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UNIVERSITY OF LOUISVILLE

THE ANTI-OXIDANT INFLUENCE OF PHENOL-
FORMALDEHYDE RESINS ON THE DRYING OF
LINSEED OIL

A Dissertation

Submitted to the Faculty

Of the Graduate School of the University of Louisville

In Partial Fulfillment of the

Requirements for the Degree

Of Master of Science

Department of Chemistry

by

Walter William Rinne

1936

14 Sept. 36 F.S.P.

Table of Contents

	Page
I Introduction -----	1
II Theories -----	5
A. Antioxidation Theory -----	5
B. The Drying of Linseed Oil -----	10
C. Composition and Structure of Resins -----	14
III Objective -----	19
IV Method -----	20
V Experimental -----	24
A. Apparatus and Reagents -----	24
B. Procedure -----	26
1. Preparation of Resin- Oil Solutions -----	26
2. Preparation of Resin- Oil Films -----	28
3. Experimental Conditions -----	30
4. Tabulation of Data -----	34
VI Tables -----	36
VII Graphs -----	77
VIII Discussion -----	92
IX A Study of the Effect of Humidity on the Resin-Linseed Oil Films -----	115
X The Influence of Natural Resins on the Oxidation of Linseed Oil -----	119
XI The Influence of Phenol-Formaldehyde Resins on the Drying of Heat-Bodied Linseed Oil	123
XII Conclusions -----	127
XIII Bibliography -----	129
XIV Acknowledgment -----	133

I Introduction

The fact that certain substances exert a marked inhibitory action toward oxidation when present in auto-oxidation processes has long been recognized by investigators in the field of catalysis. Prior to 1920 the literature discloses only a small number of isolated and apparently unrelated experiments dealing with the inhibition of auto-oxidation processes. Among the earliest contributions to this subject was the work of Thenard (1) in 1818. He found that the decomposition of hydrogen peroxide could be prevented by small amounts of acid. In 1864 Bigelow's studies (1), in preventing the oxidation of sodium sulphite with benzyl alcohol, did much to stimulate research upon the part of other scientists in this particular field. Following the work of Bigelow, Rump (2) in 1868, reported that the oxidation of chloroform to carbonyl chloride was greatly retarded by the presence of alcohol; and somewhat later, Jorissen and Reicher (3) found that the oxidation of solutions of oxalic acid by atmospheric oxygen was strongly inhibited by hydroquinone and resorcinol.

These early investigations remained, for the most part, as laboratory curiosities simply because no credible theory had been formulated by which to interpret the results of experiment. In 1920, however, two Frenchmen, Moureu and Dufraisse (3), attempting to prevent the transformation of acrolein into the stable resin, disacryl, began the first systematic and extensive study of inhibitory activity. The results of their work established the fact that certain substances having at least one free phenolic group when present in relatively minute quantities would stabilize acrolein and, what was perhaps of equal

significance, a theory explaining the mechanism of this phenomenon. This theory has been especially valuable in providing a starting point for obtaining more accurate knowledge as to the specific effects which certain substances exert upon systems of auto-oxidation.

Prior to the work of Moureu and Dufraisse inhibitory activity was regarded, in general, as an example of negative catalysis. This term, used rather indiscriminately by early workers in the field, to include all types of retarded activity, is, according to Moureu and Dufraisse, somewhat misleading especially when used in connection with oxidation reactions.

Negative catalysis, they point out, seems to imply a catalysis which would reverse the course of an otherwise spontaneous reaction; this, it is not able to do without the addition of external energy. Furthermore their results showed conclusively that inhibitors of auto-oxidation were invariably oxidizable substances and therefore they preferred to speak of them as anti-oxygens rather than negative catalysts.

Although Moureu and Dufraisse worked chiefly with aldehydes and unsaturated hydrocarbons, their principle of anti-oxygenic activity has been extended to the most diverse fields of science. Today their theory stands well supported by evidence from both chemistry and biology and has formed a working basis for subsequent investigations.

Since 1922, the date of Moureu and Dufraisse's first publication on antioxidants, there has been stimulated a vast amount of research upon this subject.

Dupont and Allard (4) studied the oxygen absorption of abietic acid as influenced by antioxidants. They concluded that the catalyst formed a chemical compound with the anti-oxygen and was thus inactivated, thereby retarding the oxidation process.

Wagner and Brier (5) studied the oxidation of linseed oil at 30 and 100 C as influenced by hydroquinone and other phenolic compounds. They found that by introducing small quantities of phenolic substances the induction period was prolonged and at the conclusion of which the oxidation is identical with that of pure linseed oil.

French, Olcott and Mottill (6) also state that the antioxidant prolongs the induction period in the oxidation of fats and oils proportionally to the amount used.

Morrell (7) found that the introduction of small quantities of either alpha- or Beta-naphthol increased the drying time of linseed oil even in the presence of strong positive catalysts.

Hilpert and Niehaus (8) studied the action of phenols on the oxidation of linseed and Tung oils with the purpose of learning the fate of such compounds over long periods of time. They too, concluded that the term negative catalyst was inappropriate for such inhibitors, as the latter disappeared more or less readily from the oils during the drying process.

The position and number of substituent groups in phenolic compounds were noted by Moureu and Duffraisie (3) to effect the degree of antioxygenic activity. Tanaka and Nakamura (9) carried out a series of investigations on the effect of phenols and substituted monohydric phenols on the oxidation of linseed oil.

They concluded that, although anti-oxygenic activity was evidenced by all phenolic compounds investigated, the potency of the effect was greater in the case of ortho and para substituted groups than with meta. Moreover, cresols and nitro-phenols showed greater anti-effect than phenol.

Greenbank and Holm (10) conclude from their work of fats and oils that only the para and ortho types of phenolic compounds are effective as antioxidants for fats and oils. They also found that certain unsaturated polybasic aliphatic acids were particularly good antioxidants.

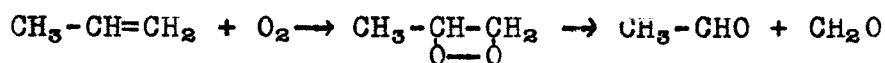
Rodgers and Taylor (11) in the course of their investigation of the effect of temperature upon the oxidation of linseed oil studied the action of diphenylamine, hydroquinone, and beta-naphthol as antioxidants. They concluded that the inhibitor and the catalyst exerted their influence independently of each other, and that the inhibitor was more effective at lower temperatures.

The foregoing investigations represent only a few of the most important contributions since Moureu and Dufraisse first enunciated their theory on antioxidation. In almost every case the study has lent support in some form or other to the basic assumptions of the theory. The wide range of substances that fall within the scope of this theory substantiates more completely the general consideration of its authors - the fact that the whole of organic matter, potentially oxidizable, and yet lying in constant contact with oxygen, validates the assumption that strong catalytic forces are everywhere present in nature opposing oxidation processes.

II Theories

A. Antioxidation Theory

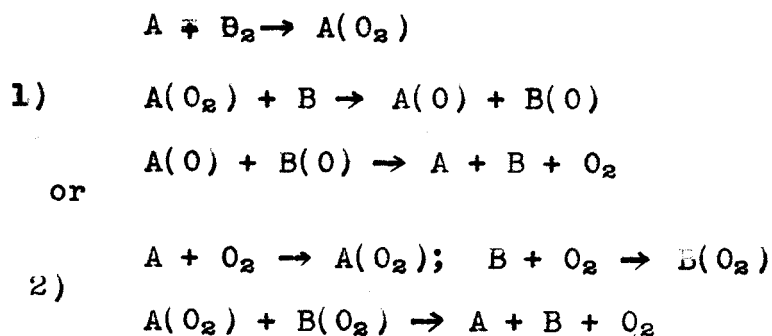
The theory proposed by Moureu and Dufraisse (3) to explain the mechanism of antioxidation has provoked a large amount of study during the last decade. This mechanism is concerned primarily with auto-oxidation processes and embraces much of what is known as the peroxide theory. The combination of an active molecule of oxygen with an active molecule of an auto-oxidizable substance, A, gives rise to an active peroxide, A(O₂). The formation of this peroxide is accompanied by an absorption rather than a liberation of energy. The active peroxide molecule represents an unstable system which, if no inhibition occurs, may break down into more stable oxidation products. Thus in the case of unsaturated hydrocarbons molecular oxygen combines at the ethenoid linkages to form peroxides (12), the latter having but a transitory existence readily decomposes into more stable products:



The resultant oxidized products are at a higher energy level and are therefore capable of further reaction with active oxygen molecules, or of collision with other inactive molecules thereby giving up their energy.

According to Moureu and Dufraisse's (3) hypothesis the antioxidant may function as an inhibitor in two different ways. First they assume the active peroxide A(O₂), oxidizes the antioxidant, B, with the formation of two peroxide molecules A(O

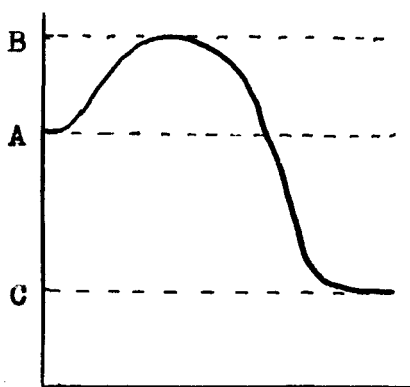
and B(O). These two peroxides are antagonistic and mutually destroy each other with the regeneration of the original components A, B, and O₂. Second they assume the possibility that the antioxidant, B, may react with an active molecule of oxygen to form a peroxide, B(O₂) which in turn would react with the peroxide A(O₂) and regenerate A, B, and O₂. The principal steps therein may be illustrated as follows:



The first reaction is doubtless predominant as the probability of an increased velocity of reaction between A(O) and B(O) is considerably enhanced due to the fact that they are produced in the same reaction and in close proximity to one another. The second reaction on the other hand is not favored by the nearness of the molecules and the probability of an increased velocity of reaction is somewhat lessened.

In the formulation of their hypothesis, Moureu and Dufraisse, not only have employed the peroxide theory but also the energy of activation concept of Arrhenius. Considering antioxygenic activity a positive catalysis rather than a negative one they assume that in the oxidation of an auto-oxidizable substance A there is not a

continual drop in potential of the system until oxidation is complete. They assume that during the course of an auto-oxidation reaction there is an increase in potential at a certain moment and that it is during this phase that the antioxidant will oppose the whole of the auto-oxidative process by favoring a lowering of potential.



Time

Figure 1

In any chemical system the molecules are distributed about a mean value with some molecules having a higher kinetic energy and some a lower. Thus molecules removed from the mean state are said to be activated. Moreover, the

velocity of a reaction is determined by the proportion of active molecules. Such molecules are said to possess the critical increment of energy.

In figure I the mean state is represented by level A. If such molecules are to react they must pass thru level B before reaching the stable state of oxidation level C. A definite quantity of energy must be absorbed in order to reach level B from which they can react to form the stable product at C. (13) Thus Moureu and Dufraisse assume that the antioxidant is effective only at level B, and at which point two catalyses are possible: the one favoring a movement to level C being pre-oxygenic in nature and the one favoring a return to level A being antioxygenic.

By such an hypothesis they were able to explain how it is

possible for relatively small amounts of a catalyst to prevent the oxidation of a large number of auto-oxidizable molecules in the presence of oxygen.

If antioxygenic activity resulted then it was assumed that the peroxide $B(O)$ had reacted with $A(O)$ regenerating the original molecules and a subsequent return to level A. On the other hand if pro-oxygenic activity resulted it was assumed that $B(O)$ had reacted with A to give B and the stable peroxide AO , favoring a movement to level C and a concomitant lowering of potential of the system. The sense of the catalysis, i.e., whether it is pro-oxygenic or antioxygenic is largely determined by such factors as light, concentration, temperature, and reaction media. The third possibility that the inhibitor, B, may be converted from the peroxide form $B(O)$ to the stable oxidized form BO resulting in a loss of antioxidant readily explained the diminution in inhibitory effect of an antioxidant over long periods of time.

The foregoing theory has led to the prediction of numerous results many of which are in accordance with experimental evidence.

A brief summary of these is as follows (3):

1. Auto-oxidizable molecules can only be inactivated by antioxidants in the presence of oxygen and conversely, oxygen can only be inactivated in the presence of an auto-oxidizable substance.
2. Antioxygenic activity is exclusively a property of oxidizable substances.
3. Antioxygenic activity is localized solely in the oxidizable portion of the molecule.

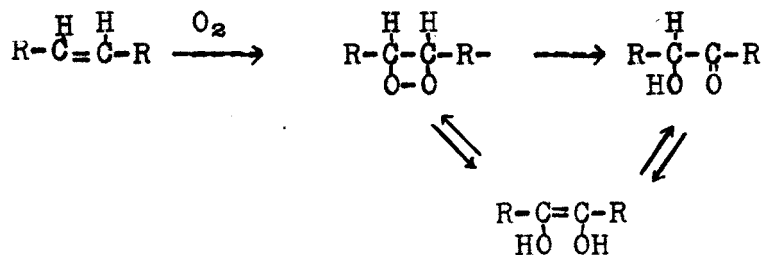
4. Antioxygenic activity increases with the increase of oxidizability.

B. The Drying of Linseed Oil

The drying of linseed oil has been studied rather extensively from the standpoint of both theoretical and practical chemistry. From early investigations upon the subject it was at first thought that the drying of an oil was simply a matter of oxidation. Within recent years it has been shown that the transition of an oil from a liquid to a solid is colloidal in nature and one that involves both the phenomena of polymerization and association (14).

Rose and Bolley (15) hold that a dried oil film consists primarily of a liquid or dispersing phase adsorbed to a variable degree by the solid or dispersed phase. They consider the film to consist of three components, namely, liquid, adsorbed liquid, and solid. The proportions in which these three are present determine in a large measure the physical nature of the film.

Lined oil is composed essentially of the mixed glycerides of linolenic, linoleic, and oleic acids, together with the glycerides of such saturated acids as myristic, palmitic, and stearic. When this oil is spread in thin films on such media as glass or wood and exposed to atmospheric conditions, oxygen is absorbed at the double bonds of the fatty acid chains. At first however, there is a slight induction period during which there is very little oxidation. Then there results a rapid increase until maximum oxygen absorption is reached. This addition of oxygen molecules to the thenoid linkages in the fatty acid chains forms peroxide groups. According to Morrell (16) three forms are possible:



These three forms are in dynamic equilibrium, any one of which may exist for an interval of time and then pass imperceptibly into another form.

Coincident with the absorption of oxygen there is an evolution of volatile decomposition products. Gardner (17) shows that these products may consist of carbon dioxide, water, and organic substances. He also holds that small quantities of carbon monoxide is evolved. This fact has been substantiated by King (18). Coffey (19) has found that these volatile products consist of aldehydes, acids, and ketones.

As the film ages it progressively loses weight due to the fact that the escape of volatile products is greater than oxygen absorption. It also increases in tackiness and softness as the aging continues (20). Rose and Bolley (15) studied this after-softening of films and showed that such factors as the composition of the oil, the degree of unsaturation, and the presence of driers profoundly affect the nature of this phenomenon.

The effect of driers is also a matter of great practical importance in the drying of oils. Not only is the induction period shortened but there are also differences in the amount of oxygen absorbed in the presence of different driers.

The function of the drier is still a matter of doubt. Aside from the intermediate compound theory and the physical absorption

theory few explanations have been offered which clearly elucidate their action. It is, however, well known that driers increase the rate of oxidation and decrease the time required for gelation. Long and his workers (14) have found that lead has a specific action in promoting the formation of groups that associate, thereby favoring gelation. Whatever their mechanism of action may be, it is well known that the different metallic oxides exert different effects on the drying rate and on the physical nature of the film. For example manganese and cobalt produce a more or less superficial oxidation, whereas lead favors a more uniform oxidation (16). The latter is also less sensitive to temperature conditions.

The oxidation of linseed oil has been regarded by Long and his workers (21) as occurring in definite steps or stages. The first stage, that of oxidation, varies, depending on the condition of the oil, whether it is blown, heat bodied, or raw. This stage in the case of the raw oil is largely a matter of oxygen absorption at the expense of the free energy of the double bonds.

In the case of bodied oils, however, a somewhat different picture is presented. During the heat bodying process the free energy of the double bonds has been partially consumed in an association phenomenon resulting in the union of the oil molecules. Long (14) found that this association or polymerization effect is greatly facilitated by increased temperature, catalysts, pressure, light, and electrical energy.

Although the first stage in the drying process varies somewhat depending on the processing of the oil the result in each case is

essentially the same, that is, larger, more complex, and more polar molecules are built up, each having the tendency to further associate or combine with other molecules to form a gel structure. Thus the second stage in the drying process has been shown by Long (22) to be one involving the orientation and association of the more complicated and polar molecules to form the solid film. Therefore from the initial setup of a film to its final failure the solidification mechanism involves a chemical change of the adsorbed, oriented liquid phase into a molecular structure resembling an association colloid gel (23). Long is of the opinion that this solid phase is one of very definite composition and that any variations in the composition of the film are due to the fact that the liquid phase has not been changed completely over into the solid phase.

He further concludes that film failure results only after the liquid phase has been changed completely over into the solid phase by reactions of an association nature and that any substance which would decrease the velocity of this change would prolong the life of the film (21).

C. Composition and Structure of Resins

A study of the products obtained by the condensation of phenols with aldehydes, especially in regard to constitution and chemical properties, is one beset with many difficulties. Such products are largely of a resinous or colloidal nature and in general are insoluble, infusible, and unreactive towards the ordinary chemical reagents. Therefore the ordinary methods of chemical analysis involving sharp melting points, crystalline structure, and similiar criteria are of no avail in the study of their constitution.

The situation is further complicated by the fact that a large number of compounds will take part in these condensation reactions. In the place of phenol may be used certain substituted phenols such as thymol, bromo-phenol, nitro-phenol, as well as cresols, naphthols, and other substances with an hydroxyl group attached to a benzene ring (24). Then too, the replacement of formaldehyde by its hydrated form or polymers as well as by acetaldehyde, benzaldehyde, and furfural has met with much success. However, HCHO , is in every case more reactive than the substituted aldehydes or aldehydes higher in the series (25). Redman (25) suggests that the oxygen to which the active methylene group is attached in aldehydes, may be replaced by sulphur or nitrogen. When ammonia is added as a catalyst to phenol and formaldehyde a compound known as hexamethylenetetramine is produced. The formation of this nitrogen compound furnishes a convenient way of applying formaldehyde both in the wet and the dry processes.

Further study of the many variations in raw materials possible

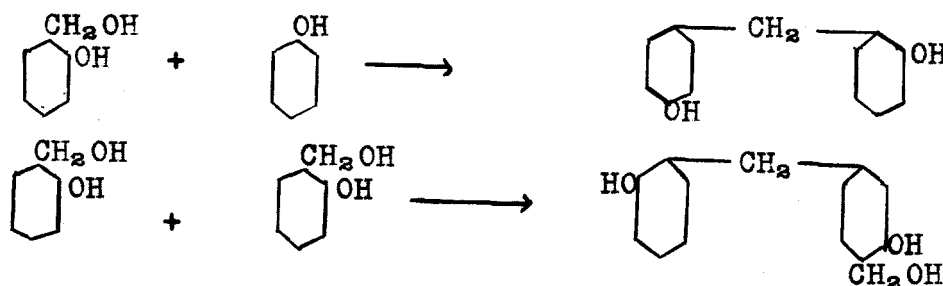
in the formation of phenolic condensates is beyond the scope of this paper. Therefore attention will be given to a few of the attempts made in the past to delineate the composition and structure of these products.

Baekeland (26), studying the nature of phenol-formaldehyde condensates, distinguishes between two types of products. To the first of these, which show distinct resin characteristics in that they are soluble and fusible and in manner ways analogous to natural resins, he gives the name Novolaks. To the other type, which are the product of the same raw materials, but decidedly insoluble and infusible, he gives the name phenolic resinoid. This latter type is known under the trade names of Bakelite, Redmanol, Amberite, Phenoform, and the like.

In recent years investigators, have attempted to throw some light upon the nature and constitution of synthetic resins by confining their study primarily to the first steps involved in resin formation. This is made possible by the fact that during the initial stages of reaction between phenol and formaldehyde substances of a relatively simple and crystalline nature are formed. The isolation and careful study of these substances has given investigators some insight into the mechanism of resinification. Moreover, by a study of these initial and intermediate products some approximation or speculation may be made as to the processes involved in the later stages.

Rachig (24) found that by carefully controlling the conditions, phenol and HCHO will react to give a crystalline compound, o-oxybenzyl alcohol along with small amounts of its para isomer. This compound

is known as saligenin and on being heated in the presence of acid is resinified. This alcohol may react in two ways: first, it may combine with a molecule of phenol, or second, it may combine with another molecule of the oxybenzyl alcohol. In both cases these results derivatives of diphenylmethane which have come to be recognized as one of the intermediate products in the formation of resinoids. These reactions may proceed as follows:



That the diphenylmethane compounds play a large part in resin formation is proved by the fact that considerable quantities of p-dihydroxydiphenylmethane has been isolated from the reaction mixture in the early stages. Rachig (24) is of the opinion that soluble resins or Novolaks are largely a mixture of the three isomeric dihydroxydiphenylmethanes which may be formed in varying amounts depending upon the concentration of the reacting substances.

Baekeland (27) also succeeded in isolating from 1 to 2 % of crystalline p-dihydroxydiphenylmethane from simple fusible resins and suggests that this is perhaps an unreacted portion still present in the resin.

Rachig further attempts to explain the difference between fusible and infusible resins on the basis that the quantities of phenol and HCHO used determines the type of resin formed. By

reacting, for example, one mol of phenol with less than one mol of HCHO would result in the formation of a fusible resin, while an infusible resin would be formed by using an excess of HCHO.

Baekeland severely criticizes Rachig's conclusions on the ground that the latter failed to take into consideration the influence of the nature of the condensing agent. He further points out that in the presence of basic catalysts infusible condensates are formed whether or not an excess of phenol is used.

