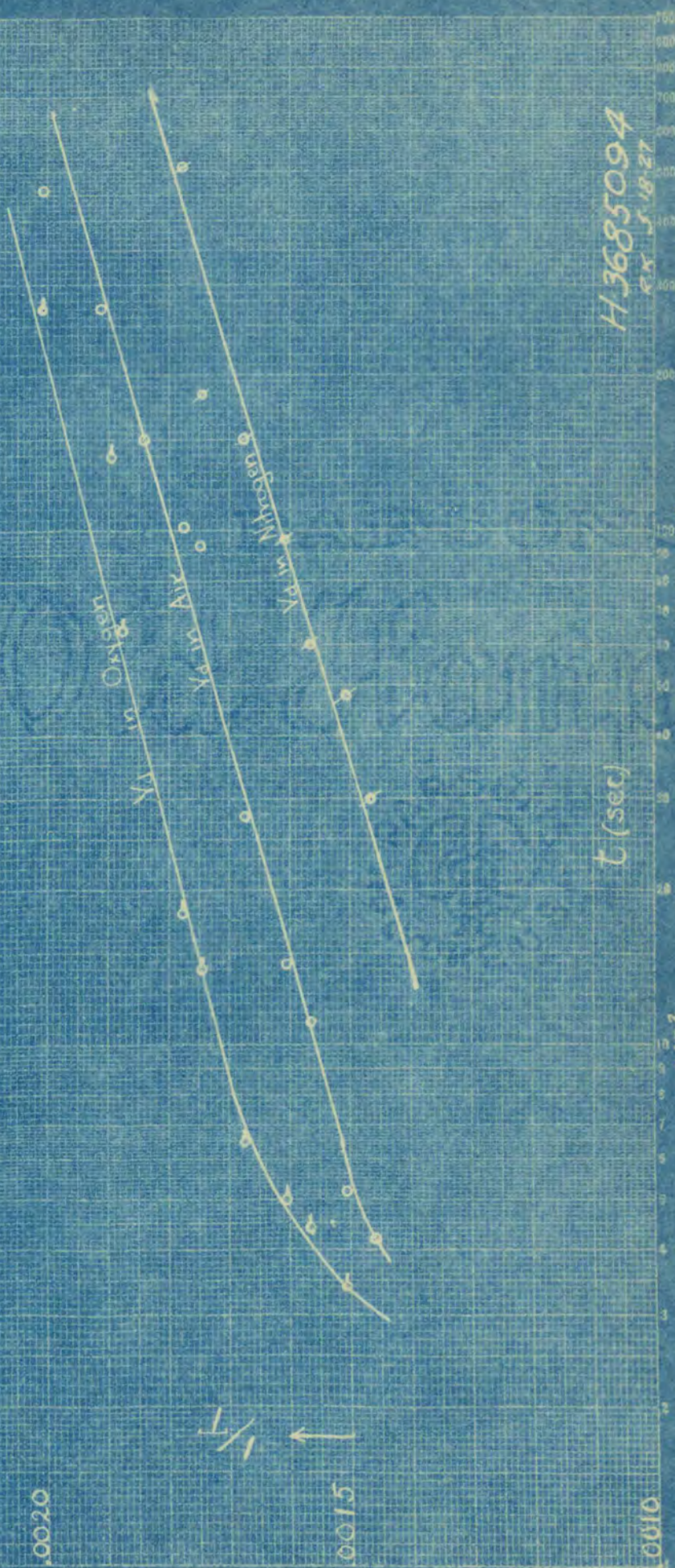
The results for N_2 ($O_2 = 0$) and pure O_2 ($O_2 = 100$) are interesting as they show the two extremes, pure polymerization and as nearly pure oxidation as it is possible to obtain.

