10-1945

Surface impregnation of wood : II. gaseous impregnation of wood : III. investigations on submarine decking : IV. investigation of marine adhesives.

Otto J. Mileti
University of Louisville

Recommended Citation

Mileti, Otto J., "Surface impregnation of wood : II. gaseous impregnation of wood : III. investigations on submarine decking : IV. investigation of marine adhesives." (1945). *Electronic Theses and Dissertations.* Paper 2016.
https://doi.org/10.18297/etd/2016

UNIVERSITY OF LOUISVILLE

I SURFACE IMPREGNATION OF WOOD
II GASEOUS IMPREGNATION OF WOOD
III INVESTIGATIONS ON SUBMARINE DECKING
IV INVESTIGATION OF MARINE ADHESIVES

A Thesis
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 CHEMICAL ENGINEERING

Department of Chemical Engineering

By
Otto J. Mileti
1945

I SURFACE IMPREGNATION OF WOOD

II GASEOUS IMPREGNATION OF WOOD

III INVESTIGATIONS ON SUBMARINE DECKING

IV INVESTIGATIONS OF MARINE ADHESIVES

Otto J. Mileti

Approved by the Examining Committee.

Director Gordon C. Williams

R. C. Ernst

W. R. Barnes

October, 1946

TABLE OF CONTENTS

Page

List of Tables v

List of Figures vi

Abstract x

I. Surface Impregnation of Wood

Introduction 1

Historical 3

Theoretical 5

Experimental 7

A. Atmospheric Immersion 9

B. Hydrostatic Pressure 20

C. Wood Compression 24

D. Comparison of Various Woods for Surface Impregnation 28

Summary and Conclusions 33

II. Gaseous Impregnation of Wood

Introduction 36

Historical 38

Theoretical 40

Experimental 42

Summary 47

III. Investigations on Submarine Docking

Introduction 49

Historical 51

Theoretical 53

TABLE OF CONTENTS - Continued.

Page

Experimental 56 42

A. Preliminary Tests 56 42

B. Extended Tests 63 64

Summary 74

IV. Investigations of Marine Adhesives

Introduction 84

Historical 87

Theoretical 89

Experimental 91

A. Acetone Extraction of Glue Films 92

B. X-ray Diffraction Procedure 106

C. Viscosity of Mixed Cascophen LT-67 Adhesives . . 118

Summary and Conclusions 124

Literature Cited 127 134

Acknowledgements . . . . 129 X

Vita . . . . 131 X

LIST OF TABLES

Table	Title	Page
I.	Pressure Curing of Impregnated Woods	16
II.	Effect of Gaseous Impregnation on Yellow Poplar	46
III.	Effect of Water Immersion (1 week) on Gaseous Treated Yellow Poplar	48
IV.	Effect of Salt Water Pressure Cycles on Various Woods	59
V.	Per Cent Weight Increase Upon Impregnation	71
VI.	Acetone Extraction of Durez 12688 and Bakelite XC 17613	98
VII.	Acetone Extraction of Bakelite XC 17540	98
VIII.	Acetone Extraction of Plyophen 6000	99
IX.	Acetone Extraction of Cascophen RS 216	99
X.	Acetone Extraction of Penacolite	100
XI.	Acetone Extraction of Lauxite PF 90 C	100
XII.	Specimens X-rayed and Their Conditions	107
XIII.	Viscosity of Mixed Cascophen LT-67 Adhesives	119

LIST OF FIGURES

Figure	Title	Page
1	The Effect of Serrations on Surface Impregnation (Mag. 3X)	12
2	Simultaneous Application of Pressure and Heat on Yellow Poplar (Mag. 4X): a) D.M.U. Impregnated; b) Water Soaked	16
3	Pressure Applied to Yellow Poplar After 5 Minutes Heating (Mag. 4X): a) D.M.U. Impregnated; b) Water Soaked	17
4	Pressure Applied to Yellow Poplar After 10 Minutes Heating (Mag. 4X): a) D.M.U. Impregnated; b) Water Soaked	18
5	Pressure Applied to Yellow Poplar After 15 Minutes Heating (Mag. 4X): a) D.M.U. Impregnated; b) Water Soaked	19
6	Cross Section of White Oak (Mag. 5X): a) Original; b) After 9 Salt Water Pressure Cycles .	60
7	Cross Section of Yellow Pine (Mag. 5X): a) Original; b) After 9 Salt Water Pressure Cycles .	61
8	Cross Section of Teak (Mag. 5X): a) Original; b) After 9 Salt Water Pressure Cycles .	62
9	Cross Section of Maple (Mag. 5X): a) Original; b) After 9 Salt Water Pressure Cycles .	63
10	Cross Section of Mahogany (Mag. 5X): a) Original; b) After 9 Salt Water Pressure Cycles .	64
11	Cross Section of Douglas Fir (Mag. 5X): a) Original; b) After 9 Salt Water Pressure Cycles .	65
12	Cross Section of D.M.U. Impregnated Yellow Pine After 9 Salt Water Pressure Cycles (Mag. 5X)	66
13	Cross Section of D.M.U. Compregnated Yellow Pine (25% Compressed) After 9 Salt Water Pressure Cycles (Mag. 5X)	67
14	Cross Section of D.M.U. Compregnated Yellow Pine (50% Compressed) After 9 Salt Water Pressure Cycles (Mag. 5X)	67