The nature of subsequent reactions following the formation of the dihydroxydiphenylmethanes is largely a matter of conjecture as the proof of such reactions is entirely beyond the scope of present scientific methods. It has been shown, however, that the gradual elimination of water from these intermediate products favors resinification processes.

Van Voorhout (24) studying the course of reaction and the effect of different catalysts on phenol and HCHO concluded that resinoids of the Bakelite type consist chiefly of dihydroxydiphenylmethane in a polymerized form.

Jablonower (28) is of the opinion that condensation occurs in the initial stages with the elimination of water followed by polymerization. However, the point at which the one ends and the other begins could not be determined.

Many hypotheses have been formulated to account for the phenomena that occurs in the latter stages of resin formation. It is the general opinion of most investigators, however, that the diphenylmethane compounds condense with the elimination of water thereby forming a more complex molecule. These molecules then

polymerize building still larger and more complex structures the nature of which remains a matter of speculation. Baekeland very aptly expresses the situation (27) "That it is very probable that they are not only very complicated (resinoids) as to molecular structure and are not very well defined chemical individuals but varying mixtures of several colloidal bodies which exist in solid solution." Therefore he continues, "one hypothesis is about as easy to propose as another as long as we are unable to use any of the methods for determining molecular size and molecular constitution.

III Objective

It has often been stated that phenol-formaldehyde resins change the properties of the oils with which they are compounded (30). Moreover, it is known that certain resins tend to accelerate both the polymerization and the drying of linseed oil (31) while certain others tend to retard the drying process. A search of the literature, however, disclosed no work wherein a quantitative study was carried out on the effect of phenolic resins on the drying of "pure" drier-treated linseed oil.

This research, therefore, was undertaken to determine the influence of different phenol-formaldehyde resins on the rate of drying of "pure" drier-treated linseed oil, and also to study what effect variations in concentration of these resins may have on the maximum oxygen absorption of the oil.

IV Method

The present investigation grew out of an attempt to study the effect of various phenolformaldehyde resins on the maximum oxygen absorption of linseed oil. The method first selected in the study was that of taking ultimate analyses of the resin-oil films at definite intervals during the drying process and in that manner determine the amount of oxygen absorbed. This method, however, presented several difficulties. Before any study of the resin-oil films could be made, it was necessary to study the composition of the resins especially with respect to their oxygen percentage composition in order to make the proper corrections for this additional oxygen when the resin became a part of the oxidized oil film. Furthermore, since all phenol-formaldehyde resins are not 100% phenolic, in that they are diluted to different percentages with ester gum, and since ester gum is an oxidizable substance it was first necessary to determine to what extent the ester gum in these resins oxidized when exposed to atmospheric oxygen. Therefore it was necessary to run an ultimate analysis on all of the resins included in the study.

For the most part these ultimate analyses gave discordant results. In fact there were no two analyses that gave identical results as to carbon percentage composition although the hydrogen checked in many instances. Therefore since the percent oxygen was determined by difference, it was virtually impossible to estimate accurately any increase in oxygen percentage if by any chance oxidation had occurred.

The results of this preliminary investigation with regard to the composition of the resins were evidence enough that such a method was beset with too great an experimental error to determine such small differences in oxygen absorption that would occur in the drying of oil films during short intervals of time.

Furthermore if this method were ever to be used in such a study it would be necessary to find some means for determining the point at which the oxygen absorption had reached its maximum and thus enable the operator to select his samples for ultimate analysis at the proper time. In much of the previous work dealing with the drying of oils this point was measured by noting the time required for the oil film to become dry to touch. This is at best, however, only an approximate indication of the extent to which an oil film has oxidized. Discussing this matter, Rhodes and Van Wirt (29), state that touch is not a satisfactory criterion since the dry point does not always coincide with the maximum oxygen absorption. Then too, the human element is always an important consideration whenever touch is used as an indication of the dry point.

Therefore in view of the foregoing difficulties the ultimate analysis method for determining the maximum oxygen absorption was discontinued. In its place three other conventional methods were suggested as possible lines of attack.

The first of these was that of exposing the oil film in a closed isothermal system and measuring volumetrically the amount of oxygen absorbed.

Although this method would give the real oxygen absorption value under accurately controlled conditions it presented numerous

disadvantages the chief of which was the fact that it would limit the study to a relatively small number of resin-oil films.

The second method considered was that of blowing the resin-oil solutions with conditioned air or oxygen under constant temperature and humidity control and measuring the degree of oxidation by iodine absorption determinations. This method has been found very practical in the study of the influence of antioxidants on the oxidation of linseed oil. However, a study of the oxidation of linseed oil by iodine number determinations would be complicated seriously by the presence of phenolic resins.

The method finally decided upon was that of determining the rate of oxidation by exposing the oil in thin films on glass plates and measuring the change in weight during definite intervals of time. Although this method has been used rather extensively in the past it has been open to much criticism. Perhaps the chief objection to this method is the fact that the change in weight of a film is not an accurate measure of the degree to which the oil has been oxidized, since oxidation is accompanied by the evolution of volatile products, the nature and amount of which vary according to the experimental conditions. This method, therefore, gives only the apparent rate of oxygen absorption.

Among other objections to the use of this method are the fact that over long periods the films readily accumulate dust, absorb gases, and water, and in general are subject to excessive handling with the attendant risks of breakage and other damage.

Despite the many disadvantages involved in the use of this method it did, however, lend itself readily to the study of a large number of resin-oil films over short periods of time.

Furthermore it was also possible to closely simulate those conditions which are to be met with in actual paint and varnish work. Thus the relative merits of this method greatly outweighed those of other methods in that it yielded data, although purely comparative in nature, which could be interpreted from a practical standpoint and which would serve as a working basis for subsequent studies of this kind.

V Experimental

A. Apparatus and Reagents

The resins, oils, and drier used in this investigation were supplied by The Devoe and Reynolds Corporation of Louisville, Ky. These materials met the usual industrial specifications.

1. Resins used:

(1) Amberol 226	45%	Phenolic
(2) Beckacite 1001	100%	"
(3) Amberol F-7	20%	"
(4) Amberol 137	100%	"
(5) Bakelite 4036	100%	"
(6) Amberol 109	14%	"

The phenolic content of these resins was based upon the degree of dilution with ester gum. That is to say a 20% phenolic resin consisted of 80% ester gum and 20% phenol-formaldehyde resin. Throughout the remainder of this paper the resins will be referred to by number rather than by name.

2. Drier:

The drier used throughout this investigation consisted of the naphthenates of cobalt, lead, and manganese. The percentages of these metals present were as follows:

0.3% Cobalt

0.3% Manganese

4.6% Lead

The density of the drier was taken as 0.855 gram per c.c.

3. Oil

The linseed oil used was alkali refined and possessed the following physical and chemical constants:

Iodine Number* = 185.3 (Wijs Method)

Saponification Value (32) = 193.2

Acid Number (33) = 0.65

Specific gravity = 0.931

* Determined in the Devoe and Reynolds Corporation laboratory.

B. Procedure

1. Preparation of Resin - Oil Solutions

The resin-oil solutions were made up in various concentrations ranging from 5% to 50%. The concentrations were calculated on a percent by weight basis. For example a 5% solution consisted of 5 grams of resin to 95 grams of oil, a 20% solution consisted of 20 grams of resin to 80 grams of oil, etc. Each resin was thoroughly pulverized and dried in a desiccator for several days before it was incorporated in the oil. The drier was kept constant throughout the experiment. The amount used was 0.04275 gram per gram of oil and was found to be adequate in all cases. The three constituents of the solutions, namely resin, oil, and drier were weighed out accurately to 0.5 milligram on an analytical balance. The three constituents were then heated together to a temperature of 150 C for five minutes. This was sufficient heating to insure complete solution. (The term solution is here used to mean the point at which no suspended matter was visible to the eye). In the case of resins No. 1 and No. 3 it was necessary to heat to 260 C for 5 minutes before complete solution resulted. The solutions were allowed to cool and then they were placed in small cork-stoppered homeopathic vials sealed with parafin. The vials were kept as much as possible out of the presence of light and in every case stood at least 2 days before using.

The nature of these solutions varied somewhat as to color and viscosity. Solutions consisting of resins #1 and #3 were dark in color and more viscous than other solutions. Solutions of resin #4 were lightest in color. This deepening in color was due somewhat to the presence of the drier as was evident from a comparison

with the drier-treated linseed oil alone. Those solutions of higher resin percentage were, as was to be expected darker and more viscous than those of low percentage.

For purposes of control two solutions of drier-treated linseed oil were made up, the one heated to 150 C and the other to 260 C for 5 minutes. Very slight differences in viscosity were evident in each case. These solutions were also kept in the same manner as the resin-oil solutions.

2. Preparation of Resin-Oil Films

The resin-oil solutions were spread out into thin films on slightly etched glass plates by means of a small camel's hair brush. No attempt was made at gauging the thickness of the films but the same technique of spreading was followed in every case. Wise and Duncan (37) carried out a study on the variations in film thickness with respect to the drying properties of linseed oil. They concluded that variations in thickness when kept within reasonable limits did not appreciably affect the rate of oxidation. Therefore in the present study the variations in film thickness were within the limits prescribed for oxidation purposes as was apparent from the results obtained.

The average size of the glass plates was 8.9 x 14.0 cm. with an average area of 125 sq. cm. A slight margin of about 0.5 cm. was left around each plate in order to prevent the oil from running over the sides. Thus the average area of the film spread was 95.0 sq. cm.

The weight of the films varied from 0.1000 to 0.2580 gram depending upon the concentration of the solution used. Those solutions of low percentage resin being of low viscosity were obviously much easier to spread. Therefore a much thinner more uniform and lighter film could be applied, while in the case of the more viscous high percentage resin solutions, where greater difficulty was experienced in applying the film, a much thicker and heavier film resulted.

The films upon application were immediately weighed to the nearest tenth of a milligram on an analytical balance. This initial weight minus the weight of the glass plate gave the weight

of the film. Thereafter weighings were made a definite intervals, the length of which depended upon the rate of drying of the film. In the case of slow drying films intervals varying from 15 to 60 minutes were found practical; while in the case of the faster drying films weighings were made at much shorter intervals. After the maximum apparent oxygen value had been attained which in most cases was reached during a period of 10 to 15 hours weighings were limited to about 1 to 3 per day.

3. Experimental Conditions

It is a well known fact that such variables as light, temperature, and humidity play an important role in the drying of an oil film. These variables are not only capable of exerting their influence individually but also conjointly so that a number of variations may be possible. Schmutz and Palmer (34) have found that the influence of humidity in retarding the drying process of an oil is accentuated by elevated temperature. Moreover, they found that the retarding effect of humidity is more pronounced in the presence of light, despite the fact that light itself is an excellent activator in the drying of oils. Rogers and Taylor (11), in the course of their investigation of the effect of temperature on the drying of linseed oil, found that increase in temperature shortened the induction period, that the effect of driers is less pronounced at high temperatures, and that the action of inhibitors is more effective at lower temperatures. Wagner and Brier (5) also found that a lowered temperature favors inhibitory action. Long (21), from his studies on drying oils, concludes that oils exposed to diffuse light and to very dry air, dry thoroughly regardless of the temperature, but at great temperature extremes the rate of oxidation or drying varies considerably.

Hence it was obvious in a study of this sort that such variables as light, temperature, and humidity had to be controlled if comparable results were to be obtained. The validity of the results were contingent upon the fact that all variables be kept at a constant value. Since the amount of drier was held constant throughout and the heating procedures were held as nearly comparable as it was possible to make them the operator was enabled to vary the amount of resin and oil

and to study their influence with regard to concentration and type of resin.

The study of this problem began in the early part of January 1936. Owing to the inclemency of the weather and the extreme cold experienced during the winter months accurate control of temperature and humidity conditions was difficult. In fact most of the data taken during the months of January and February had to be discarded because later results showed that experimental conditions had varied too much. This was due principally to the fact that during the night no heat was supplied to the laboratory at which time the temperature often fell below 18 C. Therefore the data presented in this thesis comprise for the most part the work accomplished during March, April, and May when the author was better able to control temperature and humidity conditions.

The resin-oil films were applied in most cases in the morning in order to carry out over a period of a day a complete series of weighings until the maximum apparent oxygen absorption had been attained. The plates were kept during the course of a days weighings in a small room equipped with three analytical balances. Throughout the entire experiment the films were exposed only to diffuse light and this particular variable could be considered, for the most part, as constant. The temperature of the balance room was controlled within the limits of four degrees, that is, a temperature of 27 C

2 was maintained over a day's weighings. This was obviously a wide variation in temperature for the drying of an oil film. However, a temperature of 27 C prevailed throughout the greater portion of the day with variations being most marked in the morning and late evenings.

During the night the films were kept in an improvised thermostatically controlled box where the temperature varied from 25 C to 29 C. This box was situated in the research laboratory exposed to the usual fumes and conditions of moisture characteristic of rooms of this sort. The temperature of this box could not be controlled to any greater degree of accuracy because a large opening had to be maintained in order to insure complete circulation of air.

The humidity conditions were still more difficult to control. Since the balance room was equipped with a small steam heater the humidity of this room was always high owing to a small amount of steam which invariably escaped. Then, too, when the weather was extremely humid outdoors this greatly influenced conditions indoors. This was especially pronounced when the temperature in the balance room fell to 25 C since a lower temperature favors the tendency towards a saturation condition. Under the conditions of this investigation, therefore, it was necessary to consider only the average humidity which prevailed during the course of a day's weighings. The humidity was determined whenever any fluctuation in temperature occurred. This was taken by means of a wet and dry bulb thermometer and no correction was made for barometric pressure. The average humidity for each resin-oil film is recorded in the tables. Moreover, the temperature at which each weighing was made is also recorded in the tables along side each reading taken. In this way it is possible to account for some of the minor fluctuations that may appear in the curves which have been plotted for each oil film.

It is evident that weighings made beyond 15 hours or what in most cases constituted a days work were influenced in no small

way by the conditions mentioned above. However, this investigation was concerned primarily with the initial portion of the curve from the time of spreading the film to its point of maximum gain in weight. Conditions during this period of time were fairly well controlled as is evidenced by the data obtained. In every case the resin-oil film was checked at least once. In many instances especially with the slower drying films three or more checks were necessary. When such was the case the average curve was taken as representative. Moreover, in order to obtain comparable data on a series of resin-oil films constituted of the same resin but differing in concentration, a series of these films were run on the same day under the conditions that prevailed. For example films made up say of 5, 10, 15, 20 and 30% solutions of No. 4 resin were spread together and their increase in weight was recorded under approximately identical conditions.

It might also be mentioned that the room in which the weighings were made was not entirely free from dust and fumes. The slight error obviously produced by these factors was corrected for in the final data.

4. Tabulation of Data

The present study was limited to a reaction system consisting of three components, namely, oil, drier, and resin. The amount of drier was kept constant while the oil and resin varied depending upon the concentration of the solution used. Since an interpretation of the results was to be based on the rate of oxidation of the oil and since the rate of oxidation is a function of time, it was convenient to record the data in graphical form. Therefore a co-ordinate system was used in which the abscissa represented time and the ordinate represented the percentage increase in weight.

Because of the limited size of the graph the smallest division on the paper was used to represent a time interval of 10 minutes. After 20 hours this smallest divisional unit was increased to 2 hours. Although this was not entirely an accurate representation of the drying time it served, however, for all practical purposes and placed all curves on a comparable basis. In the case of those films that dried over longer periods of time, that is, those which did not attain maximum weight within a period of 15 hours, the smallest divisional unit represented a time interval of 30 minutes.

The percentage increase in weight, represented symbolically by $\% \Delta W$, was calculated by dividing the increase in weight per unit of time by the weight of the film multiplied by 100.

In order to place all films on a comparable basis it was necessary to introduce a correction in the case of the resin-oil films. This correction was made by multiplying the actual percentage increase in weight by a factor which varied according to the percentage composition of the solution. For example, the actual

percentage increase in weight of a film constituted of a 10% solution of resin in oil was multiplied by the factor $10/9$, a 15% solution would be multiplied by the factor $100/85$, a 30% solution by $10/7$, etc. By introducing this factor all films were placed on the basis of 100% oil. For each resin-oil film a large number of weighings was taken in order to obtain a fairly representative curve.

The data were also recorded in tabular form for purposes of further reference. These tables consisted of a record of the time in hours and minutes, the increase in weight per unit of time, the percentage increase in weight, the percentage increase in weight based on 100% linseed oil, the temperature at which each weighing was made, the average humidity, and the weight of the film.

VI Tables

Table 1

Linseed Oil Heated to 150° C

Weight of Film = .1436

Average Humidity = 60

Time		ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
Hrs. - Min.					
0	10	0.0005	0.347	0.347	27.0
0	20	0.0013	0.925	0.925	27.0
0	30	0.0022	1.530	1.530	27.0
0	45	0.0049	3.400	3.400	27.0
1	10	0.0089	6.170	6.170	27.0
1	30	0.0108	7.500	7.500	27.5
1	40	0.0133	9.240	9.240	27.5
2	10	0.0163	11.300	11.300	27.5
2	40	0.0176	12.200	12.200	27.5
3	10	0.0181	12.500	12.500	27.5
3	40	0.0184	12.800	12.800	27.0
5	00	0.0187	13.000	13.000	27.0
10	00	0.0187	13.000	13.000	27.0
15	00	0.0184	12.800	12.800	26.5
20	00	0.0173	12.000	12.000	25.5
60	00	0.0159	11.000	11.000	26.5
100	00	0.0130	9.030	9.030	27.0
140	00	0.0114	7.900	7.900	27.5
180	00	0.0112	7.800	7.900	27.0

Table 2

Linseed Oil Heated to 260°C

Weight of Film = 0.1173

Average Humidity = 60

Time		ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
Hrs. - Min.					
0	10	0.0002	0.170	0.170	28.0
0	20	0.0012	1.020	1.020	28.0
0	30	0.0025	2.130	2.130	28.0
0	45	0.0040	3.420	3.420	27.5
0	55	0.0053	4.520	4.520	27.5
1	00	0.0060	5.120	5.120	27.5
1	15	0.0076	6.460	6.460	27.0
1	30	0.0096	8.200	8.200	27.0
1	45	0.0111	9.490	9.490	27.0
2	00	0.0123	10.500	10.500	27.0
2	30	0.0137	11.700	11.700	27.0
3	00	0.0148	12.600	12.600	27.5
4	00	0.0152	13.000	13.000	27.5
5	00	0.0156	13.300	13.300	27.5
6	40	0.0156	13.300	13.300	27.0
10	00	0.0153	13.100	13.100	27.0
13	20	0.0152	13.000	13.000	26.5
20	00	0.0139	11.900	11.900	27.0
60	00	0.0125	10.700	10.700	27.5
100	00	0.0117	10.000	10.000	27.5
140	00	0.0102	8.700	8.700	26.5
180	00	0.0071	8.300	8.300	27.0

Table 3

5% Solution No. 2 Resin (Oxidized)
in Linseed Oil

Weight of Film = 0.1188

Average Humidity = 50

Time Hrs. - Min.	ΔW	$\% \Delta W$	$\% \Delta W$ 100% Oil	Temp. Centigrade
0 20	0.0002	0.168	0.177	26.0
0 50	0.0005	0.420	0.443	26.5
1 25	0.0011	0.925	0.975	27.0
1 40	0.0015	1.260	1.330	27.5
2 00	0.0022	1.850	1.950	27.0
2 40	0.0035	2.940	3.100	27.0
3 10	0.0061	5.120	5.400	27.0
3 25	0.0076	6.400	6.740	27.0
4 00	0.0107	9.000	9.480	27.0
4 30	0.0131	11.000	11.600	27.0
5 00	0.0139	11.700	12.300	27.0
6 40	0.0147	12.300	13.000	27.0
10 00	0.0148	12.400	13.100	27.0
11 40	0.0148	12.400	13.100	27.0
15 00	0.0143	12.000	12.600	27.0
18 00	0.0142	11.900	12.530	27.0
24 00	0.0141	11.800	12.440	27.0
50 00	0.0136	11.410	12.040	26.5
70 00	0.0118	9.930	10.410	27.0
125 00	0.0110	9.310	9.800	27.0
145 00	0.0106	9.000	9.470	27.0
180 00	0.0098	8.240	8.670	27.0

Table 4
5% Solution No. 2 Resin
in Linseed Oil

Time		ΔW	% ΔW	Average Humidity = 55	
Hrs.	Min.			% ΔW 100% Oil	Temp. Centigrade
1	40	0.0001	0.091	0.096	26.0
2	00	0.0003	0.273	0.287	26.5
2	50	0.0006	0.545	0.575	27.0
3	30	0.0011	1.000	1.050	27.0
4	00	0.0014	1.270	1.330	27.0
5	10	0.0024	2.180	2.300	27.0
6	00	0.0034	3.090	3.260	27.0
6	20	0.0042	3.800	4.000	27.0
6	30	0.0055	5.000	5.270	27.0
7	00	0.0078	7.090	7.470	27.0
7	50	0.0104	9.500	10.000	27.0
10	00	0.0126	11.400	12.000	27.0
11	00	0.0128	11.620	12.230	26.5
15	00	0.0126	11.400	12.000	26.5
25	00	0.0118	10.720	11.300	27.0
40	00	0.0111	10.070	10.600	27.0
70	00	0.0107	9.700	10.200	26.5
120	00	0.011	9.130	9.600	27.0
180	00	0.0091	8.270	8.700	26.0