The curves show plainly the effect of the oxygen concentration and point out without question that

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Curve Sheet No 1-A

V_d curves for O_2 , Air, N_2



Velocity Reaction (3) > Velocity Reaction (6)

In the baking process as ordinarily carried out in air

$$F = aF_o + bF_o$$

where $a > b$

$$a > b$$

TABLE NO. IV

Effect of Oxygen Concentration on Baking

Gas Flow = 1.32 li. per min.

All films dried 5 min. at 125°C. in air

before baking to remove effect of solvent.

°C.	°A.	$\frac{1}{T} \cdot 10^{-5}$	V_d (Nitrogen)*	V_d (Air, $P_{ox} = .28$)	V_d (Oxy. $P_{ox} = 1.0$)
225	498	200.8	-----	4500	2700
250	523	191.0	-----	2700	-----
255	528	189.4	-----	-----	1380
260	533	187.6	-----	-----	640
270	543	184.0	-----	1500	---
290	563	177.6	5040	1020	180
300	573	174.5	1840	935	140
325	598	167.2	1500	278	65
350	623	160.8	960	144	50
365	638	156.7	600	110	44
390	663	150.8	480	52	34
410	683	146.4	300	42	---

* All values for V_d are given in seconds.

The Baking Process in Air

The results of the determination of the V_s and V_d states at various temperatures in air are given in Table 5. These results are plotted as Curve Sheet 2, using regular cross-section paper; and as Curve Sheet 3, using semi-log paper. In these curves, time is plotted as abscissa, and absolute temperature or its reciprocal as ordinate.

Curve Sheet 2 shows that the time to attain any given state of baking decreases rapidly as the temperature is increased. Curve Sheet 3 shows that this time--temperature relationship is logarithmic.

In the case of the V_s state the semi-log plot always shows a slight curvature. This curvature is probably due to the influence of the evaporation of the solvents which occurs simultaneously with the formation of the V_s film. The semi-log plot for the V_d state, however, is practically linear, and is satisfied by the equation

$$\log t = \frac{A}{T} - B \quad (9)$$

where

t represents the time necessary to reach the V_d state,

T " the absolute temperature, and

A, B are constants.

Given the data at three or four temperatures for any desired state of the baking process, it is possible by use of this equation to calculate the time when this same state is reached at any other temperature. Applying this test to the data in Table 4 and calculating the V_d

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Curve Sheet No 2

Baking Process in Air to V_s, V_d states

680°A (407°C)

700

600

500

400

V_s

V_d

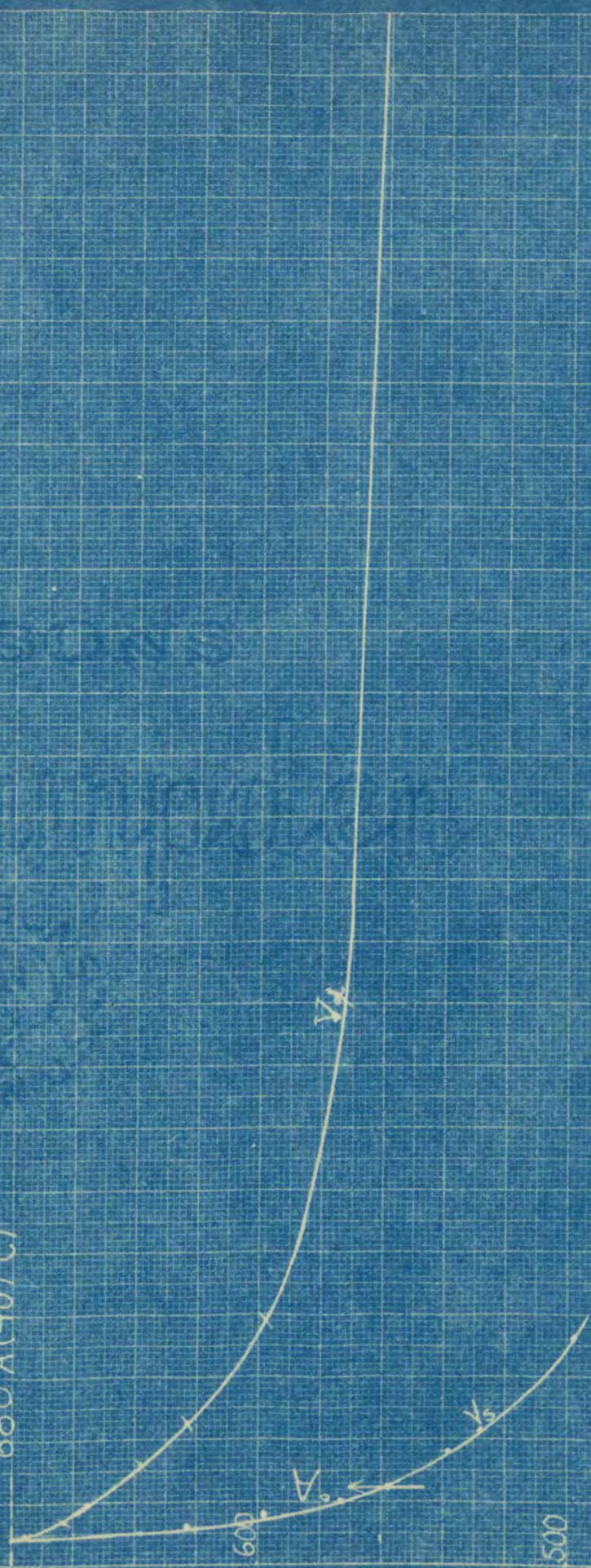
t (sec)