LIST OF FIGURES - Continued.

Figure	Title	Page
15	Weight Increase of Wood During Pressure Cycles in Salt Water	72
16	Weight Increase of Treated Mahogany During Pressure Cycles in Salt Water	73
17	Weight Increase of Treated Birch During Pressure Cycles in Salt Water	75
18	Weight Increase of Treated Laminate (Maple Faces, Mahogany Core) During Pressure Cycles in Salt Water	76
19	The Effect of Species on Weight Increase of Rez Sealer Impregnated Woods	77
20	The Effect of Species on Weight Increase of Copper Naphthenate Impregnated Woods	78
21	The Effect of Species on Weight Increase of Paraffin Oil Impregnated Woods	79
22	The Effect of Species on Weight Increase of Linseed Oil Impregnated Woods	80
23	The Effect of Species on Weight Increase of Tung Oil Impregnated Woods	81
24	The Effect of Species on Weight Increase of Oleic Acid Impregnated Woods	82
25	Final Dimensional Changes of Impregnated Woods After Pressure Cycles in Salt Water	83
26	Acetone Extractions of Durez Adhesive (12688 Resin, #12689 Hardener)	101
27	Acetone Extraction of Bakelite Adhesive (XC 17613 Resin, XK 17618 Hardener)	102
28	Acetone Extraction of Bakelite Adhesive (XC 17540 Resin, XK 17545 Hardener)	103
29	Acetone Extraction of Plyophen Adhesive (#6000 Resin, #6001 Hardener)	104

LIST OF FIGURES - Continued.

Figure	Title	Page	
30	Acetone Extraction of Laurite Adhesive (PF 90 C Resin and Hardener)	105	101
31	X-ray Diffraction Pattern of Uncured Cascophen LT-67 Adhesive	109	106
32	X-ray Diffraction Pattern of Cascophen LT-67 & M-18 Adhesive (Uncured)	109	106
33	X-ray Diffraction Pattern (Powder Method) of Cascophen LT-67 & M-18 Adhesive (Uncured)	110	107
34	X-ray Diffraction Pattern of Cascophen LT-67 & M-18 Adhesive (24 Hours at 25°C.)	110	107
35	X-ray Diffraction Pattern of Cascophen LT-67 & M-18 Adhesive (6 Hours at 100°C.)	111	108
36	X-ray Diffraction Pattern of Cascophen LT-67 & M-18 Adhesive (24 Hours at 120°C.)	111	108
37	X-ray Diffraction Pattern of Oak Shavings	112	109
38	X-ray Diffraction Pattern of Oak Shavings Heated 24 Hours at 120°C.	112	109
39	X-ray Diffraction Pattern of Oak Shavings and Cascophen LT-67 & M-18 Adhesive (Uncured)	113	110
40	X-ray Diffraction Pattern of Oak Shavings and Cascophen LT-67 & M-18 Adhesive (24 Hours at 25°C.).	113	110
41	X-ray Diffraction Pattern of Oak Shavings and Cascophen LT-67 & M-18 Adhesive (6 Hours at 100°C.).	114	111
42	X-ray Diffraction Pattern of Oak Shavings and Cascophen LT-67 & M-18 Adhesive (24 Hours at 120°C.)	114	111
43	X-ray Diffraction Pattern of α - Cellulose	116	112
44	X-ray Diffraction Pattern of α - Cellulose Heated 24 Hours at 120°C.	115	112
45	X-ray Diffraction Pattern of α - Cellulose and Cascophen LT-67 & M-18 Adhesive (Uncured)	116	113

LIST OF FIGURES - Continued.