Table 5

10% Solution No. 2 Resin
in Linseed Oil

Weight of film \Rightarrow 0.1471

Average Humidity = 55

Time		ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
Hrs.	Min.				
4	10	0.0001	0.068	0.075	26.5
4	40	0.0005	0.340	0.370	27.5
5	20	0.0007	0.475	0.520	27.0
5	50	0.0010	0.680	0.750	28.0
7	20	0.0022	1.490	1.600	27.0
8	00	0.0026	1.780	2.000	27.0
9	10	0.0047	3.180	3.540	27.0
10	20	0.0079	5.400	6.000	27.5
11	40	0.0108	7.360	8.200	27.0
13	00	0.0134	9.100	10.100	27.0
15	50	0.0154	10.450	11.600	27.5
18	00	0.0159	10.800	12.000	27.0
30	00	0.0159	10.800	12.000	27.0
100	00	0.0156	10.600	11.800	27.5
140	00	0.0145	9.900	11.000	27.0
180	00	0.0131	8.900	9.900	27.5

Table 6

15 % Solution No. 2 Resin
in Linseed Oil

Weight of Film = 0.1145

Average Humidity = 60

Time		ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
Hrs.	Min.				
0	20	-0.0001	-0.087	-0.102	26.0
2	30	-0.0003	-0.260	-0.306	26.0
6	00	0.0001	0.087	0.102	26.5
10	30	0.0009	0.782	0.920	27.0
14	00	0.0017	1.475	1.74	27.0
23	00	0.0043	3.740	4.400	27.5
26	00	0.0053	4.600	5.400	27.0
32	30	0.0073	6.350	7.500	28.0
40	00	0.0095	8.250	9.700	27.5
42	30	0.0106	9.190	10.800	28.0
50	00	0.0120	10.48	12.300	27.0
60	00	0.0124	10.80	12.700	27.0
75	00	0.0121	10.52	12.400	27.5
100	00	0.0110	9.60	11.200	27.0
160	00	0.0104	9.04	10.6	26.5
180	00	0.0098	8.50	10.00	26.0

Table 7

20% Solution of No. 2 Resin
in Linseed Oil

Weight of Film = 0.1378

Average Humidity = 55

Time		ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
Hrs. - Min.					
0	20	-0.0001	-0.073	-0.092	26.0
5	00	-0.0003	-0.217	-0.271	27.0
9	00	-0.0002	-0.145	-0.181	27.0
12	30	0.0000	0.000	0.000	27.5
15	00	0.0003	0.217	0.271	27.0
20	00	0.0010	0.725	0.905	27.5
23	00	0.0017	1.230	1.540	27.0
26	30	0.0027	1.950	2.400	27.5
28	00	0.0031	2.240	2.800	27.5
40	00	0.0067	4.850	6.050	27.0
50	00	0.0099	7.160	8.950	27.5
57	30	0.0117	8.500	10.600	27.0
65	00	0.0124	9.000	11.200	27.5
75	00	0.0124	9.000	11.200	27.0
120	00	0.0116	8.400	10.500	26.5
140	00	0.0115	8.350	10.400	27.0
180	00	0.0104	7.550	9.500	27.0

Table 8

5% Solution of No.4 Resin
in Linseed Oil

Weight of Film = .1065

Average Humidity = 55

Time		ΔW	% ΔW	% ΔW 100% Dil	Temp. Centigrade
Hrs. - Min.					
0	20	0.0002	0.189	0.199	26.5
0	35	0.0006	0.560	0.590	26.5
0	50	0.0009	0.842	0.886	26.5
1	10	0.0014	1.310	1.380	26.5
1	40	0.0025	2.340	2.460	27.0
2	00	0.0036	3.360	3.540	27.0
2	20	0.0051	4.760	5.01	27.0
2	35	0.0063	5.880	6.20	27.0
2	50	0.0072	6.720	7.06	27.0
3	00	0.0081	7.560	7.99	27.0
3	25	0.0097	9.02	9.50	27.0
3	50	0.0112	10.49	11.02	27.5
4	00	0.0120	11.20	11.80	27.5
5	00	0.0130	12.12	12.80	27.5
6	00	0.0135	12.60	13.30	27.0
6	50	0.0136	12.70	13.40	27.0
10	00	0.0135	12.60	13.30	26.5
15	00	0.0131	12.22	12.90	26.0
24	30	0.0119	11.10	11.70	27.0
50	00	0.0108	10.10	10.61	27.0
100	00	0.0098	9.15	9.65	27.0
120	00	0.0094	8.80	9.27	28.0
170	00	0.0083	7.75	8.18	27.0
180	00	0.0083	7.75	8.18	27.0

Table 9

7% Solution of No.4 Resin
in Linseed Oil

Weight of Film = 0.1116

Average Humidity = 55

Time		ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
Hrs. - Min.					
0	20	0.0001	0.089	0.096	26.5
0	30	0.0003	0.267	0.288	26.5
0	50	0.0005	0.446	0.480	26.5
1	10	0.0008	0.715	0.770	26.5
1	30	0.0015	1.340	1.400	26.5
2	00	0.0025	2.230	2.400	26.5
2	20	0.0037	3.300	3.530	27.0
3	00	0.0063	5.610	6.050	27.0
3	20	0.0074	6.600	7.100	27.0
4	10	0.0097	8.65	9.320	27.0
4	30	0.0109	9.75	10.500	27.0
5	10	0.0125	11.15	12.000	27.0
5	50	0.0131	11.70	12.600	27.5
7	30	0.0136	12.14	13.050	27.5
10	00	0.0134	12.00	12.900	27.5
13	20	0.0134	12.000	12.900	27.5
30	00	0.0124	11.000	11.900	26.5
50	00	0.0117	10.400	11.200	27.5
100	00	0.0098	8.800	9.500	27.5
140	00	0.0094	8.360	9.000	28.0
180	00	0.0088	7.810	8.4	26.5

Table 10

10% Solution No.4 Resin
in Linseed Oil

Weight of Film = 0.1604

Average Humidity = 55

Time		ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
Hrs. - Min.					
0	50	0.0004	0.250	0.300	26.5
1	10	0.0009	0.560	0.600	26.5
1	30	0.0013	0.813	0.904	26.5
2	10	0.0023	1.440	1.600	27.0
2	30	0.0032	2.000	2.200	27.0
3	00	0.0046	2.880	3.200	27.0
3	30	0.0063	3.940	4.370	27.5
4	10	0.0088	5.500	6.100	27.5
4	40	0.0115	7.200	8.000	27.0
5	50	0.0144	9.000	10.000	27.0
6	40	0.0166	10.300	11.600	27.0
8	10	0.0182	11.340	12.600	27.0
10	00	0.0183	11.400	12.700	26.5
13	00	0.0182	11.340	12.600	26.0
20	00	0.0173	10.800	12.000	26.5
50	00	0.0161	10.050	11.200	27.0
100	00	0.0148	9.250	10.270	27.5
120	00	0.0144	9.000	10.000	27.0
170	00	0.0129	8.060	8.900	27.5
180	00	0.0129	8.060	8.900	27.0

Table 11

15% Solution No. 4 Resin
in Linseed Oil

Weight of Film = 0.1574

Average Humidity = 53

Time		ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
Hrs. - Min.					
0	50	0.0004	0.254	0.299	28
1	30	0.0008	0.510	0.600	28
2	20	0.0017	1.080	1.270	28
3	00	0.0028	1.780	2.100	27.5
4	10	0.0050	3.180	3.740	27.5
4	30	0.0057	3.630	4.280	27.0
5	00	0.0067	4.260	5.020	27.0
6	25	0.0100	6.360	7.500	27.0
7	00	0.0113	7.200	8.470	27.0
8	30	0.0147	9.350	11.000	27.0
12	00	0.0164	10.400	12.300	26.5
16	00	0.0164	10.400	12.300	26.5
20	00	0.0160	10.200	12.000	26.5
40	00	0.0156	9.940	11.700	27.0
86	00	0.0153	9.750	11.400	27.0
115	00	0.0150	9.550	11.200	25.0
180	00	0.0131	8.350	9.800	26.0

Table 12

20% Solution No. 4 Resin
in Linseed Oil

Weight of Film = 0.1593

Average Humidity = 55

Time		ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
Hrs. - Min.					
0	50	0.0001	0.063	0.080	27.0
2	00	0.0008	0.503	0.600	27.5
2	40	0.0013	0.820	1.020	27.5
3	30	0.0023	1.440	1.800	27.5
5	00	0.0048	3.020	3.770	27.0
6	00	0.0063	3.960	4.900	27.0
7	00	0.0079	4.960	6.200	27.0
7	30	0.0089	5.600	7.000	26.0
8	40	0.0108	6.800	8.500	27.0
9	30	0.0122	7.670	9.600	27.0
10	10	0.0136	8.550	10.700	26.5
11	00	0.0146	9.200	11.500	26.5
13	20	0.0155	9.760	12.200	26.0
18	20	0.0156	9.820	12.300	27.0
20	00	0.0156	9.820	12.300	27.5
40	00	0.0151	9.500	11.800	28.0
100	00	0.0145	9.130	11.400	27.0
120	00	0.0145	9.130	11.400	28.0
160	00	0.0133	8.400	10.400	27.0
180	00	0.0127	8.000	10.000	27.5

Table 13

30% Solution of No. 4 Resin
in Linseed Oil

Weight of Film - 0.1640

Average Humidity - 55

Time		ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
Hrs. - Min.					
1	50	0.0002	0.122	0.174	25.0
2	50	0.0008	0.481	0.697	26.0
3	20	0.0012	0.731	1.040	26.5
4	20	0.0021	1.280	1.830	27.0
5	00	0.0029	1.770	2.520	27.0
5	20	0.0038	2.320	3.310	27.0
6	20	0.0045	2.740	3.910	27.0
6	50	0.0053	3.210	4.600	27.5
7	30	0.0061	3.720	5.300	27.5
8	10	0.0068	4.150	5.920	27.0
9	00	0.0082	4.970	7.120	27.0
10	20	0.0101	6.150	8.800	27.0
12	00	0.0119	7.260	10.340	27.0
12	50	0.0129	7.900	11.300	27.0
14	50	0.0137	8.350	11.900	27.5
15	00	0.0140	8.550	12.200	27.0
30	00	0.0141	8.600	12.300	27.5
60	00	0.0140	8.550	12.200	28.0
100	00	0.0137	8.350	11.900	27.0
140	00	0.0132	8.050	11.500	27.5
160	00	0.0126	7.700	11.000	27.5
180	00	0.0122	7.420	10.600	27.0

Table 14

5% Solution #5 Resin

Weight of Film = 0.1501

Average Humidity = 55

Time		ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
Hrs. - Min.					
0	20	-0.0002	-0.133	-0.140	27.0
0	50	-0.0001	-0.066	-0.070	27.0
1	10	0.0003	0.200	0.211	27.0
1	30	0.0005	0.333	0.350	27.0
1	50	0.0014	0.935	0.983	27.0
2	10	0.0023	1.530	1.610	27.0
2	30	0.0040	2.670	2.810	27.0
2	55	0.0061	4.070	4.300	27.0
3	20	0.0085	5.650	5.950	27.0
3	45	0.0113	7.550	7.940	27.0
4	35	0.0148	9.870	10.40	27.0
4	55	0.0158	10.500	11.00	27.5
5	20	0.0165	11.000	11.60	27.5
6	00	0.0171	11.400	12.00	28.0
7	30	0.0177	11.800	12.400	28.0
10	50	0.0176	11.700	12.300	27.0
14	10	0.0174	11.600	12.200	26.5
16	40	0.0171	11.400	12.000	26.0
20	00	0.0161	10.700	11.300	26.0
60	00	0.0150	10.000	10.500	25.0
100	00	0.0135	9.000	9.500	26.0
110	00	0.0134	8.94	9.400	27.0
150	00	0.0121	8.06	8.500	28.0
180	00	0.0111	7.40	7.800	26.0

Table 15

5% Solution No. 5 Resin (Oxidized)
in Linseed Oil

Weight of Film - 0.1277

Average Humidity - 60

Time Hrs. - Min.	ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
0 30	0.0004	0.312	0.330	26.0
1 15	0.0017	1.320	1.390	26.0
2 00	0.0045	3.510	3.700	26.0
2 30	0.0073	5.700	6.000	26.5
3 10	0.0102	7.980	8.400	26.5
3 15	0.0110	8.600	9.040	26.5
4 00	0.0140	10.920	11.500	27.0
5 05	0.0152	11.850	12.500	26.5
7 00	0.0158	12.350	13.000	26.0
11 40	0.0158	12.350	13.000	26.0
20 00	0.0143	11.150	11.700	25.0
90 00	0.0122	9.540	10.010	27.0
120 00	0.0119	9.300	9.800	27.5
160 00	0.0110	8.600	9.040	27.0
180 00	0.0097	7.580	8.000	26.5

Table 16

10% Solution No. 5 Resin
in Linseed Oil

Weight of Film - 0.1141

Average Humidity - 55

Time Hrs. - Min.	ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
0 20	-0.0001	-0.088	-0.098	25.0
0 40	-0.0002	-0.175	-0.195	25.0
0 50	-0.0002	-0.175	-0.195	26.0
1 20	0.0000	0.000	0.000	26.0
2 00	0.0002	0.175	0.195	27.0
2 50	0.0006	0.525	0.585	27.0
3 20	0.0009	0.790	0.880	27.0
3 40	0.0013	1.140	1.200	27.0
4 20	0.0019	1.670	1.800	27.5
4 40	0.0022	1.930	2.100	27.0
5 00	0.0028	2.450	2.730	27.0
5 35	0.0038	3.330	3.700	26.5
6 40	0.0063	5.500	6.000	26.5
7 00	0.0070	5.850	6.500	27.0
7 25	0.0077	6.740	7.500	27.0
8 30	0.0097	8.500	9.400	27.0
8 45	0.0101	8.810	9.800	26.5
9 10	0.0105	9.200	10.200	27.0
9 40	0.0110	9.650	10.700	27.0
10 10	0.0114	10.000	11.100	27.0
13 00	0.0127	11.100	12.300	27.0
20 00	0.0127	11.100	12.300	
40 00	0.0117	10.27	11.400	27.0

Table (Continued)

10% Solution No. 5 Resin
in Linseed Oil

Weight of Film - 0.1141

Average Humidity - 55

Time		ΔW	$\% \Delta W$	$\% \Delta W$	Temp.
Hrs. - Min.				100% Oil	Centigrade
80	00	0.0112	9.82	10.900	27.0
120	00	0.0103	9.05	10.050	28.0
180	00	0.0093	8.10	9.00	27.5

Table 17

15% Solution No. 5 Resin in Linseed Oil

Weight of Film = 0.1712

Average Humidity = 55

Time Hrs. - Min.	ΔW	$\% \Delta W$	$\% \Delta W$ 100% Oil	Temp. Centigrade
0 30	-0.0002	-0.117	-0.138	27.0
3 00	-0.0002	-0.117	-0.138	27.5
4 00	0.0000	0.000	0.000	27.0
5 30	0.0004	0.230	0.270	27.0
6 00	0.0008	0.468	0.550	27.0
7 30	0.0016	0.935	1.100	27.0
9 00	0.0028	1.635	1.920	27.0
10 00	0.0036	2.100	2.480	27.0
11 00	0.0045	2.640	3.100	26.0
12 30	0.0059	3.450	4.070	26.5
15 00	0.0073	4.260	5.030	26.0
20 00	0.0113	6.620	7.800	26.5
25 00	0.0149	8.720	10.260	27.0
30 00	0.0164	9.600	11.300	26.5
31 30	0.0164	9.600	11.300	27.0
35 00	0.0163	9.530	11.190	27.0
45 00	0.0157	9.200	10.800	26.5
60 00	0.0152	8.800	10.450	27.0
100 00	0.0149	8.720	10.260	26.0
120 00	0.0145	8.540	10.000	27.0
150 00	0.0145	8.540	10.000	26.5
180 00	0.0137	8.000	9.400	27.0
220 00	0.0130	7.650	9.000	27.0

Table 18

20% Solution No. 5 Resin in Linseed Oil

Weight of Film = .1295

Average Humidity = 55

Time Hrs. - Min.	ΔW	$\% \Delta W$	$\% \Delta W$ 100% Oil	Temp. Centigrade
1 00	-0.0002	-0.154	-0.193	25.0
2 30	-0.0002	-0.154	-0.193	26.5
4 30	-0.0002	-0.154	-0.193	27.0
5 30	0.0000	0.000	0.000	27.5
9 00	0.0010	0.770	0.900	27.0
12 30	0.0026	2.000	2.500	27.0
13 30	0.0032	2.460	3.060	26.5
14 30	0.0036	2.770	3.440	26.0
15 00	0.0038	2.920	3.600	26.0
20 00	0.0062	4.800	6.000	26.5
25 00	0.0083	6.400	8.000	27.0
27 30	0.0099	7.600	9.500	27.0
31 00	0.0115	8.850	11.000	27.0
35 00	0.0121	9.300	11.600	26.5
40 00	0.0122	9.400	11.700	27.0
50 00	0.0115	8.850	11.000	26.5
75 00	0.0112	8.640	10.800	27.0
170 00	0.0103	7.920	9.900	26.5
220 00	0.0098	7.540	9.400	27.5

Table 19

30% Solution No. 5 Resin in Linseed Oil

Weight of Film = 0.1312

Average Humidity = 55

Time Hrs. - Min.	ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
1 30	-0.0003	-0.231	-0.330	26.5
3 30	-0.0003	-0.231	-0.330	27.0
6 00	-0.0003	-0.231	-0.330	27.0
7 30	0.0000	0.000	0.000	27.5
10 00	0.0005	0.381	0.540	27.0
11 30	0.0010	0.765	1.090	27.0
12 30	0.0012	0.919	1.310	27.0
20 30	0.0039	2.990	4.250	26.0
23 30	0.0055	4.200	6.000	27.0
30 00	0.0080	6.100	8.700	26.5
35 00	0.0097	7.400	10.500	27.5
40 00	0.0102	7.850	11.200	27.0
50 00	0.0104	7.950	11.400	27.5
55 00	0.0100	7.620	10.900	26.0
100 00	0.0100	7.620	10.900	27.5
140 00	0.0097	7.400	10.500	27.0
180 00	0.0091	7.000	10.000	27.5
220 00	0.0090	6.860	9.800	27.0

Table 20

10% Solution of Ester Gum

Weight of Film = 0.1419

Average Humidity = 55

Time		ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
Hrs.	Min.				
0	10	0.0003	0.211	0.232	27.5
0	15	0.0007	0.493	0.540	28.0
0	30	0.0033	2.320	2.500	28.0
1	00	0.0068	4.780	5.300	28.0
1	30	0.0112	7.890	8.700	27.5
2	00	0.0145	10.200	11.300	27.5
2	30	0.0160	11.200	12.500	27.5
4	00	0.0169	11.900	13.200	27.0
5	00	0.0170	12.000	13.300	27.0
8	40	0.0170	12.000	13.300	26.5
10	00	0.0170	12.000	13.300	26.5
16	40	0.0165	11.600	12.900	27.0
40	00	0.0160	11.200	12.500	27.0
60	00	0.0153	10.800	12.000	27.0
100	00	0.0141	9.940	11.000	26.5
150	00	0.0126	8.900	9.900	27.0
180	00	0.0119	8.380	9.300	27.5

Table 21

30% Solution of Ester Gun in Linseed Oil

Weight of Film = 0.1610

Average Humidity = 50

Time Hrs. - Min.	ΔW	$\% \Delta W$	$\% \Delta W$ 100% Oil	Temp. Centigrade
0 25	0.0003	0.186	0.276	26.0
0 40	0.0015	0.930	1.320	27.0
1 00	0.0035	2.170	3.100	27.0
1 10	0.0052	3.230	4.600	26.5
1 30	0.0073	4.530	6.500	27.0
1 40	0.0082	5.100	7.200	27.0
2 00	0.0106	6.590	9.400	27.0
2 20	0.0131	8.200	11.700	27.0
3 20	0.0148	9.170	13.100	27.0
4 30	0.0152	9.490	13.500	27.0
5 30	0.0154	9.560	13.700	27.0
13 20	0.0154	9.560	13.700	27.0
40 00	0.0154	9.560	13.700	27.0
100 00	0.0149	9.250	13.200	26.5
149 00	0.0141	8.760	12.500	27.0
160 00	0.0139	8.650	12.300	27.0
180 00	0.0139	8.650	12.300	27.5

Table 22

5% Solution No. 1 Resin
in Linseed Oil

Weight of Film = 0.1103

Average Humidity = 60

Time Hrs. - Min.		ΔW	$\% \Delta W$	$\% \Delta W$ 100% Oil	Temp. Centigrade
0	15	0.0005	0.455	0.479	27.0
0	30	0.0009	0.817	0.862	27.0
0	40	0.0017	1.540	1.620	27.0
1	10	0.0042	3.820	4.020	27.0
1	40	0.0066	6.000	6.300	27.0
2	00	0.0078	7.100	7.500	27.0
2	20	0.0099	9.000	9.599	27.0
3	30	0.0131	11.900	12.500	27.0
4	40	0.0138	12.500	13.200	27.0
5	20	0.0139	12.610	13.300	27.0
10	00	0.0138	12.500	13.200	27.0
12	00	0.0138	12.500	13.200	27.0
15	00	0.0135	12.250	12.900	26.5
20	00	0.0132	11.960	12.600	26.0
70	00	0.0103	9.400	9.900	27.0
90	00	0.0103	9.400	9.900	27.0
120	00	0.0096	8.750	9.200	27.0
170	00	0.0094	8.550	9.000	27.0
180	00	0.0090	8.160	8.600	27.0

Table 23

10% Solution No. 1 Resin (Boiled)
in Linseed Oil

Weight of Film = 0.1430

Average Humidity = 60

Time Hrs. - Min.	ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
0 40	0.0008	0.560	0.600	27.0
1 15	0.0018	1.260	1.400	27.0
1 30	0.0023	1.620	1.800	26.5
1 40	0.0032	2.240	2.490	26.5
1 50	0.0039	2.720	3.030	26.5
2 00	0.0059	4.120	4.500	26.5
2 20	0.0079	5.500	6.100	26.5
2 40	0.0103	7.200	8.000	26.6
3 00	0.0127	8.890	9.800	26.5
3 20	0.0141	9.900	11.000	26.5
3 45	0.0148	10.350	11.500	26.5
4 15	0.0155	10.800	12.000	26.5
5 20	0.0165	11.500	12.800	26.0
6 10	0.0167	11.700	13.000	26.0
10 00	0.0168	11.720	13.100	26.0
13 20	0.0166	11.600	12.900	26.0
20 00	0.0160	11.200	12.400	26.0
70 00	0.0143	10.000	11.100	26.5
100 00	0.0138	9.650	10.700	27.5
140 00	0.0122	8.550	9.500	27.0
170 00	0.0119	8.320	9.250	27.0
180 00	0.0116	8.100	9.000	27.0