500

1000

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Curve Sheet No 3

Baking Process In Air to V_s , V_d States

V_d state (coeff)

V_s state

V_s state

(410°C)

t (sec)

0010

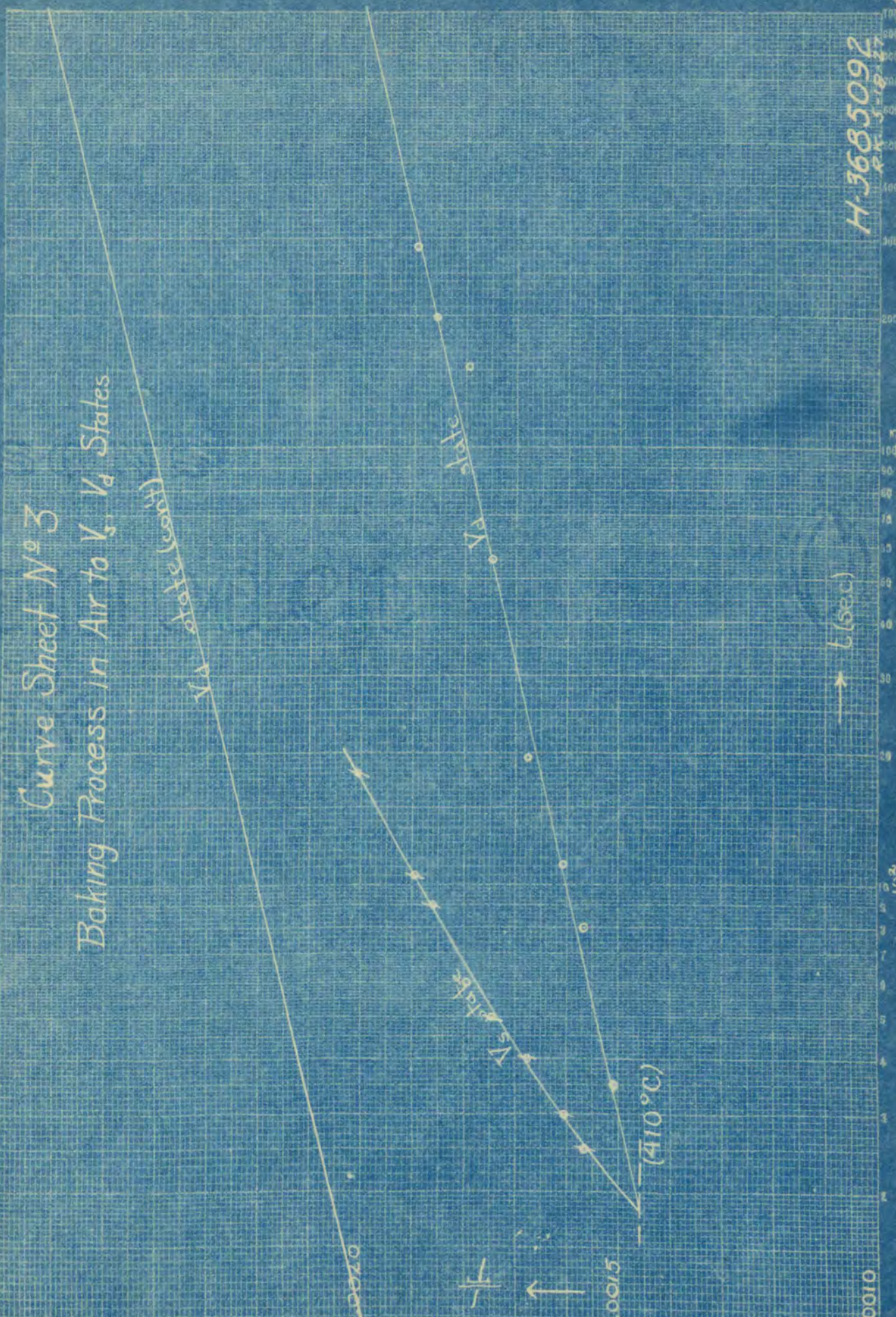
10^2

10^3

1000

1000

H-3685092



state for 110°C, the equation was found to be reasonably accurate, especially when all the variables are considered.

Hansen⁽²⁶⁾, in an investigation of baking of core oils, further tests this formula. He takes as his values of t the time required to develop maximum strength in a standard oil-sand mixture, and finds that the formula "agrees remarkably well" with his experimental results.

TABLE NO. V

Baking Process in Air

Air Flow = 1.82 li. per min.

°C	°A	$\frac{I}{T} \times 10^{-5}$	V_s	V_d (abs)	V_d (calc)
110	383	261.0	--	64-130 days*	104 days
225	498	200.8	180 sec.	21600	
255	528	189.4	105	2880	
265	538	185.9	90	1984	
285	558	179.2	60	1530	
300	573	174.5	50	451	
325	598	167.2	40	195	
350	623	160.5	30	111	
365	638	156.7	25	80	
390	663	150.8	--	35	
405	678	147.6	ignited	--	

* Depending on observer.

The temperature at the point of intersection of the V_s and V_d curves, see Curve Sheet 3, is interesting as it (410°C) agrees fairly well with the experimentally determined flash point, 405°C .

Reaction Velocity of the Baking Process in Air

Tables 6 to 9, inclusive, give the data for the rate at which baking process progresses with time as determined by the spectrophotometer at respectively 275° , 295° , 315° and 335°C .

The reaction velocity constants as calculated, using the formula for a first order reaction; namely,

$$k = \frac{2.3}{t} \log \frac{a}{a-x}$$

$$= \frac{2.3}{t} \log \frac{a_0 - a_{\infty}}{a_t - a_{\infty}}$$

are included. Except for the initial and final readings, where the difficulty in reading the spectrophotometer accurately is great, the values, as thus calculated, are fairly constant. This indicates that the process is essentially a first order reaction.

In one case, Table 8, the reaction velocity constants, k_2 , as calculated on the basis of a bi-molecular reaction of the type $2A \longrightarrow A + B$ are given. These values are certainly not constant.

The various results are summarized in Curve Sheet 4.

Reaction Velocity and Temperature

In Curve Sheet 5, the logarithms of the reaction velocity constants, as determined above, are plotted against the reciprocal of the corresponding absolute temperatures,

a linear relationship resulting. This is in agreement with the Arrhenius⁽²²⁾ relationship

$$\log k = C - a/T \quad (10)$$

where c , a are constants

T is the absolute temperature

k the reaction velocity constant.