Figure **Title** **Page**

46 X-ray Diffraction Pattern of α - Cellulose and Cascophen LT-67 & M-18 Adhesive (24 Hours at 120°C.) 116 113

47 Viscosity Changes of Mixed Cascophen LT-67 Adhesives at 87°F. (50 ml. Thru #4 Ford Cup) 121 118

48 Viscosity Changes of Mixed Cascophen LT-67 Adhesives at 87°F. (50 ml. Thru #4 Ford Cup) 122 119

ABSTRACT

This thesis presents results on methods used to produce a hard surfaced wood product. The methods involve the parting of the wood fibers on the surface by a special serrating tool, followed by surface impregnation and final curing. The serrations on the wood surface produce an artificial grain upon curing.

A preliminary investigation was made to improve the rot-resistance of wood by a gaseous treatment. Results of such treatments show some limited success with formaldehyde on yellow poplar and warrant further study.

An investigation was made to find a substitute for teak wood used on submarine decking. A number of combinations of woods and impregnating agents were prepared and tested under simulated ocean conditions. The results of these tests indicate that a maple-mahogany laminate, when treated with the proper agent, will compare favorably with teak.

The optimum curing conditions of several phenolic resin adhesives are presented as determined by an acetone extracting procedure.

The results are presented for an attempt to replace the acetone extraction procedure by an x-ray diffraction method. X-ray diffraction patterns are presented of wood, α-cellulose, and a phenolic adhesive.

The viscosity charactistics of mixed Cascophen LT-67 phenolic adhesive are given. These viscosity correlations are based on the flow of material through an orifice.

I. SURFACE IMPREGNATION OF WOOD

INTRODUCTION

Wood is one of our most abundant natural resources. However it has been limited in its uses because of certain inherent properties, such as low strength and low resistance to dimensional changes, decay, and chemicals.

It has been found that impregnating wood with synthetic resins greatly improves the properties and produces a hard, dimensionally stable product, with a high compressive strength. Such products, though having innumerable uses, are brittle, low in resilience, and difficult to glue or fasten.

It was therefore desired to produce a product having a hard, dense, water repellent surface, resistant to marring and grain raising, and with a soft core to provide the desired resilience. This has been accomplished by producing a plywood of compressed resin treated face plies with an uncompressed core in a single operation. Such an assembly is made possible by the plasticising action of the resin forming constituents in the treated plies. Little or no compression takes place in the dry, untreated core.

The object of this research was to simplify this procedure for producing such a product by impregnating the surface layers of a solid piece of wood and to produce the hardened surfaces as an integral part of the wood section.

HISTORICAL

Many materials and methods to improve the properties of wood have been investigated. Creosote has been used for years as a successful wood preservative and many other chemicals have been found to be toxic to certain wood destroying organisms. However not until recent years with the development of synthetic resins has any definite step been made to improve wood to the extent of producing a strong, uniform, and durable material which could take its place along side that of plastics and metals.

Salt solutions (1), oils, waxes (2), and many other materials have been found to retard the rate of absorption of moisture in wood, thereby causing a temporary reduction in swelling and shrinkage. Later, Stamm and Seborg (3) report a permanent decrease in the dimensional change of wood by synthetic resin impregnation. They (4) have reported a method of producing compregnated wood using a phenol formaldehyde type resin and have demonstrated many uses for such a product.

The DuPont de Nemours Company (5) has produced a dimensionally stable wood by impregnating it with dimethylolurea in a method similar to that of the phenol-formaldehyde resin.

Recently Stamm and associates (6) have succeeded in utilizing the resin properties of the lignin to produce a heat-stabilized compressed wood. The wood is compressed under such conditions that will cause a sufficient flow of lignin to relieve the internal stresses. The product is not so stable as compregnated wood, but it does possess several superior qualities including a notably greater impact strength.

Bailey and associates (7) have presented data comparing the relative merits of various resin treated wood products.

THEORETICAL

Wood is composed of microscopic crystallites, (micelles) linked together to form cells, in the shape of hollow spindle-shaped, closed end tubes. Sine the material composing the cell walls is primarily cellulose, it is very hygroscopic and susceptible to swelling with moisture.