Table 24

10% Solution No. 1 Resin in Linseed Oil

Weight of Film = 0.1469

Average Humidity = 60

Time Hrs. - Min.	ΔW	$\% \Delta W$	$\% \Delta W$ 100% Oil	Temp. Centigrade
0 40	0.0005	0.340	0.377	27.0
1 00	0.0011	0.750	0.800	27.0
1 30	0.0017	1.150	1.200	27.0
2 00	0.0024	1.630	1.800	27.5
2 40	0.0036	2.450	2.700	27.0
3 30	0.0062	4.230	4.700	26.5
3 40	0.0075	5.100	5.600	27.0
4 40	0.0115	7.830	8.700	27.0
5 10	0.0134	9.110	10.100	27.0
5 40	0.0148	10.000	11.100	27.0
6 20	0.0157	10.700	11.900	26.5
7 30	0.0168	11.400	12.700	27.0
9 00	0.0175	11.900	13.200	27.0
10 00	0.0176	11.960	13.300	26.5
11 00	0.0176	11.960	13.300	26.0
16 20	0.0174	11.800	13.100	26.0
20 00	0.0169	11.500	12.700	26.0
60 00	0.0155	10.500	11.600	27.5
120 00	0.0137	9.340	10.350	27.0
140 00	0.0129	8.800	9.800	27.0
170 00	0.0124	8.450	9.400	27.0
180 00	0.0123	8.380	9.320	27.5

Table 25

15% Solution No. 1 Resin
in Linseed Oil

Time		ΔW	$\% \Delta W$	Average Humidity \Rightarrow 60	
Hrs. - Min.	$\% \Delta W$ 100% Oil			Temp. Centigrade	
1	10	0.0005	0.359	0.423	27.0
2	10	0.0013	0.935	1.100	27.0
3	00	0.0021	1.510	1.770	27.0
4	40	0.0046	3.310	3.900	27.0
6	00	0.0078	5.580	6.200	27.5
6	50	0.0084	6.040	7.100	27.0
7	20	0.0094	6.750	7.950	26.5
8	10	0.0109	7.850	9.240	27.0
8	30	0.0123	8.850	10.400	27.5
9	10	0.0133	9.570	11.210	27.0
10	00	0.0145	10.400	11.280	27.0
12	10	0.0154	11.020	13.000	27.0
12	50	0.0154	11.020	13.000	26.5
20	00	0.0154	11.020	13.000	26.0
60	00	0.0154	11.020	13.000	27.0
120	00	0.0144	10.340	12.200	27.0
150	00	0.0141	10.100	11.900	27.0
180	00	0.0126	9.060	10.630	27.0

Table 26
 10% Solution No. 3 Resin
 in Linseed Oil

Time		ΔW	% ΔW	Average Humidity = 55	
Hrs. - Min.	% ΔW 100% Oil			Temp. Centigrade	
0	30	0.0005	0.437	0.486	27.0
0	50	0.0011	0.965	1.070	27.0
1	15	0.0032	2.800	3.000	27.0
1	30	0.0046	4.040	4.480	27.0
2	05	0.0076	6.650	7.300	27.0
2	30	0.0092	8.060	8.960	27.0
2	40	0.0113	9.900	11.000	27.0
3	10	0.0125	10.980	12.200	27.0
4	00	0.0132	11.600	12.800	27.0
5	50	0.0135	12.050	13.400	27.0
7	30	0.0135	12.050	13.400	27.0
10	00	0.0134	11.900	13.200	27.0
20	00	0.0128	11.200	12.500	26.5
80	00	0.0114	10.000	11.100	27.5
120	00	0.0114	10.000	11.100	26.5
150	00	0.0103	9.040	10.000	27.0
180	00	0.0086	7.550	8.500	27.5

Table 27

20% Solution No. 3 Resin
in Linseed Oil

Weight of Film = 0.1555

Average Humidity = 55

Time Hrs. - Min.	ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
0 50	0.0005	0.320	0.400	27.0
1 10	0.0014	0.896	1.120	27.0
1 30	0.0024	1.540	1.900	27.0
1 50	0.0038	2.430	3.000	27.5
2 10	0.0058	3.720	4.600	27.5
3 10	0.0106	6.800	8.500	27.0
3 40	0.0138	8.850	11.000	27.0
4 40	0.0160	10.200	12.500	27.5
5 00	0.0170	10.900	13.610	27.0
5 30	0.0173	11.100	13.840	27.0
7 00	0.0179	11.420	14.300	27.0
10 00	0.0178	11.360	14.200	27.5
20 00	0.0176	11.300	14.000	27.0
80 00	0.0165	10.600	13.250	27.5
100 00	0.0152	9.750	12.300	27.0
160 00	0.0140	8.950	11.200	26.5
180 00	0.0133	8.500	10.6	27.0

Table 28

30% Solution No. 3 Resin
in Linseed Oil

Weight of Film = 0.2485

Average Humidity = 55

Time Hrs. - Min.		ΔW	$\% \Delta W$	$\% \Delta W$ 100% Oil	Temp. Centigrade
0	50	0.0003	0.120	0.173	27.5
1	20	0.0007	0.281	0.400	27.0
1	40	0.0011	0.442	0.630	27.0
2	30	0.0026	1.040	1.560	27.0
3	20	0.0051	2.044	2.930	27.5
3	30	0.0059	2.370	3.400	28.0
3	50	0.0088	3.530	5.000	27.5
4	10	0.0108	4.340	6.200	27.5
4	40	0.0144	5.790	8.200	27.0
5	10	0.0180	7.240	10.300	27.0
6	00	0.0208	8.350	11.900	27.0
7	00	0.0229	9.200	13.100	26.5
9	00	0.0244	9.820	14.000	26.5
11	00	0.0254	10.200	14.500	26.5
25	00	0.0254	10.200	14.500	27.0
100	00	0.0254	10.200	14.500	27.0
140	00	0.0244	9.820	14.000	27.0
180	00	0.0232	9.340	13.300	27.0

Table 29

10% Solution No. 6 Resin
in Linseed Oil

Weight of Film = 0.1050

Average Humidity = 60

Time		ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
Hrs. -	Min.				
0	15	0.0003	0.286	0.317	27.5
0	30	0.0010	0.950	1.060	27.0
1	00	0.0036	3.420	3.800	27.0
1	30	0.0058	5.520	6.150	27.0
2	00	0.0083	7.900	8.800	27.0
2	30	0.0109	10.350	11.500	27.0
3	00	0.0123	11.700	13.000	27.0
5	00	0.0132	12.600	14.000	27.0
10	00	0.0132	12.600	14.000	26.5
20	00	0.0129	12.250	13.600	27.5
50	00	0.0115	11.100	12.200	27.0
70	00	0.0115	11.100	12.200	27.0
90	00	0.0106	10.100	11.200	27.0
120	00	0.0101	9.650	10.700	27.5
150	00	0.0091	8.650	9.600	27.0
180	00	0.0087	8.270	9.200	27.5

Table 30

20% Solution No. 6 Resin
in Linseed Oil

Weight of Film = 0.1622

Average Humidity = 60

Time Hrs. - Min.		A W	% Δ W	% Δ W 100% Oil	Temp. Centigrade
0	35	0.0006	0.370	0.460	26.0
1	00	0.0021	1.280	1.600	26.5
1	40	0.0056	3.460	4.300	27.0
2	30	0.0104	6.410	8.030	27.0
3	10	0.0146	9.010	11.200	27.0
3	40	0.0161	9.950	12.400	27.5
4	00	0.0174	10.650	13.300	27.0
6	00	0.0182	11.200	14.100	27.0
10	00	0.0186	11.500	14.300	26.5
20	00	0.0182	11.200	14.100	27.0
60	00	0.0174	10.650	13.300	27.5
90	00	0.0152	9.400	11.700	26.5
170	00	0.0147	9.100	11.300	27.0
180	00	0.0140	8.660	10.800	27.0

Table 31

30% Solution No. 6 Resin
in Linseed Oil

Weight of Film = 0.1846

Average Humidity = 60

Time Hrs. - Min.		ΔW	$\% \Delta W$	$\% \Delta W$ 100% Oil	Temp. Centigrade
0	40	0.0004	0.216	0.309	26.5
1	00	0.0009	0.486	0.695	27.0
1	30	0.0024	1.290	1.840	27.0
2	30	0.0065	3.510	5.020	27.5
3	00	0.0095	5.130	7.340	27.0
3	30	0.0122	6.590	9.400	27.0
4	00	0.0153	8.280	11.200	27.5
5	00	0.0169	9.150	13.020	27.0
8	00	0.0190	10.200	14.500	27.0
10	00	0.0190	10.200	14.500	26.5
20	00	0.0190	10.200	14.500	26.5
90	00	0.0190	10.200	14.500	26.0
180	00	0.0181	9.800	14.000	26.5

Table 32

40% Solution No. 6 Resin
in Linseed Oil

Weight of Film = 0.2152

Average Humidity = 60

Time Hrs. - Min.	ΔW	$\% \Delta W$	$\% \Delta W$ 100% Oil	Temp. Centigrade
1 00	0.0004	0.186	0.310	28.0
1 40	0.0012	0.558	0.931	27.5
2 00	0.0022	1.020	1.700	27.0
2 50	0.0051	2.370	3.900	27.0
3 30	0.0074	3.400	5.700	27.0
4 10	0.0097	4.500	7.500	27.5
4 20	0.0120	5.580	9.900	27.5
5 20	0.0155	7.220	12.000	26.5
7 10	0.0181	8.400	14.000	27.0
10 20	0.0192	8.950	14.700	27.0
20 00	0.0192	8.950	14.700	27.0
90 00	0.0192	8.950	14.700	27.0
180 00	0.0185	8.600	14.300	26.5

Table 33

50% Solution No. 6 Resin
In Linseed Oil

Weight of Film = 0.1989

Average Humidity = 55

Time Hrs. - Min.	ΔW	$\% \Delta W$	$\% \Delta W$ 100% Oil	Temp. Centigrade
1 20	0.0003	0.151	0.320	26.0
2 00	0.0007	0.350	0.700	26.0
2 50	0.0018	0.905	1.800	27.0
3 50	0.0040	2.000	4.000	27.0
4 40	0.0055	2.760	5.500	27.5
5 10	0.0071	3.560	7.100	27.0
5 50	0.0088	4.420	8.840	27.0
6 20	0.0098	4.950	9.900	26.5
7 00	0.0115	5.750	11.500	26.5
7 50	0.0124	6.200	12.400	26.5
9 10	0.0137	6.900	13.800	26.5
12 00	0.0147	7.400	14.800	29.0
22 00	0.0147	7.400	14.800	26.5
100 00	0.0147	7.400	14.800	26.5
180 00	0.0144	7.250	14.500	27.5

Table 34

10% Solution Kauri Resin
in Linseed Oil

Weight of Film = 0.1434

Average Humidity = 50

Time Hrs. - Min.		ΔW	$\% \Delta W$	$\% \Delta W$ 100% Oil	Temp. Centigrade
0	20	0.0009	0.629	0.700	26.0
0	40	0.0024	1.680	1.870	26.5
0	50	0.0052	3.640	4.050	26.5
1	20	0.0084	5.850	6.500	26.5
1	50	0.0122	8.540	9.460	26.5
2	00	0.0134	9.370	10.400	26.5
2	20	0.0149	10.400	11.580	26.5
3	00	0.0160	11.180	12.410	26.0
3	30	0.0168	11.750	13.100	26.0
5	50	0.0175	12.200	13.600	26.5
7	30	0.0175	12.200	13.600	26.0
20	00	0.0172	12.200	13.310	26.0
50	00	0.0164	11.450	12.700	26.5
70	00	0.0161	11.250	12.500	27.0
120	00	0.0136	9.530	10.580	27.0
180	00	0.0124	8.670	9.650	27.5

Table 35

10% Solution East India Resin
in Linseed Oil

Weight of Film = 0.1467

Average Humidity = 50

Time Hrs. - Min.	ΔW	$\% \Delta W$	$\% \Delta W$ 100% Oil	Temp. Centigrade
0 20	0.0005	0.342	0.381	26.0
0 40	0.0013	0.885	0.984	26.5
0 50	0.0026	1.770	1.970	26.5
1 00	0.0046	3.130	3.480	26.5
1 10	0.0059	4.000	4.450	26.5
1 20	0.0069	4.690	5.210	26.5
1 25	0.0076	5.170	5.750	26.5
1 40	0.0095	6.450	7.170	26.5
1 45	0.0101	6.870	7.640	26.5
1 50	0.0116	7.900	8.780	26.5
2 10	0.0129	8.790	9.770	26.0
2 40	0.0139	9.460	10.500	26.0
3 40	0.0153	10.400	11.550	26.0
5 20	0.0159	10.800	12.000	26.0
10 00	0.0159	10.800	12.000	26.0
16 40	0.0155	10.500	11.700	26.0
20 00	0.0154	10.450	11.600	27.0
70 00	0.0144	9.800	10.900	27.0
120 00	0.0136	9.250	10.280	27.0
180 00	0.0124	8.450	9.400	27.0

Table 36

10% Solution Congo Resin
in Linseed Oil

Weight of Film = 0.1203

Average Humidity = 50

Time Hrs. - Min.	ΔW	$\% \Delta W$	$\% \Delta W$ 100% Oil	Temp. Centigrade
0 20	0.0002	0.166	0.185	26.0
1 10	0.0008	0.666	0.742	26.0
1 30	0.0012	1.000	1.110	26.5
1 55	0.0030	2.500	2.700	27.0
2 10	0.0056	4.660	5.100	27.0
2 30	0.0085	7.060	7.700	26.5
3 00	0.0114	9.500	10.500	26.5
3 30	0.0127	10.600	11.700	26.5
3 50	0.0131	10.900	12.100	26.5
4 30	0.0136	11.300	12.500	26.5
5 20	0.0138	11.500	12.800	26.0
6 10	0.0140	11.700	13.000	26.0
10 00	0.0140	11.700	13.000	26.0
15 00	0.0136	11.300	12.500	26.0
23 00	0.0129	10.700	11.900	26.0
70 00	0.0119	9.930	11.000	27.0
112 00	0.0115	9.600	10.600	27.5
145 00	0.0110	9.170	10.200	27.0
180 00	0.0103	8.600	9.550	27.5

Table 37

Heat Bodied in Linseed Oil

Weight of Film = 0.1854

Average Humidity = 60

Time Hrs. - Min.	ΔW	% ΔW -	% ΔW 100% Oil	Temp. Centigrade
0 30	0.0002	0.108	0.108	24.0
1 10	0.0005	0.270	0.270	24.0
2 00	0.0020	1.080	1.080	25.0
2 30	0.0024	1.570	1.570	25.0
2 45	0.0042	2.270	2.270	25.5
3 10	0.0061	3.300	3.300	27.0
3 30	0.0076	4.100	4.100	27.0
3 45	0.0087	4.700	4.700	27.0
4 00	0.0097	5.250	5.250	26.5
5 00	0.0124	6.720	6.720	26.5
5 20	0.0131	7.100	7.100	27.0
5 50	0.0139	7.520	7.520	27.0
6 10	0.0141	7.620	7.620	27.0
6 40	0.0148	8.000	8.000	27.0
7 10	0.0151	8.150	8.150	27.0
7 50	0.0157	8.500	8.500	27.0
9 30	0.0168	9.100	9.100	26.5
10 50	0.0170	9.200	9.200	26.5
15 00	0.0170	9.200	9.200	27.0
40 00	0.0170	9.200	9.200	27.0
70 00	0.0166	9.000	9.000	26.5
100 00	0.0165	8.900	8.900	27.0
140 00	0.0161	8.700	8.700	27.0
180 00	0.0157	8.500	8.500	27.5

Table 38

5% Solution No. 5 Resin
in Heat Bodied Linseed Oil

Weight of Film = 0.1462

Average Humidity = 60

Time Hrs.- Min.	ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
1 50	0.0003	0.205	0.216	24.0
2 30	0.0008	0.547	0.575	24.0
3 10	0.0014	0.960	1.010	25.0
4 40	0.0039	2.660	2.800	26.0
5 00	0.0050	3.420	3.600	27.0
5 30	0.0061	4.170	4.400	27.0
6 10	0.0082	5.600	5.900	26.5
6 40	0.0090	6.60	6.500	26.5
8 20	0.0111	7.600	8.000	26.0
10 00	0.0120	8.230	8.700	26.0
12 00	0.0129	8.850	9.300	26.0
30 00	0.0129	8.850	9.300	26.0
70 00	0.0128	8.770	9.200	26.5
110 00	0.0126	8.630	9.050	27.0
180 00	0.0118	8.020	8.450	27.5

Table 39

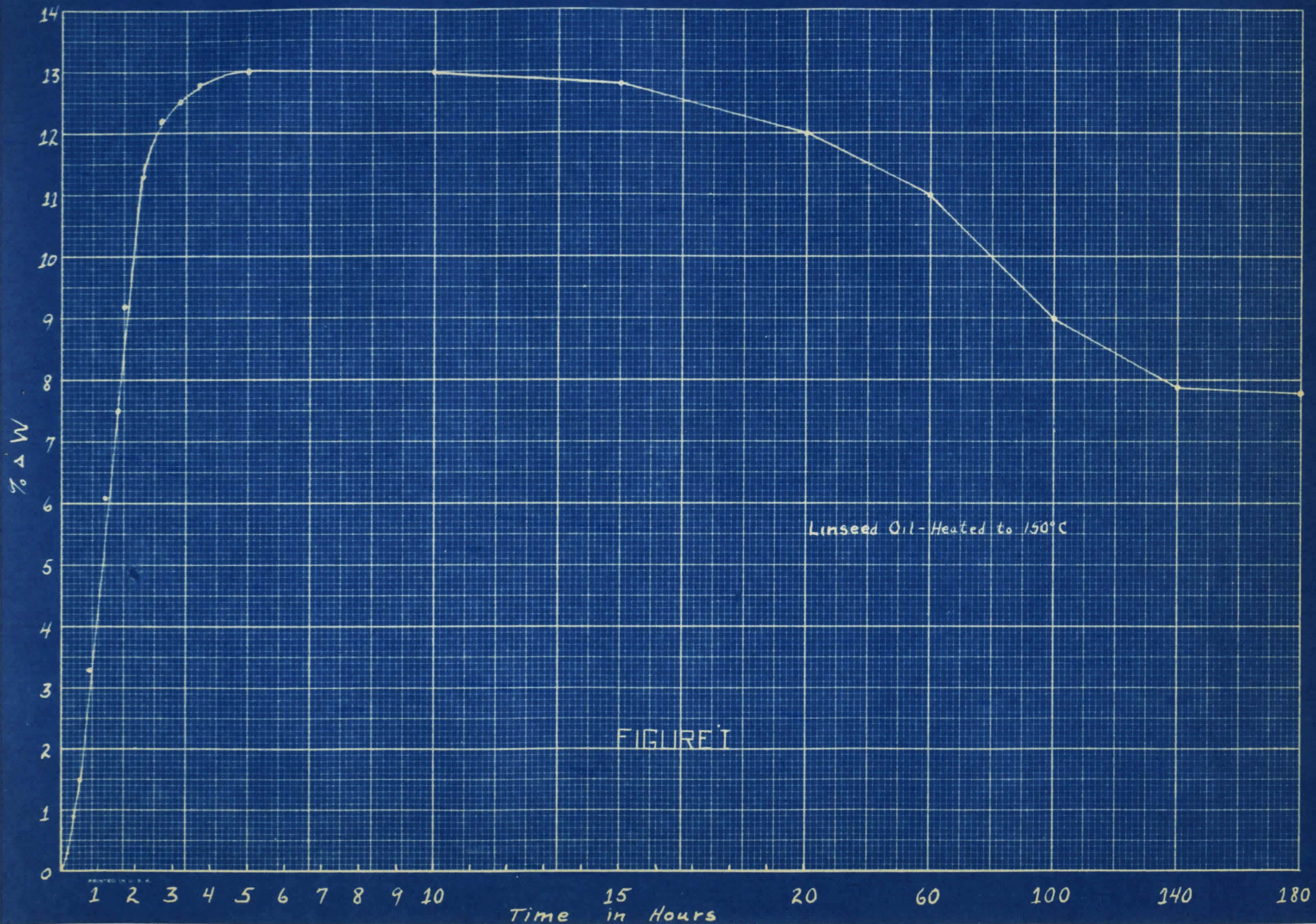
5% Solution No. 2 Resin in
Heat Bodied Linseed Oil