The fact that the experimental results obey this equation, together with the knowledge that the baking process obeys the laws of a first order reaction, explains equation 9. Thus we can write

$$k = \frac{1}{t} \ln \frac{a}{a-x}$$

for any temperature. Now, by always carrying the baking process to the same degree of bake, such as the V_d state,

$$k_1 = \frac{1}{t_1} \ln \frac{a}{a-x} \quad \text{at } T_1^0$$

$$\text{and } k_2 = \frac{1}{t_2} \ln \frac{a}{a-x} \quad \text{at } T_2^0$$

Dividing one equation by the other we have

$$\frac{k_1}{k_2} = \frac{t_2}{t_1} \quad (11)$$

which says that the reaction velocity constant is inversely proportional to the time.

Substituting $1/t$ for k in (10) we get

$$\log 1/t = C - a/T$$

and, rearranging,

$$\log t = \frac{A}{T} - B$$

which is equation 9.

TABLE NO. VI

 $T = 275^{\circ}\text{C} (548^{\circ}\text{A}), \quad \lambda = 6600 \text{ \AA}$

t (sec)	R (reflected)	R_c^*	()**	log ()	k
0	94	86	---	---	---
30	89	81	1.061	.0267	.0020
90	80	72	1.194	.0770	.0020
120	75	65	1.322	.1212	.0023
180	61	53	1.621	.2008	.0026
240	50	42	2.045	.3107	.0029
300	46	38	2.260	.3543	.0027
360	43	35	2.453	.3906	.0025
480	40	32	2.684	.4283	.0021
600	30	22	3.910	.5927	.0023
1200	28	20	4.300	.6335	<u>.0014</u>

Ave. k = .0022

* refers to $a_t - a_{\infty}$

** refers to $a/a-x$ i.e. $\frac{a_0 - a_{\infty}}{a_t - a_{\infty}}$

TABLE NO. VII

t	R	R _c	()	T = 295°C (568°A) log ()	$\lambda = \frac{6600}{k}$
0	94	86	-----	-----	-----
30	85	77	1.118	.048	.0037
60	72	64	1.342	.128	.0049
90	62.5	54	1.582	.199	.0051
120	52.5	45	1.910	.281	.0054
150	48.	40	2.125	.327	.0050
180	40	32	2.685	.429	.0055
240	33	30	2.865	.457	.0044
300	32	24	3.580	.554	.0043
360	27	19	4.525	.646	.0042
600	23	15	5.74	.759	.0030
1200	21	13	6.61	.820	---
2400	13	5	-----	-----	-----

Ave. k = .0046

TABLE NO. VIII

T = 315°C (598°A)

t	R	R _c	()	log ()	k ₂	k
0	94	86	---	----	----	---
30	82	74	1.270	.1038	.000063	.0087
60	62	54	1.740	.2406	.000115	.0092
90	49	41	2.292	.3692	.000142	.0092
120	36	28	3.360	.5263	.000201	.0101
150	26	18	5.22	.7177	.000291	.0108
180	25	17	5.54	.7135	.00262	.0092
240	24	16	5.88	.7694	.000212	.0074
300	21	13	7.24	.8596	.00218	.0066
360	14.25	6.25	15.02	1.177	.000364	<u>.0076</u>