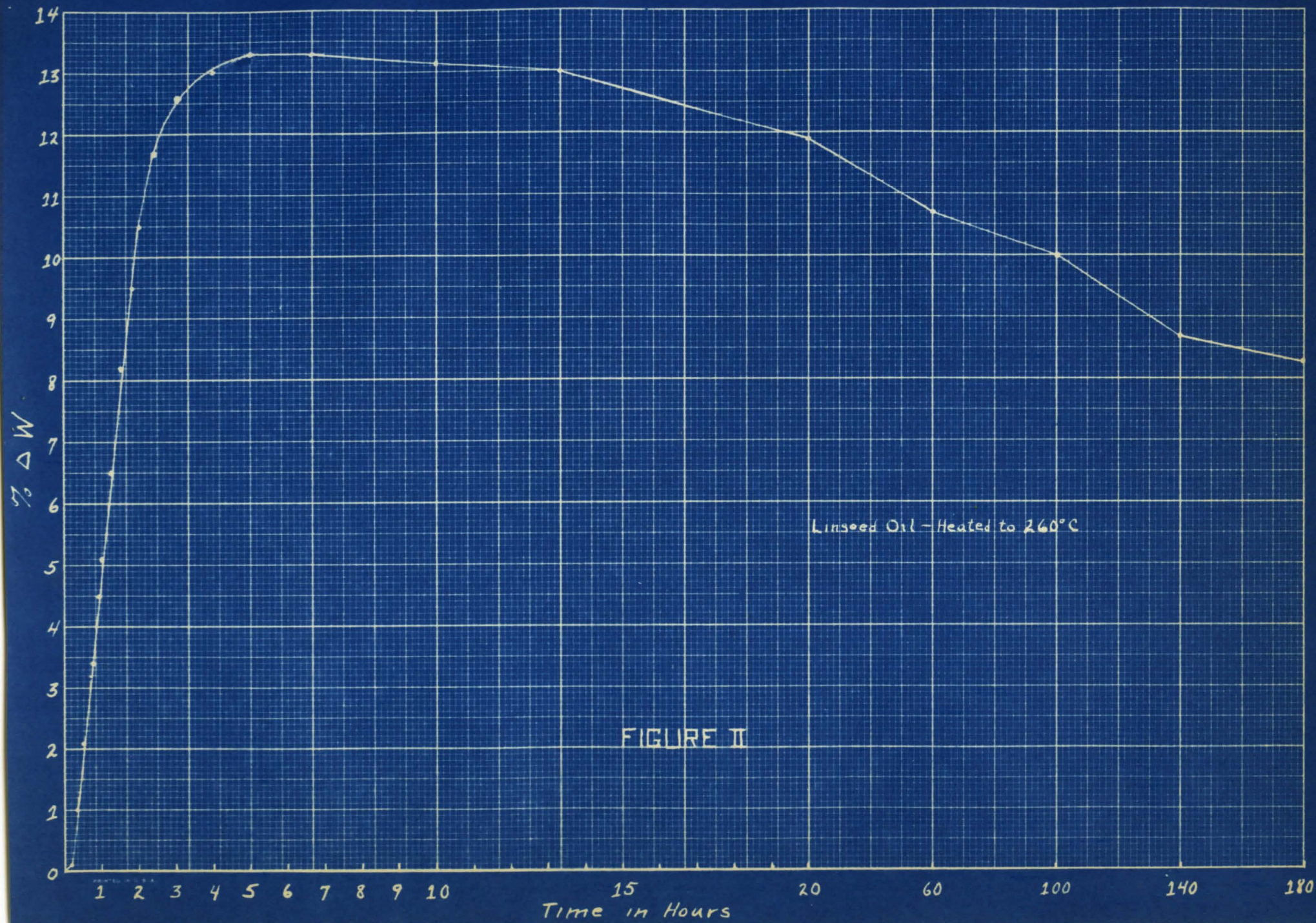
Weight of Film = 0.1300

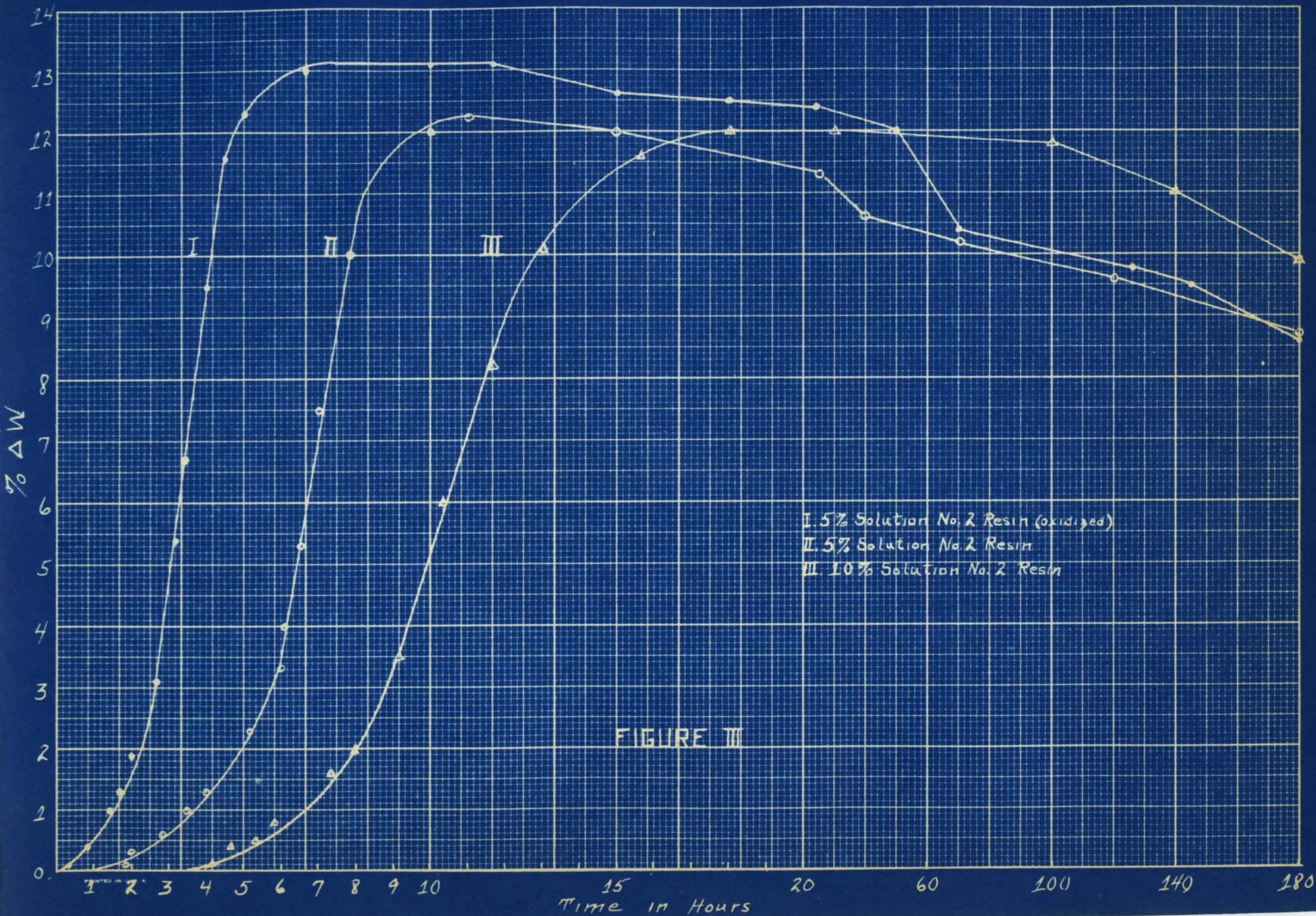
Average Humidity = 60

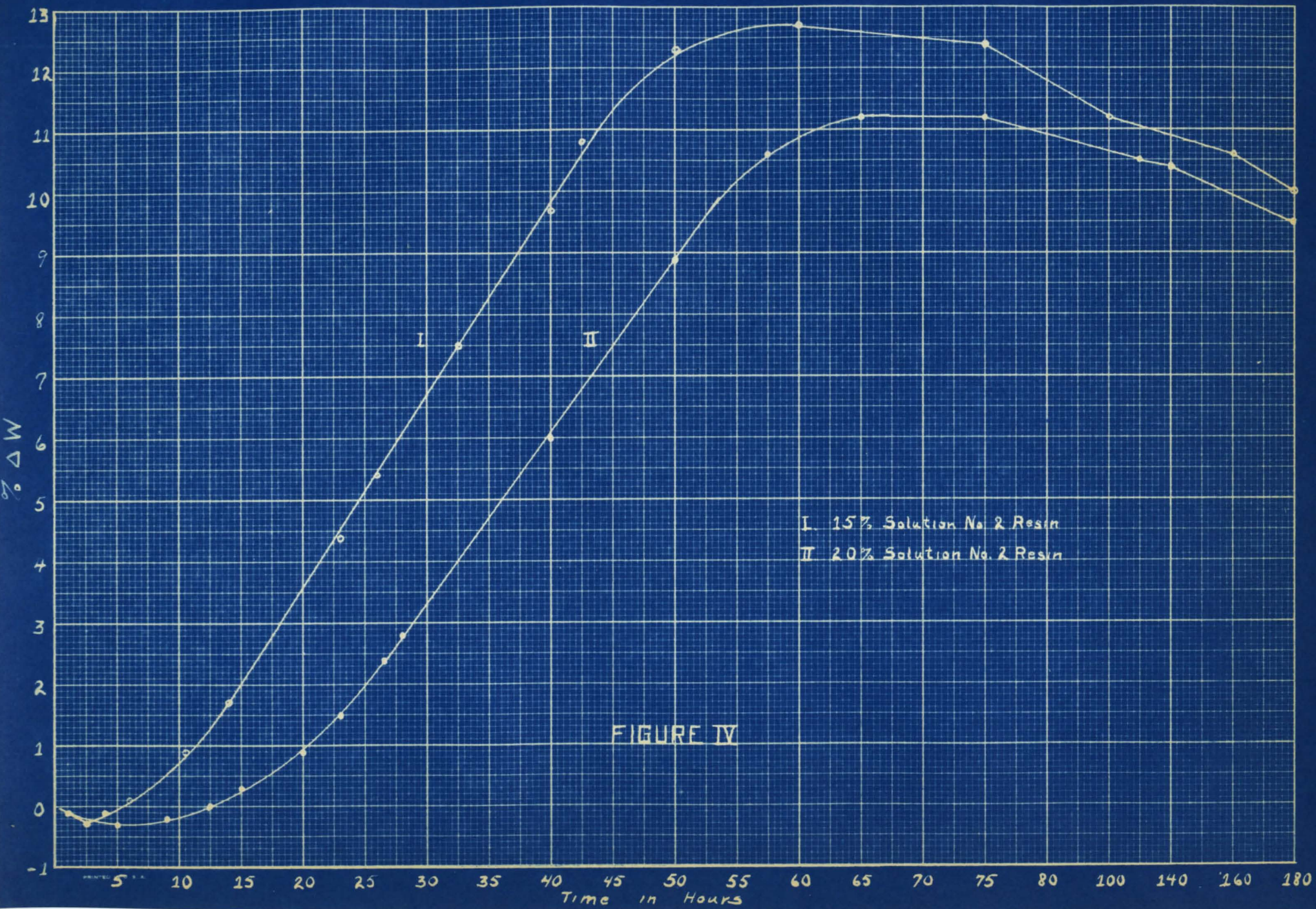
Time Hrs. - Min.	ΔW	% ΔW	% ΔW 100% Oil	Temp. Centigrade
3 00	0.0003	0.231	0.243	24.0
4 40	0.0010	0.790	0.8090	24.0
6 10	0.0021	1.610	1.700	25.0
6 40	0.0031	2.380	2.520	26.5
7 40	0.0052	4.000	4.200	26.5
8 10	0.0062	4.750	5.000	27.0
8 40	0.0070	5.400	5.700	27.0
9 55	0.0087	6.680	7.000	26.5
11 00	0.0100	7.700	8.100	26.0
12 30	0.0109	8.350	8.800	26.0
15 00	0.0117	9.000	9.500	26.0
40 00	0.0117	9.000	9.500	27.0
110 00	0.0110	8.450	8.900	27.5
180 00	0.0104	7.980	8.400	27.0