Ave. k = .0090

TABLE NO. IX

T = 335°C (638°A), $\lambda = 6600 \text{ \AA}$

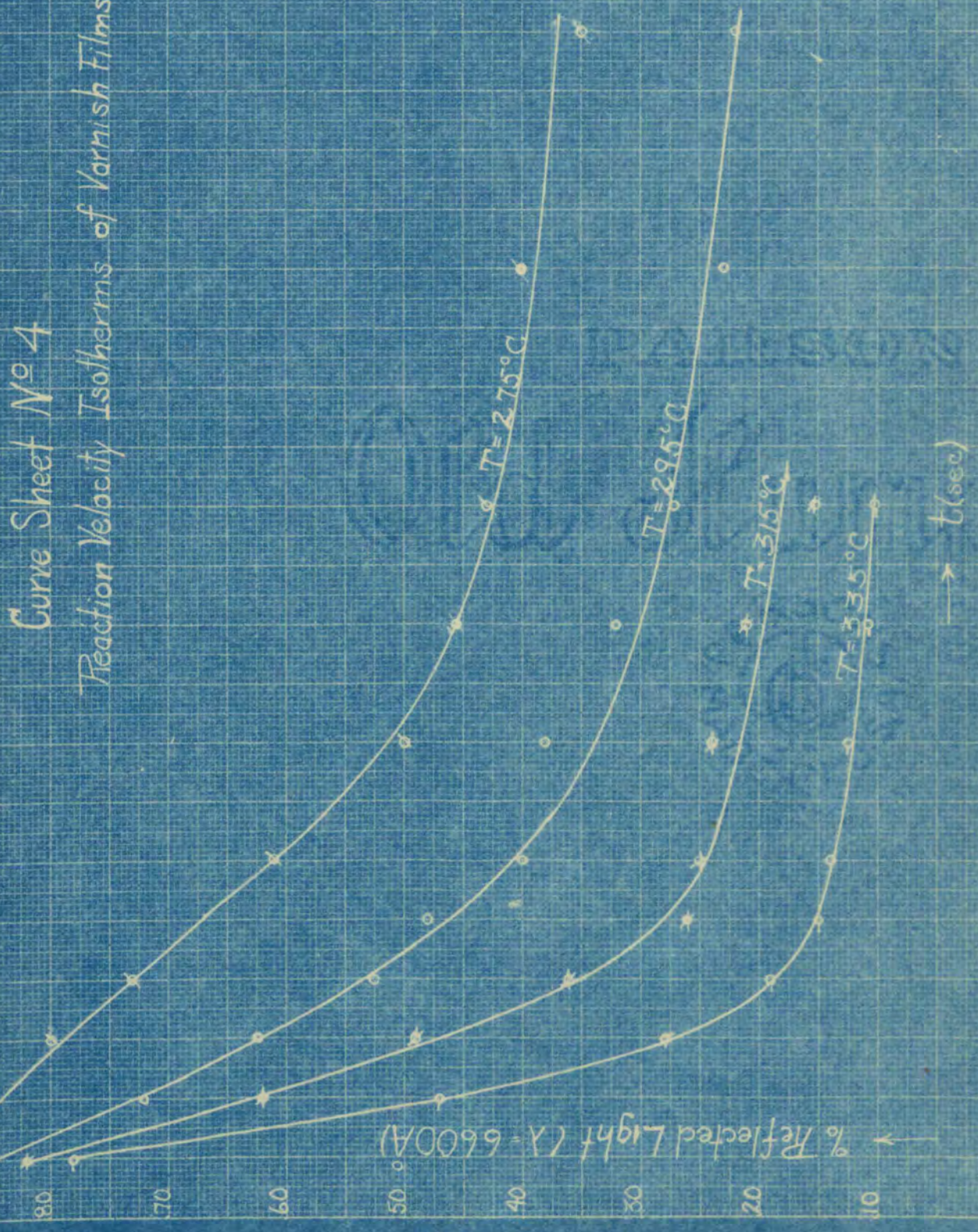
t	R	R _c	()	log ()	k
0	94	86	---	----	---
30	78	70	1.342	.028	.0098
60	47	39	2.205	.343	.0132
90	28	20	4.300	.634	.0162
120	19	11	8.55	.932	.0179
150	15	7	13.41	1.127	.0179
180	14	6	15.68	1.196	.0157
240	12.25	4.25	22.10	1.344	.0129
300	10.50	2.50	37.60	1.564	.0119
360	10.25	2.25	41.80	1.621	<u>.0105</u>