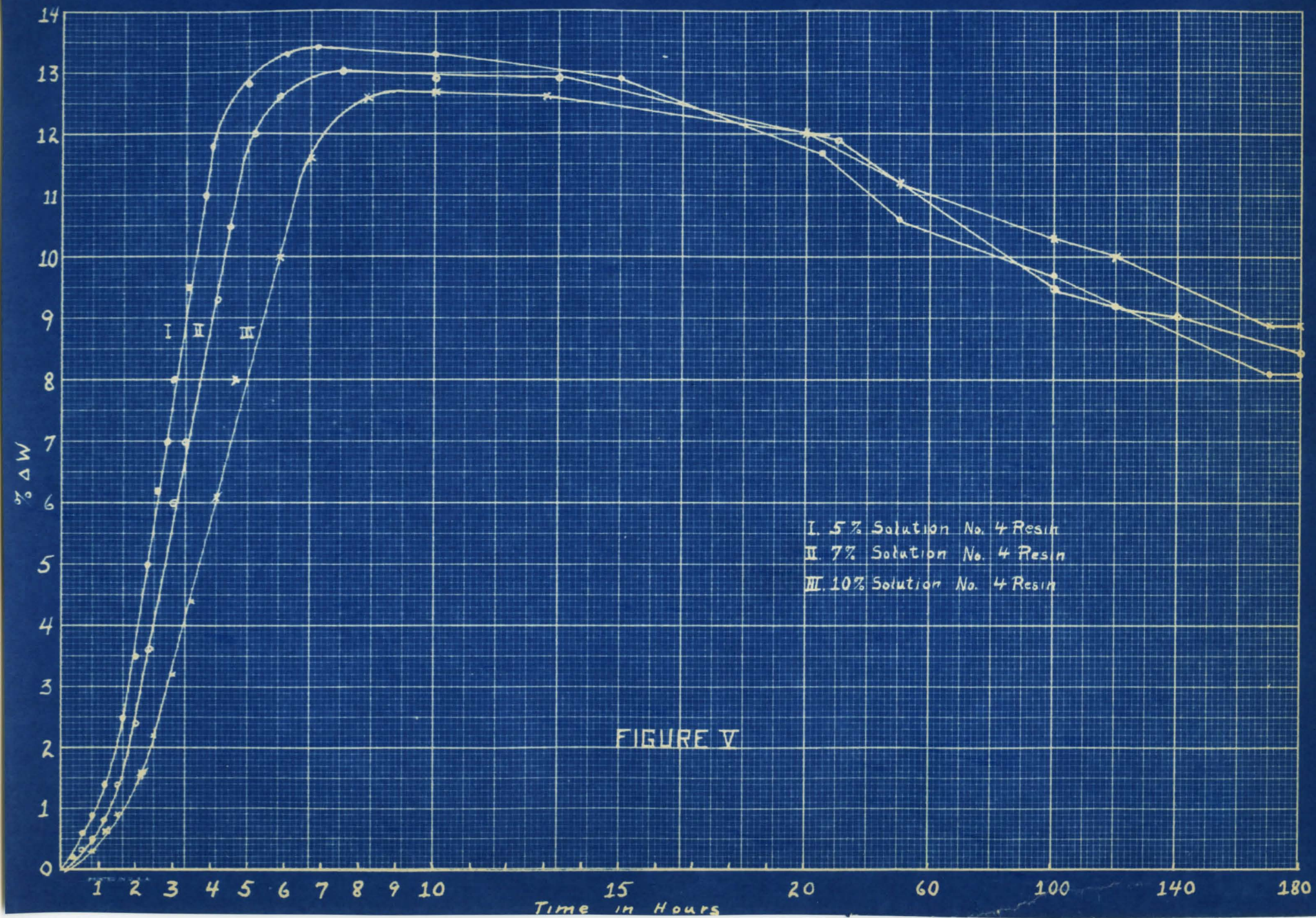
VII. Graphs

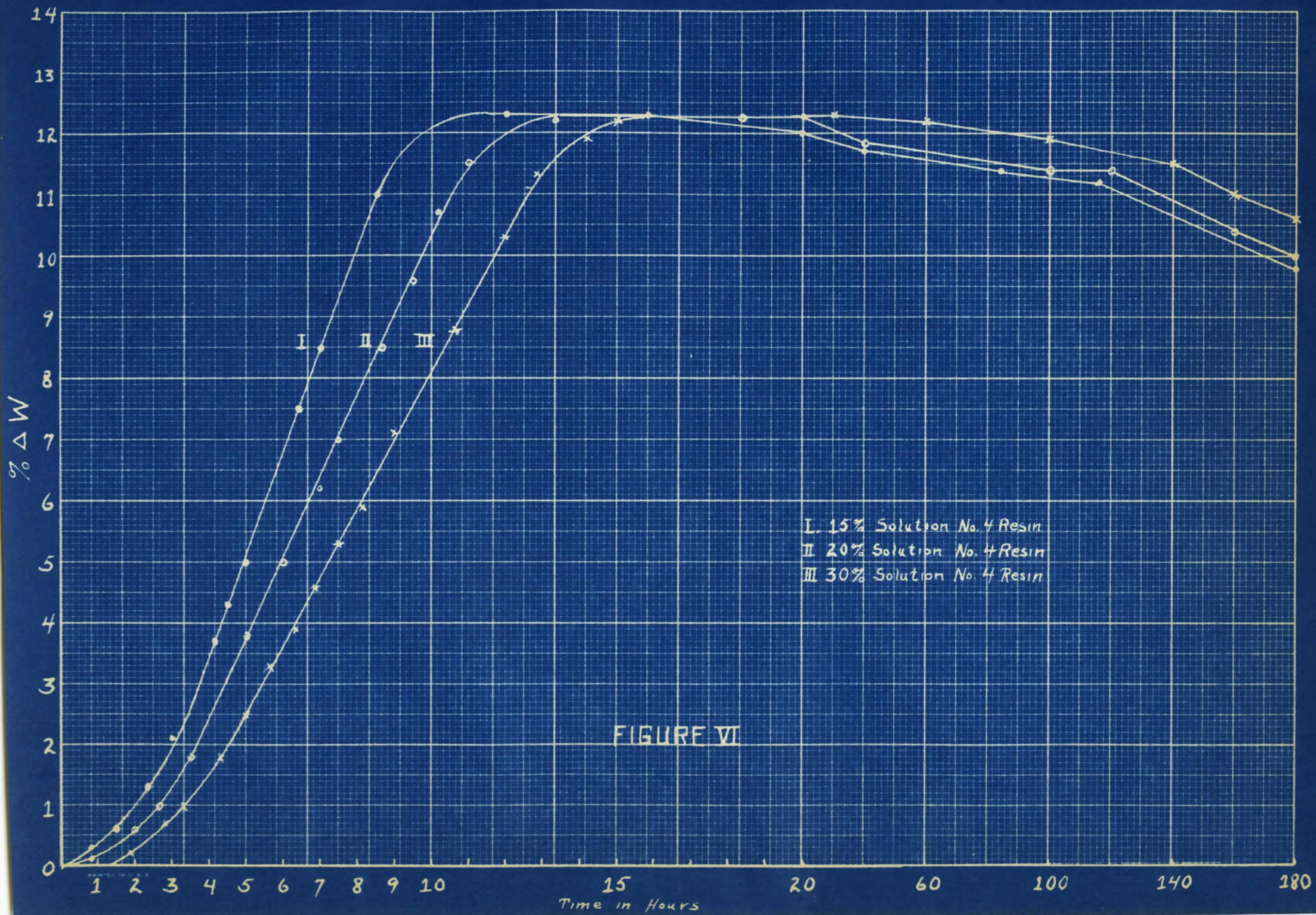


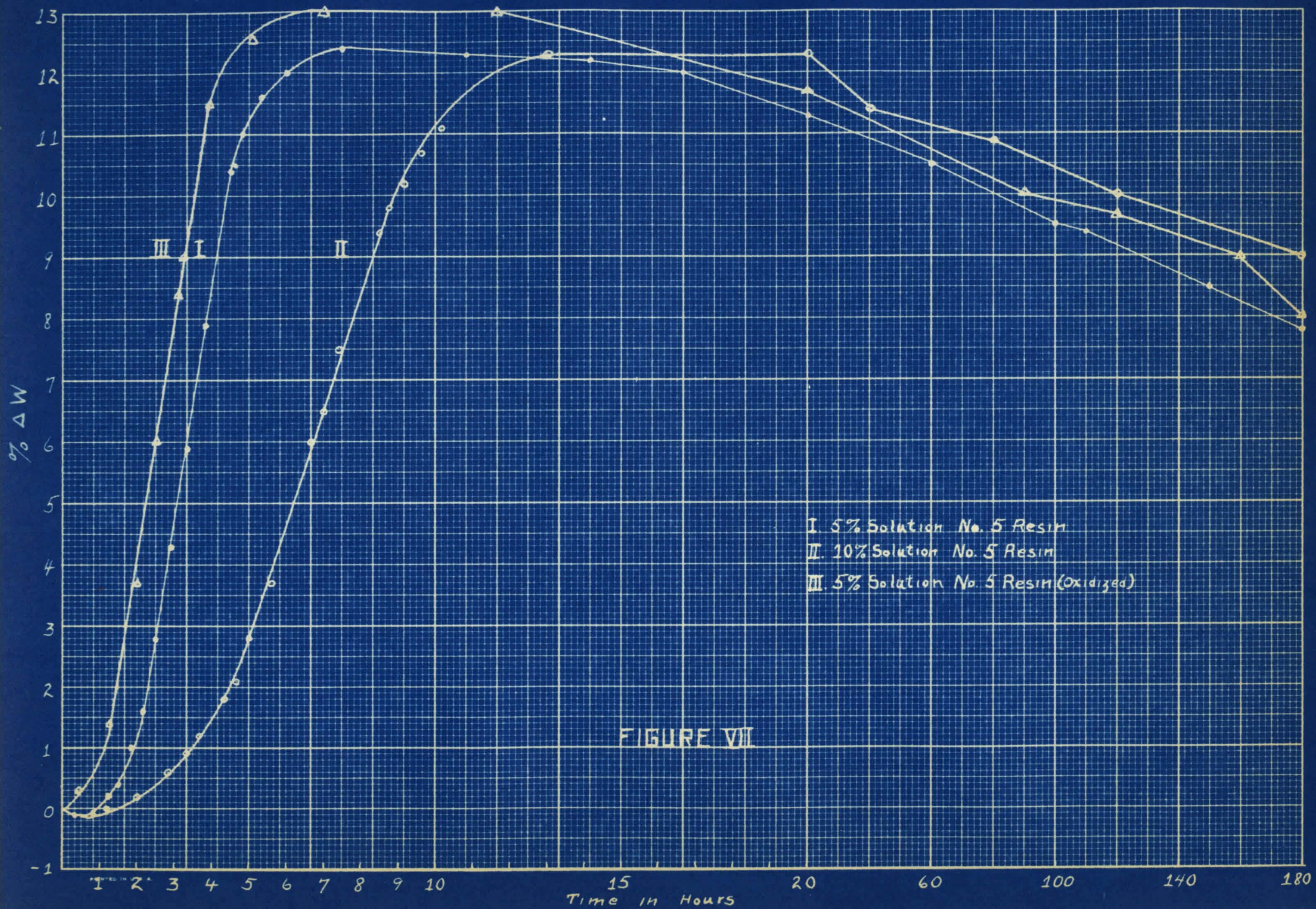


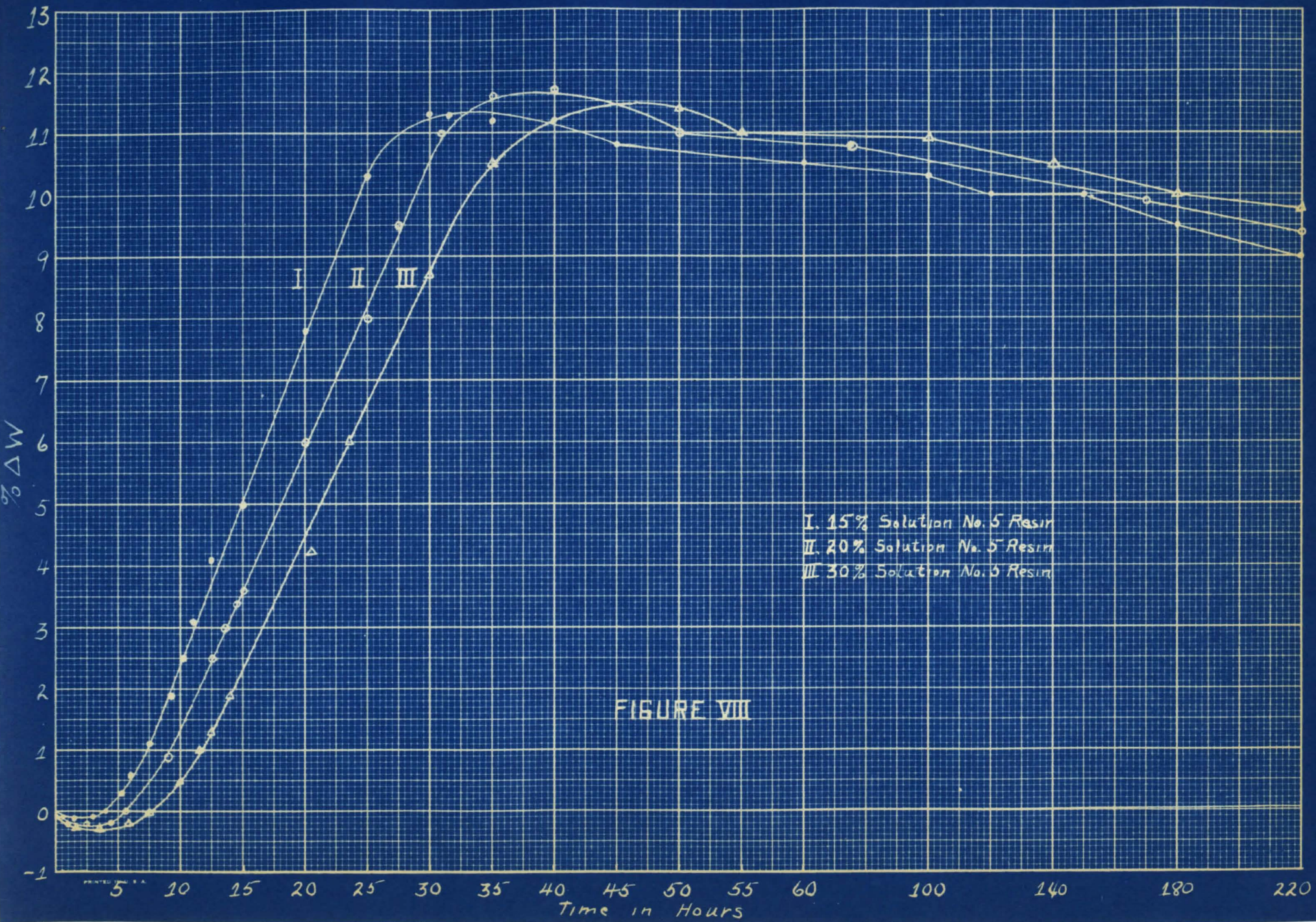


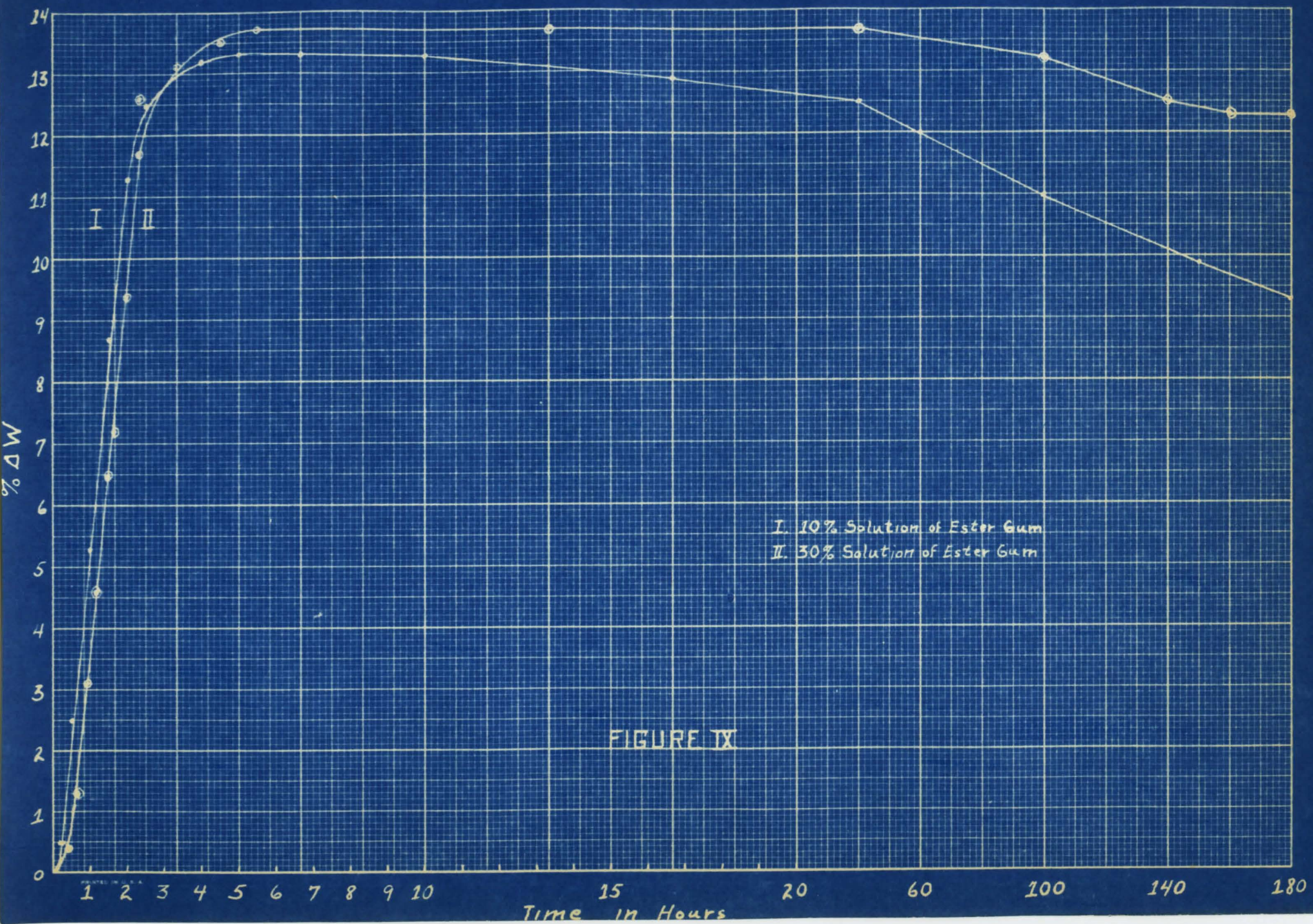


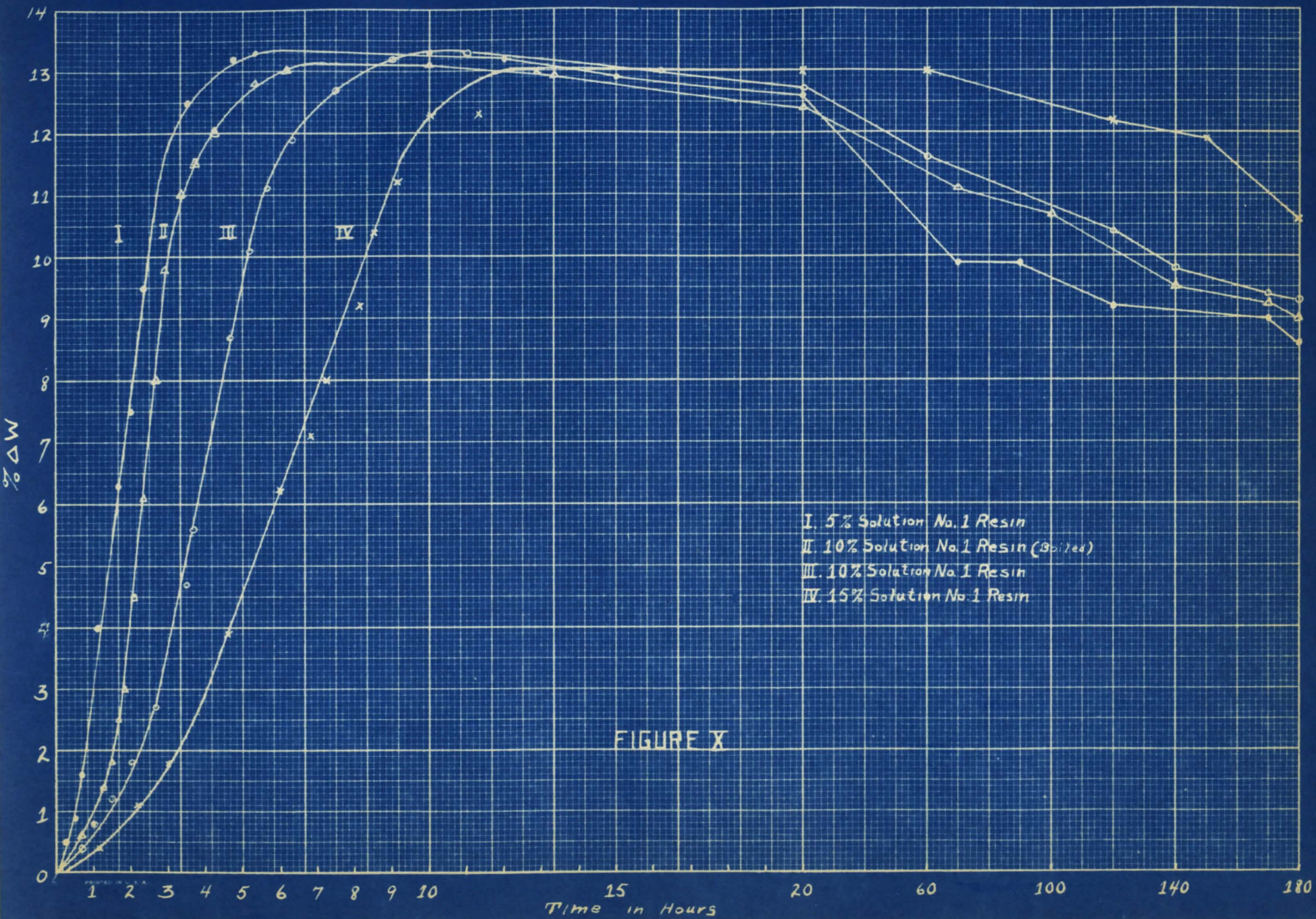


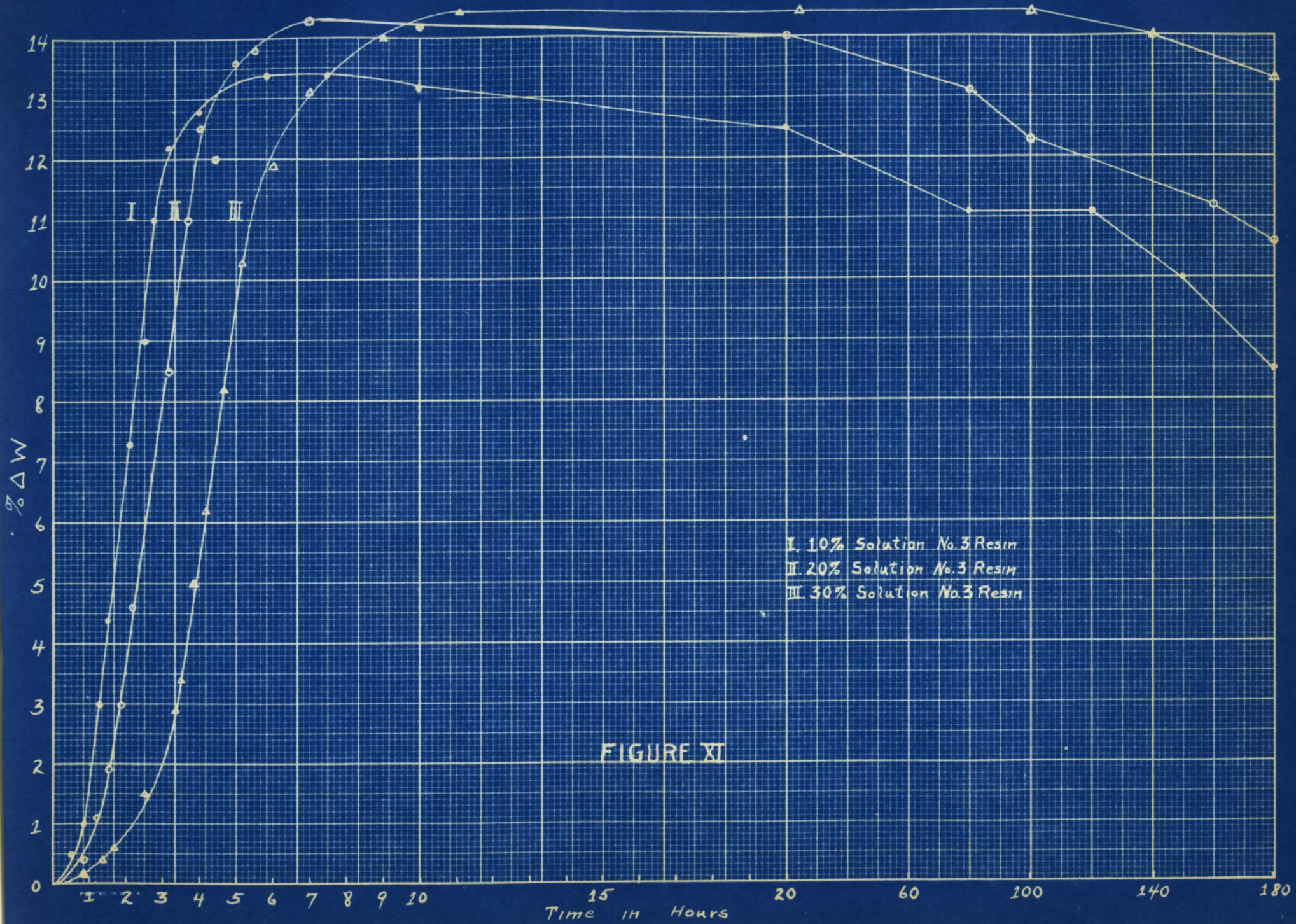


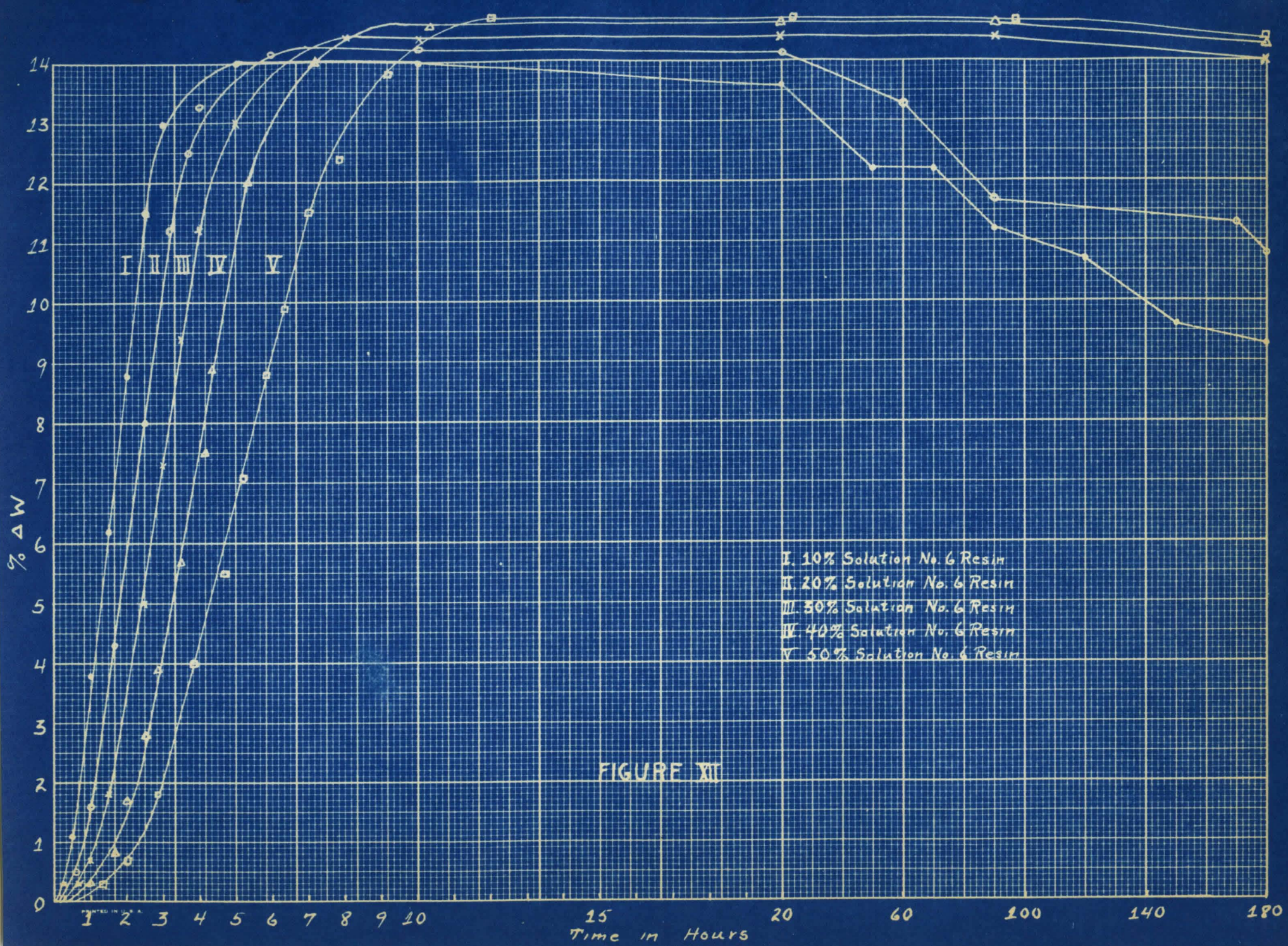


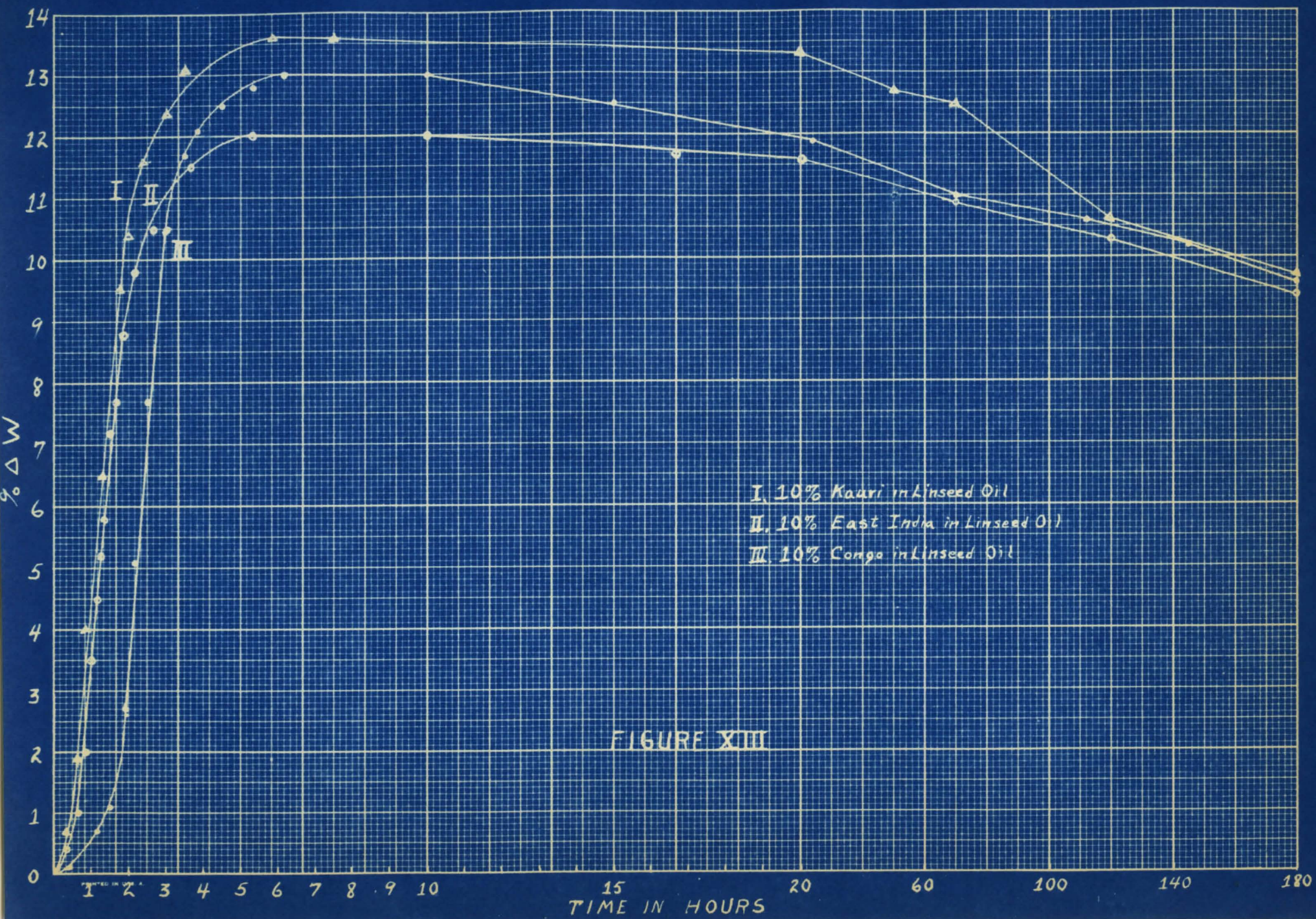


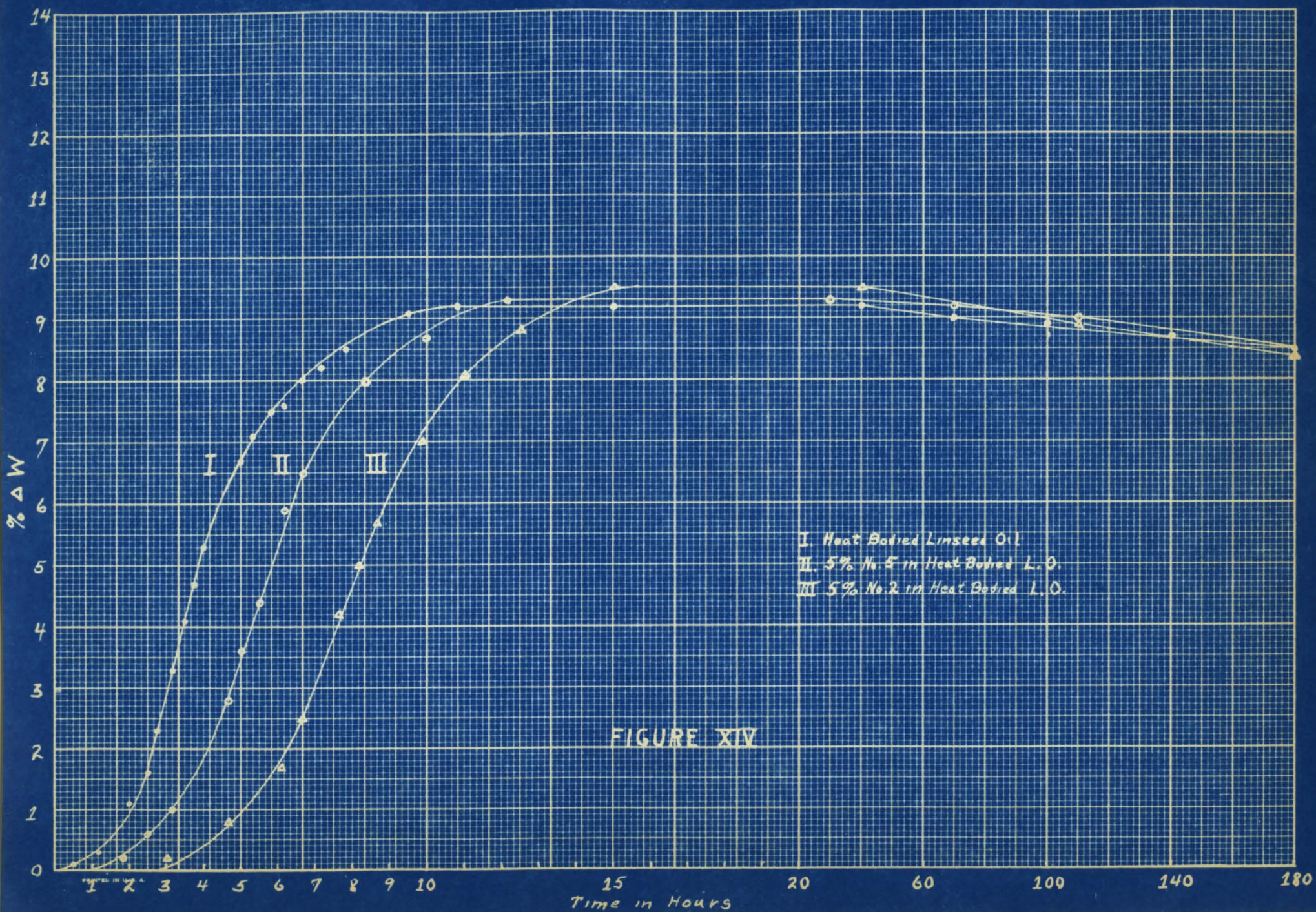












VIII Discussion

The opinion has generally prevailed among many investigators that phenol-formaldehyde resins influence the rate of oxidation of drying oils. This influence has been reported in some cases to accelerate the drying while in others it has been said to retard the drying.

The retarding influence of the resins on the drying of linseed oil may be attributed to the fact that these resins still retain phenolic characteristics. The fact that phenolic substances in general exert an antioxidant effect upon auto-oxidation processes makes this assumption all the more probable. Therefore this study has been carried out upon the basis that phenol-formaldehyde resins do exert an antioxygenic influence upon the oxidation of linseed oil.

Since this investigation is confined to measurements of the rate of oxidation of a phenol-formaldehyde resin linseed oil systems it was necessary for purposes of comparison to make a preliminary study of the rate of oxidation of a "pure" drier-treated linseed oil system.

1. Pure Drier-Treated Linseed Oil

In figures I and II are shown the drying curves of linseed oil. The same amount of drier was used as in the case of the resin treated oil. In the case of figure I the oil and drier were heated to 150°C while in figure II the oil and drier were heated to 260°C. The oils were held at their respective temperatures for 5 minutes. This preliminary heating was necessary in order to place the results on a comparable basis, because all of the

resin-oil solutions were treated in like manner. The two curves within the limits of experimental error evidence little difference. The two films gained weight at approximately the same rate attaining their maximum increase at around 13%. This maximum percentage gain in weight is only a relative value and by no means is it an indication of the total amount of oxygen absorbed. This is due to the fact that the absorption of oxygen is accompanied by a chemical change which decomposes the oil film and causes volatile products to be given off. Moreover, the presence of metallic driers increases the amount of volatile products evolved during the initial stages of oxidation (21). The latter portion of the curves representing the stage at which maximum oxidation had been reached and the stage at which oxygen absorption was gradually being exceeded by the escape of volatile products is approximately the same. At the end of 180 hours the percentage gain in weight of both curves had fallen to nearly the same value, namely, 8%.

The induction period of these two curves is extremely short. The conclusion of this period in both cases may be taken as the point at which the percentage gain in weight had reached 1.5%. This point was reached in about $\frac{1}{2}$ hour. The brief duration of the induction period may be attributed largely to the presence of driers which probably function in accelerating the formation of active peroxides which in turn catalyze further oxidation (40). Moreover, since the induction period is due ordinarily to the presence of natural antioxidants (35), probably sterols with free hydroxyl groups, and since purification tends to remove these sterols, a short induction

period would be expected in the present instance, because the oil used was of a highly purified, alkali-refined variety. Therefore it is obvious from the close similarities of the two curves that the difference in heat treatment of the two oils had little or no effect on the rate of oxidation.

2. The 100% Phenolic Resin-Linseed Oil Solutions

The study of the resin treated oil films presents some rather marked differences. The 100% phenolic resins were first to be studied. These resins consisted of 100% phenol-formaldehyde undiluted with ester gum. Hence if antioxygenic activity was to be evidenced at all then these 100% phenolics should be expected to exert it in the most pronounced degree. In figure III is shown the curves representing films consisting of 5 and 10% solutions of #2 resin respectively. This particular resin exerted the greatest antioxygenic activity of any in the series. The induction period is very markedly increased in both cases. In the 5% solution it was extended to more than 6 hours while for the 10% solution it was concluded at about 10 hours. The remaining portion of the curves simulate that of the linseed oil curve in that the rate of oxidation steadily increased after the induction period. However, the middle portion of the curve is not quite as steep as that of the linseed oil curve. The latter portion of the curve tapers off in the usual manner showing a decrease in percentage gain in weight.

In figure IV is given the drying curves for a 15 and 20% solutions of #2 resin. The most interesting feature in connection with the drying of these two films is the fact that the curves indicate

a loss of weight during the early stages of the induction period. This fact will be considered later. The middle portion of these curves is representative of a fairly straight line but is less steep than the curves representing the 5 and 10% solutions. Then, too, the curves at the point of maximum gain in weight are not as sharp as in the preceding cases showing a marked tendency to level out. The two curves also evidence a rather wide variation in the maximum gain in weight, the 15% solution film attaining its maximum at 12.7% in 57 hours while the 20% solution film reached its maximum at 11.2% in 65 hours. This variation of 1.5% may be explained on the basis of the time factor in that the 20% solution, requiring 8 hours longer to reach its maximum, obviously suffered a greater loss in volatile products, which in turn affected the maximum gain in weight. (Other factors, such as temperature and humidity, played, in all probability, a rather important role in determining the nature and shape of the curves representing high resin percentages.) Therefore, the validity of such curves whose drying time extended over long periods might be open to question.

Further attempts at increasing the concentration of #2 resin beyond 20% failed to give comparable results.

The case of #4 resin presented a somewhat different picture. In the first place the antioxygenic action was not nearly so pronounced as in the case of #2 resin. From the curves in figure V, which represent 5, 7, and 10% solutions of this resin respectively, it is evident that the drying rate is more rapid. In figure VI are included the curves for a 15, 20, and 30% solution of this resin. The drying time of these curves is progressively increased as the

concentration of the resin increases. In every case the induction period is lengthened and can approximately be taken at the point where 1.5% increase in weight has been reached.

It was also attempted in the case of this particular resin to note the effect of an intermediate concentration between the limits of 5 and 10%. Therefore a 7% solution was arbitrarily selected. Its drying curve is shown in figure V. The proportional increase in drying time with increase in concentration is rather well marked in this instance, and as would be expected the 7% solution curve lies nearer the 5% solution curve than it does the 10% solution curve.

The next series of curves, figure VII, constitute those of #5 resin, another 100% phenolic. As in the case of #2 the films of this resin-oil solution evidenced a decrease in weight immediately after their application. This phenomenon, characteristic only of these two 100% phenolics, was first thought to be due to the antioxygenic power of these resins. Since solutions constituted of 100% phenolic resins would actually contain more phenol-formaldehyde resin for a given concentration than the diluted resins, the antioxidant effect should obviously be greater. Therefore it was concluded that the inhibition of oxidation in such instances was so great that the escape of volatile products would exceed any oxygen absorption that would take place, thus permitting a measurable decrease in weight during the initial stages of the induction period. Moreover, that this is not an altogether unusual phenomenon in oxidation studies, is apparent from the work of Elm (36), who reports that the drying curve of trilenolenic glyceride shows a loss in weight immediately after the application of the film, but offers no explanation for his observation. However, if the above reasoning were entirely

sound, then it would be logical to expect that the curves for the 5 and 10% solutions of #2 resin should likewise show a slight decrease in weight due to their rather prolonged induction period. This, however, was not found to be true.

Dr. J. S. Long of Devoe and Reynolds Corporation offered the suggestion that this decrease in weight, before the incipency of oxidation, is probably due to the escape of free formaldehyde which often remains occluded in small amounts in these resins because of insufficient washing during their manufacture. In order to verify this suggestion the author carried out an experiment to determine whether or not the free HCHO could be removed from the resin prior to its solution in the oil. The following work was attempted on #2 and #5 resins:

2 grams of pulverized resin were accurately weighed to the nearest tenth of a milligram in a tared porcelain crucible. The crucible was then placed in a 6 x 2 inch test tube which was connected to a suction pump. The tube was placed in an oil bath and the temperature was slowly raised until the resin just showed signs of melting. A small suction was applied sufficient to remove any escaping vapors. This heating procedure was carried out for one hour. The crucible was allowed to cool in a desiccator and then weighed.

The loss in weight in every case was greater than could be accounted for by the escape of free HCHO. This was due to the fact that a small portion of the resin invariably vaporized and was carried away. The resin was then incorporated in the oil in 10, 15, and

20% solutions and the rate of oxidation of each was studied. In every case the initial decrease in weight was eliminated, but the remainder of the curve was identical to the curve of the untreated resin of the same percentage. Therefore it was found unnecessary to plot these curves. The results of this experiment seem to strengthen the statement made by Dr. Long to the effect that this decrease in weight is due to the presence of free HCHO. Moreover, on the basis of this assumption it is possible to account for the anomalous behavior of the 5 and 10% solutions of #2 resin in that they did not evidence a decrease in weight, because the percent resin in these particular solutions was small compared with the 15 and 20 % solutions. Then, too, this assumption allows for variations in the amount of free HCHO, which in turn would affect the general nature of the curve with regard to different resins.

Further study of the curves of #5 resin-oil solutions show that the antioxidant effect of this resin, while not as potent as that of #2, is greater than that of #4 resin. The curves of the 5 and 10% solutions of #5 are shown in figure VII. Both curves reach practically the same maximum despite the fact that the 10% solution curve, by virtue of its slower drying, should evidence a much lower maximum than the 5% solution. This may be accounted for by the fact that as the concentration of the resin increases the percent of oil in the surface film is proportionately decreased, thereby preventing a rapid escape of volatile products. This fact must also be considered when interpreting the latter portion of the curves.

The percentage gain in weight of the curves representing the more concentrated resin solutions do not fall to as low a value as in the

case of the less concentrated solutions. A comparison of the 15, 20, and 30% solutions of #5 resins, figure VIII, with the 5 and 10% solutions of the same resin evidence this fact. At the end of 180 hours the 5% solution curve fell to 7.8% while the 30% solution at the end of 180 hours fell only to 10%. By extending the time of the 30% solution curve to 220 hours only a 0.2% decrease was observed. Therefore it may be concluded that as the percentage of resin in the film increases, the chances for the escape of volatile products is greatly lessened with the attendant result that the decrease in percentage gain in weight is not nearly so marked.

To summarize briefly a few points of interest with regard to the 100% phenolics, it may be said that the data strengthens the assumption that the antioxygenic activity of a particular resin is specific for that resin. Furthermore, when it is considered that the characteristic properties of the different phenol-formaldehyde resins may vary according to their constitution and structure and that the nature of the constituents of these resins vary widely it is not at all improbable that this would influence in no small way their anti-oxidant affect on the oxidation of linseed oil.

The study of these three 100% phenolic resins namely, #2, #4, and #5 clearly indicates that they profoundly influence, not only in a qualitative manner but in a quantitative as well, the rate of oxidation of a linseed oil reaction system.

3. The Diluted Phenol-Formaldehyde Resin-Linseed Oil Solutions

In the paint and varnish industry the use of 100% phenolic resins is not always desirable. This is especially true when lower material cost is demanded. Therefore, in what is known as reduced types of

varnish formulation, the 100% phenolic resins are diluted with ester gum or some natural resin.

The present study included several of these diluted resins in which the phenolic resin content was given at 14, 20, and 45%.

An investigation of these diluted resins first necessitated a preliminary study of ester gum. Ester gum is the glycerol ester of rosin, an oleo-resinous substance consisting chiefly of abietic acid. This acid by virtue of its unsaturation is capable of oxidation. Thus in order to determine its degree of oxidizability under ordinary atmospheric conditions the same method employed in the study of the resin-oil films was used.

About 3 grams of ester gum were dissolved in 10C.c. of ethyl ether. This solution was quickly spread by means of a camel's hair brush on weighed glass plates and placed immediately in a vacuum desiccator. After the ether had evaporated and a constant weight was attained, the plates were weighed twice a day over a period of one month. The results obtained are as follows:

Time Hours	ΔW	% ΔW	Wt. of Film - .2006
26.5	0.0004	0.20	
52.0	0.0013	0.65	
74.0	0.0023	1.15	
121.5	0.0034	1.70	
290.0	0.0060	3.00	
386.0	0.0069	3.46	
410.0	0.0075	3.75	
463.0	0.0092	4.60	
597.0	0.0106	5.30	
720.0	0.0107	5.35	

These results were subject to the usual laboratory conditions. The relatively large value at the end of 720 hours is no doubt due to the accumulation of dust, the absorption of water and gases, and handling in general. These results were checked within a fair degree of accuracy by subsequent studies.

The oxidation of the diluted phenol-formaldehyde resins was studied in the same manner. Although the ester gum alone had oxidized to 5.35% of its weight it was logical to assume that when it became a part of a phenol-formaldehyde resin its oxidation would be prevented by its phenolic counterpart. This assumption was partially substantiated by the previously attempted work of ultimate analysis which for the most part had yielded no consistent results. Therefore the oxidation of these resins was determined by the change in weight method. After exposing the films of these resins to the atmosphere over a period of a month it was found that, aside from the accumulation of dust and fumes, these films showed no appreciable gain in weight. Therefore these results were evidence enough that these diluted resins had not undergone oxidation when exposed to atmospheric oxygen.

A study of the effect of ester gum on the oxidation of linseed oil was made in order to determine whether or not this substance exerted any inhibitory effect. In figure IX is shown the curves for a 10 and a 30% solution of ester gum in linseed oil. The 10% solution curve is practically identical with that of the linseed oil curve after allowing for experimental error. However, there is some difference in the latter portions of the two curves; the one representing ester gum did not fall as rapidly nor to as low a value as in the case of linseed oil. This is apparently due to the fact

that the surface concentration of oil in the ester gum film has been decreased. Another significant point to be mentioned here is the influence of the oxidation of the ester gum on the maximum gain in weight. The data on the oxidation of ester gum alone indicate that up to 26 hours very little oxidation had taken place. Therefore it would be expected that its influence up to this point would be practically negligible. However, it was found that at 70 hours the oxidation of ester gum was quite evident and in view of the fact that the latter portion of the 10% ester gum-linseed oil solution curve did not fall to as low a value as in the case of pure linseed oil, it is not at all improbable that the oxidation of the ester gum itself was of some consequence.

The oxidation curve for the 20% solution of ester gum was practically identical with that of the 10% solution curve. Therefore this curve was not included in the series.

A comparison of the 30% solution curve with the 10% reveals some slight variations. In the first place the induction period for the 30% solution curve is more prolonged. A time interval of about 40 minutes was required for the latter film to conclude its induction period; whereas, in the case of the former it was concluded at the end of 20 minutes. The drying time of the 30% solution curve is for the most part increased by 20 minutes over the 10% solution curve. Moreover, the 30% solution not only attains a greater maximum increase in weight, but this maximum does not fall to as low a value at the end of 180 hours as in the case of the 10% solution curve. Therefore, the two factors mentioned above, i. e., the actual decrease of linseed oil in the surface film and

the oxidation of the ester gum present in the film, are significant in explaining these differences.

The fact that little or no inhibition of oxidation occurred in the ester gum-linseed oil series is to be expected since the presence of hydroxyl groups is rather uncertain. However, it often happens that ester gum is composed of considerable quantities of the diglyceride of abietic acid which, in that event would present a free hydroxyl group. Because no work was attempted on the diglycerol ester, a conclusion in this regard is not wholly warranted; but, this does not preclude a general statement to the effect that the presence of a free hydroxyl might exert some influence on the rate of oxidation of linseed oil.

The drying curves for the diluted phenol-formaldehyde resins also showed comparable results. The first of these, #1 resin, a 45% phenolic, had to be heated to 260°C before solution resulted. Moreover, the resulting solutions were highly viscous, thus presenting difficulties in applying a uniform film. For this reason the study included only 5, 10, and 15% solutions. The curve representing the 5% solution (see figure X) exhibits a slight retardation in drying rate. The induction period, although slightly more prolonged than in the case of the linseed oil heated to 260°C, was relatively short. Then, too, the middle portion of the curve evidenced a more pronounced slope than did the linseed oil curve. The latter portion of the curve dropped rapidly at 70 hours and then continued fairly straight to 180 hours. The final decrease in percentage gain in weight was approximately the same for both curves.

Further study of the curves of #1 resin brings out some interesting points. The amount of phenol-formaldehyde resin in these solutions is small compared with solutions of like concentrations of the 100% phenolics. A 10% solution of #1 resin, which being a 45% phenolic, would actually be constituted of 4.5% phenol-formaldehyde resin. The 15% solution would contain 6.75% phenol-formaldehyde, while the 5% would contain 2.25%. Therefore, this fact must be kept in mind when comparing the diluted phenolic resins with the 100% phenolics. The 10 and 15% curves are proportionately moved to the right. Their induction periods are also more pronounced as would be expected when the concentration of the resin is increased.

The drying curves for #3 resin, a 20% phenolic, are given in figure XI. These curves represent 10, 20, and 30% solutions of resin in linseed oil or 2.0, 4.0, and 6.0% solutions based on the amount of phenol-formaldehyde resin. A comparison of the 10% solution curve of #3 resin with the 5% solution curve of #1 resin evidences close similarities which are consistent with the percentage of phenolic resin present. The difference in concentration between the two solutions amounts to 0.25% of phenolic resin.

A comparison of the more concentrated solutions of these two resins does not show such striking resemblances. In figure XI the curve representing the 20% solution of #3 resin lies closer to the 10% solution curve. Apparently it should have fallen midway between the two curves.