Ave. k = .0158

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Curve Sheet No 4

Reaction Velocity Isotherms of Varnish Films



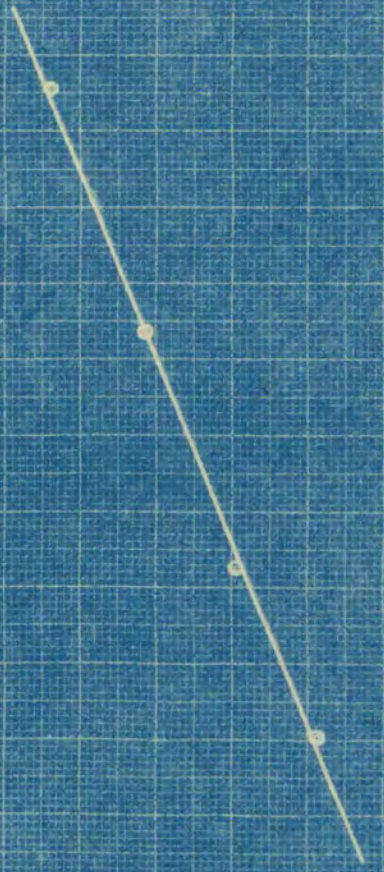
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THIS MARGIN RESERVED FOR BINDING

Curve Sheet No 5

Plot of $\log k$ vs $1/T$



$\log k$

$1/T$

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-3.00

-2.00

VIII TEMPERATURE COEFFICIENT AND HEAT OF ACTIVATION

Temperature Coefficient

The experimental data allow calculation of the temperature coefficient of the baking process. Expressing the temperature coefficient, as is customary, in terms of a 10° temperature rise, using data from Curve Sheet 5, we calculate

$$\frac{k_{305}}{k_{295}} = 1.352$$

Referring to equation (11) where it was shown that

$$\frac{k_1}{k_2} = \frac{t_2}{t_1}$$

and using the data in Curve Sheet 1-A, we calculate:

	Oxygen	Air	Nitrogen
$\frac{k_{305}}{k_{295}}$	1.421	1.342	1.300

Heat of Activation

Using the Arrhenius⁽²⁷⁾ equation

$$\ln \frac{k_1}{k_2} = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

where ΔH = heat of activation calcs per gm. mol. Using the above ratios, the heats of activation of the baking reaction in oxygen, air and nitrogen were calculated. For air, the value of 1.352 was used as this value is probably the more accurate one, being based on better data. The calculations are given in Table 10.

TABLE X

Heats of Activation Baking Reaction

ΔH	Cals. per gm. mol.		
	In Oxygen	In Air	In Nitrogen
	+22,500	+19,500	+16,800

VIII SUMMARY

1. The baking of an oil base varnish is the result either of an oxidation process, a polymerization process, or both.
2. The polymerization process is dependent only on heat.
3. Baking proceeds independently of the gas atmosphere in which it is carried out, provided no oxygen is present and such vapors as are formed are removed.
4. With oxygen present, the rate of baking, at any temperature, increases as the oxygen concentration is increased.
5. The baking process follows a general chemical equation which takes into account the above facts. Baking can be studied on the basis of this equation.
6. The structure of the films produced by polymerization differs from the films produced when oxygen is present.
7. A spectrophotometer can be used to judge the degree of bake of a clear varnish, and thus affords a method for studying the velocity of the baking process.
8. The baking process follows essentially the laws of a first order equation.

9. The reaction velocity constants for the baking process in air of a type varnish have been calculated. The relationship between the logarithm of the reaction velocity constant and the reciprocal of the absolute temperature is linear.

10. A linear relationship also holds between the logarithm of the time required to reach any desired baked state and the reciprocal of the absolute temperature. This relationship can be used to calculate the time required for baking if data at a few temperatures are known.

11. The temperature coefficients and heats of activation of the baking process, as carried out in oxygen, air and nitrogen have been calculated for a type varnish.