Further examination of the curves of this series brings out several interesting points. In the first place the 10% solution curve reached its maximum gain in weight at 13.4%. This is in close

agreement with the 10% solution curves of other resins. However, the 20 and 30% solution curves reached their maximas at 14 and 14.5% respectively. These high maximas are not quite consistent with those of other resin-oil solutions of like concentration. An explanation of this anomalous behavior may be found in the fact that this resin is largely made up of ester gum which in a 30% solution would amount to 24%. Furthermore, it is to be recalled that the 30% solution of ester gum reached a maximum of nearly 14% and evidenced little or no inhibitory activity. Since solutions constituted of this resin would therefore contain only small quantities of phenolic resin, it is reasonable to expect them to show little antioxidant effect. The fact is apparent from the nature of the curve which, after the conclusion of the induction period, evidences a fairly rapid increase in weight.

Another significant point to be considered in the study of these curves, especially with regard to the 20 and 30% solutions, is that the percent of oil has been considerably reduced at the surface interface. The presence of a large amount of resin at the surface would obviously retard the escape of volatile products and thus permit a higher maximum gain in weight to be attained. Then, too, these curves did not fall to as low a value at the end of 180 hours as the 10% solution curve a fact which is consonant with the above reasoning.

Finally, it must be mentioned that solutions of #3 resin had to be heated to 260°C before complete dispersion resulted. This fact may also be useful in interpreting the nature of these curves. In the case of the 20 and 30% solutions, this heat treatment produced a thick, heavy, and viscous solution which was difficult to spread. Therefore the films would naturally be heavier and thicker than those of other resins..

The prolonged induction period of the 30% solution curve is probably due to the thickness of the film which did not permit a uniform penetration of oxygen. At the conclusion of the induction period, however, the rate of oxidation proceeded in the usual manner. Therefore it was apparent that there were two factors responsible for the retarded drying rate of the 30% solution film, i. e., the increased thickness of the film and the decrease in amount of oil present at the interface of the film. Owing to the viscous nature of solutions of this resin, concentrations greater than 30% were not studied.

The curves of #6 resin (see figure XII), a 14% phenolic, were somewhat analogous to those of #3 resin in that a high maximum gain in weight was attained. Here again the amount of phenolic resin present is comparatively small and as would be expected the anti-oxidant effect exerted was small. However, by way of contrast to #3 resin, #6 resin was readily dispersed in the oil at 150°C. Hence it was possible to increase the concentration up to 50% before the viscosity of the solutions became too great for uniform spreading.

The high maximum gain in weight and the rather slow decrease in weight after the maximum had been reached as evidenced by the more concentrated solutions in this series is obviously due to the large percentage of ester gum present in these solutions. Since the amount of oil has been reduced materially from the surface interface of the film and replaced by the resin, the escape of volatile products is largely prevented, and this in turn would allow for a greater increase in weight. A study of the 40 and 50% solution-curves of #6 resin is rather indicative of this fact because, after the maximum

value has been reached, it is held fairly constant until about 60 hours when a small decrease in weight becomes apparent. After 180 hours the 40 and 50% solution curves fell only slightly to about 13%.

4. The Oxidation of Phenol-Formaldehyde Resins

The theory of antioxygenic activity as formulated by Moureu and Dufraisse (3) predicated the hypothesis that the power of inhibiting the action of free oxygen in auto-oxidation processes belonged to oxidizable substances. Furthermore their theory assumes that the antioxygenic activity is localized in the oxidizable portion of the molecule and that the degree of this activity is dependent upon the state of oxidation of this portion of the molecule. In the course of their investigations they found that di-methyl sulphide retards the oxidation of benzaldehyde and that the antioxygenic activity was due to the sulphur group and not to the methyl groups. By oxidizing dimethyl sulphide to dimethyl sulphone, they were able to suppress its antioxygenic influence.

Upon this assumption it was decided to attempt the oxidation of phenol-formaldehyde resins with an oxidizing agent and note what effect the resulting product would have on the drying of linseed oil.

The oxidation of phenol-formaldehyde resins with oxidizing agents has been known for a long time. Blumer (38) oxidized phenolic resins with persulphates and perborates. Ellis (39) reports that the ordinary oxidizing agents such as MnO_2 , $KMnO_4$, K_2CrO_4 , and H_2O_2 can be used satisfactorily to oxidize these resins. In this particular study the resultant product produced by the reduction of the oxidizing agent was an important consideration. The use of manganese and chromium compounds would be barred owing to the fact that they would

be difficult to remove and their presence, even in small amounts, would probably act as an accelerator on the drying of the oil. Therefore hydrogen peroxide was found to be the only practical oxidizing agent that could be used.

The oxidation was carried out using 60 c.c. of 30% H_2O_2 to 4 grams of pulverized resin. The mixture was made alkaline with 5c.c. of 10% NaOH. The reaction mixture was heated gently under reflux for 1 hour after which the liquid portion was discarded. The resin was then boiled in three 50c.c. portions of water for a period of 10 minutes each. After cooling, the resin was pulverized and dried for 5 days in a desiccator and was then dispersed in the usual manner in the linseed oil.

This study was confined to resins #2 and #5, the two which had evidenced the greatest antioxidant effect. A study of the drying curves for 5% solutions of these resins, shown in figures III and VII, indicate that in both cases the drying time was greatly decreased. Although the antioxidant effect of the resins was not completely eliminated, the difference between the curves of the untreated resins and those of the oxidized resins is of sufficient magnitude to conclude that the potency of the antioxygenic activity of the resins had been diminished by treatment with an oxidizing agent. These results, therefore, are in close agreement with the hypothesis of Moureu and Dufraisse.

5. The Effect of Boiled Resins on the Oxidation of Linseed Oil

The data of this investigation seem to strengthen the general premise that phenol-formaldehyde resins exert an antioxygenic influence on the oxidation of linseed oil. Since phenolic compounds possessing at least one free hydroxyl group (i. e., the hydroxyl attached to the benzene ring) prevent the oxidation of Auto-oxidizable substances, it is reasonable to assume that phenol-formaldehyde resins either possess phenolic characteristics which would account for this activity, or else they contain small quantities of free phenol which is responsible for their antioxidant effect.

The fact that little is known concerning the structure and constitution of these resins makes the first of these assumptions rather vague and indefinite. The second assumption, however, has been held by a number of investigators. Ellis (39), discussing the discoloration of phenol-formaldehyde resins under the influence of light and air, attributes this effect to the presence of uncombined phenol retained in the resin.

Herzog (41) is also of the opinion that a portion of the phenol is rather loosely combined by the resin complex, probably in the form of a phenyl ether.

Bradley (42) reports the removal of free phenols from phenolic resins by repeated boiling in water, while Seebach (43) reports the use of fluxing agents in order remove the free phenol from fusible resins.

On the basis of these results the author attempted to remove the free phenol present in the phenolic resins used in the investigation and to determine whether or not they were responsible for the antioxygenic activity. In view of the fact that the resin itself could not be seriously altered since it was later to be incorporated in the oil,

a method had to be selected which would meet this requirement. The method suggested by Bradley, that of boiling the resin in water, seemed to be the most practical for this purpose.

From 2 to 5 grams of the resin were boiled in 75 c.c. of water for 3 hours after which the water extract was poured off and tested for free phenol. The resin was pulverized and dried in a desiccator.

In every case with the exception of #1 resin the test for free phenol was inconclusive. The reagent used in this test was p-nitroaniline hydrochloride. This reagent was diazotized and the resulting diazonium salt coupled with the phenol in the presence of NaOH. A red coloration resulted in case phenol was present.

The resins treated in this manner and made up into oil solutions showed no appreciable effect on their drying curves. However, in the case of #2 and #5 resins the decrease in weight, which was observed at the beginning of the induction period and which was attributed to the presence of free HCHO, was not apparent after treatment with boiling water. The boiling obviously removed the free HCHO present in the resin.

From the water extracts of #1 resin there was observed to precipitate out on cooling a white crystalline substance. This substance was identified as 4,4-dihydroxy-diphenylmethane according to the following data:

Observed	Literature (44)
M. P. = 156.5°C (uncorrected)	M. P. = 158°C
Molecular Weight = 199.9	Molecular Weight = 200
Solubility - Sol. in Et OH, Et O,	Solubility - Sol. in EtOH, Et O,
KOH; Slightly sol. in CHCl ₃ ;	KOH; Slightly sol. in CHCl ₃ ;

Observed	Literature (44)
Insol. in CS ₂	Insol. in CS ₂
Derivatives;-	Derivatives:-
Diacetyl - prisms from EtOH,	Diacetyl - prisms from EtOH,
M. P. = 69°C (uncorrected)	M. P. = 69°C
Dibenzoyl - needles from EtOH	Dibenzoyl - needles from EtOH
M. P. = 156°C (uncorrected)	M. P. = 156°C

The molecular weight was determined by the camphor method (45).

The following data was recorded:

Temperature Readings

Melting Point °C	Freezing Point °C
158.5	155.0
158.5	155.5
158.5	155.5
<hr style="width: 50%; margin: 0 auto;"/> 158.5	<hr style="width: 50%; margin: 0 auto;"/> 155.3

Average = 156.9

Weight of Unknown = 0.0034 gm.

Weight of Camphor = 0.0346 gm.

Melting Point of Camphor = 176.4°C

Lowering of Melting Point = 19.5°

$$\text{M. W.} = \frac{1000 \times 39.7 \times \text{wt. of sample}}{\Delta t \times \text{wt. of camphor}}$$

Molecular Weight determined = 199.9

In order to determine the amount of this compound that could be extracted by boiling, 5 grams of the resin were boiled until no further precipitate appeared in the water extractions. The 5 gram sample yielded 0.9965 gram of the substance or 19.93% by weight.

Since the water extracts from #1 resin had given a heavy deep red precipitate on treatment with p-nitroaniline reagent, it was apparent that this was due to the 4,4-dihydroxydiphenylmethane which was extracted from the resin. Therefore the azo derivative of this compound was prepared in the following manner:

0.10 gram of 4,4-dihydroxydiphenylmethane was dissolved in 5 c.c. of 10% NaOH. 10c.c. of p-nitroaniline hydrochloride was diazotized with 8 c.c. of a 20% solution of NaNO_2 . This solution was added to the alkaline solution of the 4,4-dihydroxydiphenylmethane and the resulting mixture shaken vigorously. There immediately formed a heavy dark red precipitate which upon acidification with 10% HCl changed over to an orange yellow precipitate. The precipitate was suction filtered and dried and recrystallized twice from alcohol.

The fact that the ordinary physical constants are of little value in dye analysis and that a complete analysis of this dye was beyond the scope of the present study, no further examination was made.

The remaining portions of resin #1 from which the above mentioned compound was extracted was dispersed in linseed oil in the usual manner. The drying curve for a 10% solution of this resin is shown in figure X. When compared with the 10% solution curve of the untreated resin it is obvious that the drying time has been considerably reduced. Therefore the resulting data is highly suggestive of the fact that the antioxygenic activity of phenolic resins is to some extent, at least, due to the presence of uncombined or free phenol

which is present in varying degrees in the different resins. Although this was the only resin in which an actual test for phenolic compounds was obtained this in no wise precludes the possibility that the other resins may have contained free or uncombined phenols. A continuation of this phase of the work will present an interesting study.

IX A Study of the Effect of Humidity on
the Resin-Linseed Oil Films

The retarding effect of humidity on the oxidation of linseed oil has been pretty well established. In the present study the humidity conditions were subject to control only within relatively wide limits and for this reason only the average humidity was considered in the drying of each resin-oil film. That this factor was of great importance is apparent from the following observation. When the films which had already attained their maximum gain in weight were taken from the thermostatically controlled box into the balance room and immediately weighed they suffered a decrease in weight from the previous days weighing. That this was not due entirely to the loss of volatile products is evident from the fact that after remaining in the balance room for one hour the films increased in weight to a value which often exceeded that of the previous days' weighing. A check on the humidity showed that in such cases the amount of moisture in the air had invariably increased.

This increase in moisture content of the air was also dependent upon the temperature.

The unvarying occurrence of this phenomenon led the author to believe that there was an equilibrium established between the water content of the film and the amount of water present in the air. Eibner (46) reports in his studies on auto-oxidation that linseed oil in moist air absorbs water with attendant film swelling, whereas in dry air it gives up water. Moreover, he holds that this water is both chemically and physically held by the film. Gardner (47) also maintains that in moist air the film increases in weight.

In order to test these conclusions the films were weighed at a definite humidity. They were then placed in the apparatus shown in figure A, which consisted of a vacuum desiccator connected to a

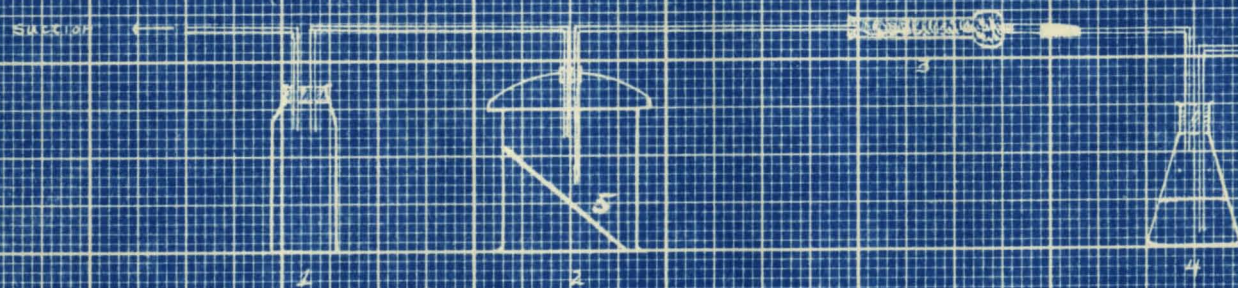


FIGURE A

- 1. Trap
- 2. Vacuum Desiccator
- 3. CaCl_2
- 4. Conc. H_2SO_4
- 5. Oil Film

suction pump, a calcium chloride drying tube, and a flask containing concentrated sulphuric acid. The air was then drawn into the desiccator through the H_2SO_4 and $CaCl_2$ for 30 minutes after which the film was removed and immediately weighed. No attempt was made to measure the humidity of the air after it passed through the desiccants. The results obtained are given in the table below:

Type of film	Initial Wt. of film	ΔW	ΔW after air treatment	Humidity	% loss in Wt.
5% #4 resin	0.1301	0.0152	0.0139	55	1.00
20% #5 resin	0.1410	0.0121	0.0106	55	1.06
30% #4 resin	0.2010	0.0176	0.0158	50	0.90
10% #3 resin	0.1123	0.0131	0.0116	55	1.35
10% #1 resin	0.1434	0.0164	0.0143	60	1.45
15% #2 resin	0.1150	0.0120	0.0109	60	1.10

It is also of interest to note that these films regained the weight lost by treatment with dry air after remaining in the balance room for one hour.

Time was not available to develop adequately this phase of the investigation with the various films of different resin concentrations. Those films selected were fairly representative and the results obtained seem to strengthen the assumption that there is an equilibrium maintained between the water in the film and the water present in the atmosphere. Moreover, the question of whether the water is absorbed or adsorbed by the film is one that requires additional investigation but is, nevertheless, of sufficient interest and importance to be mentioned at this time.

X The Influence of Natural Resins on
the Oxidation of Linseed Oil

The term natural resin embraces a large class of substances which occur as exudations from the cells of certain plants. These substances may be obtained from the living plant or from the remains of plants which have long been dead. In the latter case they are termed fossil resins.

The structure and constitution of these products are not definitely known but it is generally accepted that they are composed of a number of organic substances of terpene derivative, among which have been isolated certain aromatic acids, alcohols, resenes, and essential oils. The nature and amount of these substances present determines in a large measure the characteristic properties of the resin. Therefore the use of natural resins in the paint and varnish industry has been limited to a relatively small number of these products.

The consideration of the nature of these substances has been one of the importance to the varnish maker. Before a natural resin can be dispersed in an oil it is necessary to remove certain of its constituent products. This is accomplished by what is known as a gum-running process which consists of heating the resin in an open vessel at 360°C until it has lost approximately 25% of its weight. The exact nature of these decomposition products is still a matter of opinion since they vary considerably with regard to the botanical origin of the resin. Barry (48) holds that these products are largely carbon dioxide and hydrocarbons which result from the decomposition of certain di- and polycarboxylic acids. The complete removal of these acids is necessary in order to insure solubility of the resin in the oil.

The influence of natural resins on the rate of drying of linseed

was included in the present study merely for purposes of comparison.

The three natural resins selected - Kauri, Congo, and East India - were supplied by the Devoe and Reynolds Corporation. After the preliminary running process each resin was dispersed in the oil at 360°C. The drier was added while the oil was still hot, the amount used being the same as in the previous work. After the solution had cooled sufficiently it was filtered through cheese cloth into small homeopathic vials sealed with parafin.

The drying curves of 10% solutions of these resins are shown in figure XIII. The Kauri and East India oil solutions dried at a fairly rapid rate, their curves simulating very closely that of the linseed oil curve. Their induction periods were relatively short. Their values for maximum gain weight, however, varied considerably. The Kauri-oil solution reached a maximum of 13.6% in 6 hours while that of the East India-oil solution attained a 12% maximum in 5 hours. No reason has been offered to explain this difference in percentage gain in weight.

The drying curve for the Congo-oil solution presents a rather marked difference in regard to the induction period which was concluded after an hour and forty minutes. The gain in weight then proceeded rapidly until a maximum gain in weight of 13% was reached. An interesting point in connection with this curve and that of the Kauri-solution curve is that both attain approximately the same maximum weight during the same period of time despite the longer induction period of the Congo-oil solution film. In order for this to be possible the Congo-oil film had to oxidize at a more rapid

rate. No explanation is offered for this anomaly.

The latter portions of the three curves were quite similar in that their maximum increase in weight fell to about 9.5% in 180 hours.

Any conclusions regarding the inhibitory effect of natural resins on the oxidation of linseed oil are not entirely warranted on the basis that the structure and constitution of these substances are not definitely known. However, it is possible in the case of the Congo resin, which evidenced the greatest inhibitory effect, that certain substances of antioxygenic nature are present in small amounts. Evidence of this fact is not presented in this study.

XI The Influence of Phenol-Formaldehyde

Resins on the Drying of Heat

Bodied Linseed Oil

In order to present a more comprehensive study of the influence of phenol-formaldehyde resins on the oxidation of linseed oil it was decided to extend the investigation to include bodied linseed oil.

Heat bodied oils are those oils that have been thickened by heat at a temperature ranging from 500° to 550° F. The oils are usually heated out of contact with air until the desired consistency is obtained. The changes in properties of the oil resulting from this heat treatment may be briefly summarized as (16): (1) a large increase in viscosity, (2) an increase in density, (3) a decrease in the iodine value, and (4) an increase in acid number.

According to Long (23) the heat bodying process causes the molecules to couple at their double bonds thereby leading to molecules of a complex structure. This is evidenced by a decrease in unsaturation and an increase in molecular weight. Long further assumes that such products should approximate closely a gel structure with an interlacing network of carbon chains. Therefore it is apparent from these changes that occur in the oil that the drying curves for heat-bodied linseed oil should exhibit rather wide deviations from the drying curves of the raw oil.

This investigation was limited to the study of the influence of resins #2 and #5 on the oxidation of heat bodied linseed oil. These two resins were selected as they had been found to exert the most potent antioxidant effect of any of the resins in the series. Moreover, since the viscosity of heat bodied oil is rather large thus making the application of its films a difficult matter, the concentrations of the resins in the oil were limited to 5% solutions. It was felt that the observations made at this concentration would

afford a reasonable basis for comparison with the curves of the raw linseed oil of the same resin percentages. Therefore the resin-solutions of the heat bodied linseed were made up in identically the same manner as were those of the raw linseed oil.

The three curves shown in figure XIV represent oxidation of the heat bodied oil alone, the 5% solution of #5 resin, and the 5% solution of #2 resin.

A comparison of these curves with those of the raw linseed oil of the same concentrations exhibits some rather striking differences. In the first place the induction periods have been considerably increased. As a matter of fact the entire curve may be considered as the induction period. In the second place the maximum increase in weight reached a much lower value than in the case of the raw oil. All three curves averaged a little better than a 9.0% maximum value. At the end of 180 hours this maximum fell to 8.5% which is a relatively small decrease in comparison to the raw oil. The low oxygen absorption in the case of heat bodied oil is obviously due to its decrease in unsaturation. Although the middle portions of the curves show a slight tendency towards a straight line it is not as pronounced as in the case of the raw oil. As to a comparison of the antioxidant effects of these two resins, namely, #2 and #5, on the rate of oxidation of the bodied oil, it is as would be expected, that #2 resin shows the strongest influence. This effect when compared with that on the raw oil evidences rather close similarities in that the retarding effect is in somewhat the same proportions.

Although this experiment did not include all the resins in the series nor all of the concentrations used, the results do, nevertheless, seem to strengthen the general premise that

phenol-formaldehyde resins exert an antioxygenic influence on the oxidation of linseed oil.

XII Conclusions

1. Phenol-formaldehyde resins definitely show an antioxidant effect on the drying of "pure" drier-treated linseed oil.
2. The degree of the antioxidant effect is a specific property of the resin itself.
3. The presence of phenol-formaldehyde resins prolongs the induction period to an extent which is proportional to the concentration of the resin in the oil.
4. At the conclusion of the induction period the rate of oxidation of the resin-oil system closely simulates that of the "pure" linseed oil system.
5. The antioxidant effect of phenol-formaldehyde resins seems to strengthen the general premise that these products still retain some of their phenolic properties. Whether this effect is due to the structure and constitution of the resin molecule or to the presence of free phenol, was not definitely ascertained in this investigation.
6. The oxidation of phenol-formaldehyde resins with hydrogen peroxide suppresses the antioxygenic activity of the resin.
7. Phenol-formaldehyde resins exert an antioxidant effect on the oxidation of heat bodied linseed oil.

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