This swelling and shrinkage can be reduced considerably by impregnation with a synthetic resin. However since the cell wall is the hygroscopic material, it is not sufficient to diffuse the resin into the cavities, for this would produce only a number of hard non-hygroscopic resin particles held together by a non-conforming, hygroscopic matrix. It is necessary to diffuse the resin into the cell walls where it can either form a bond with the wood fibers and thereby eliminate the hygroscopity of the micelles, or completely bind the entire structure. The penetration of these cell walls requires a polar or semipolar substance of low molecular size with an affinity for cellulose and lignin molecules. Such a substance has been found in the synthetic resin of the phenol formaldehyde type on which the condensation has been arrested at an early stage.

Such a resin may be used for surface impregnation; however unlike total impregnation, the penetration must be wholly from the face of the wood since it is desired to harden just the surface. The surface hardening could be realized by curing the product under elevated pressures and temperatures. Since only the surface is treated, upon applying heat and pressure the plasticizing action of the resin should cause the surface to be compressed and hardened. The untreated core should retain its original softness and resilience.

EXPERIMENTAL

This work is a continuation of the preliminary investigations of Saora (8) to determine a method of surface impregnating wood. In his investigation Saora found that serrating or separating the wood fibers at the surface greatly aided resin penetration, and upon curing, it produced an artificial grain. However he tried only atmospheric soaking of the wood in the resin solution and failed to get a uniformly impregnated surface.

In this investigation three methods of impregnation were tried in an attempt to acquire a uniformly surface impregnated product:

1) Atmospheric immersion i.e., immersing the sample in the resin solution for a given length of time at atmospheric pressure.

2) Hydrostatic pressure i.e., immersing the sample in resin solution for a given length of time under pressure.

3) Wood compression, i.e., the wood sample is compressed and released in a resin solution.

A comparison of various resins and different woods was also made using the 3 methods.

In all three methods surface serrated wood samples were tested. These serrations were made in the fiber direction on both faces by passing the samples between two rollers each having a series of circular knives. These knives were of hardened saw steel and were ground to a fine edge.

A. ATMOSPHERIC IMMERSION

APPARATUS:

Laboratory electric ovens were used as kiln driers. A manually operated hydraulic press, made by the Charles E. Frances Company, was used to cure the treated samples. The press had electrically heated platens controlled by thermostats and was capable of standing a 50 ton total pressure.

MATERIALS:

Finished yellow poplar (6 x 3.5 x .9 inches) having V shaped serrations 0.08 inches apart and 1/16 inch deep running the length of the wood was used as test specimens.

Amberlite PR23, a phenol formaldehyde type resin containing 30 per cent solids in a water solution, was used first as impregnating agent; and later PR50, a similar resin, was also used.

Dimethylolurea (D.M.U.), containing three parts dimethylolurea, one part urea, and twelve parts water by weight, was also used as an impregnating agent.

TEST PROCEDURES AND RESULTS:

A. Amberlite, PR23

Two series of wood samples were immersed in the resin, one completely and the other to one half the thickness, for 6, 12, and 24 hour periods. After immersion, all samples were subjected to a 24 hour diffusion period in a non-drying atmosphere and then oven heated for 24 hours at 145°F. Following this drying period, the samples were compressed one half hour at 300° F. with a pressure of 1000 psi. In the curing of the samples impregnated on one side, only the treated side was subjected to the high temperature. The other was held at room temperature. All heated platens were cooled below 220° F. before the pressure was released.

All samples had a hard, reddish brown high gloss surface. However in every case the penetration was never deeper than the serration, and the diffusion in the lateral direction was very slight. Thus the wood between the serrations had only a thin coat of resin analagous to a protective coating and was totally unsatisfactory as an impregnated surface.

Impregnation at elevated temperatures (100° F.) was tried but without any better results. The resin diffused into the serrations but penetrated the wood only slightly.

Since penetration was unsatisfactory, the same two series of tests at room temperature were run again but with some fresh PR23. The samples were cured by compressing quickly from 0.9 to 0.6 inches at 300° F. and held for one half hour; then the platens were cooled to 220° F. and the pressure released.

The resulting penetration was only slightly better with this newer resin. Also examination of the cross section of the specimens under a low power microscope indicated that the resin was not so fully cured as the first batch under the same conditions. It still had its original red color as compared to the black color of the cured older resin.

These tests indicate quite conclusively that atmospheric immersion, using PR23 on yellow poplar having the described serration, is unsatisfactory.

Aluminum, tin, and steel were tested for use as cauls to distribute the heat evenly and to impart a smooth, hard, glossy surface to the wood upon curing. All three imparted very good surface, if they were polished, but both the aluminum and tin had more of a tendency to stick to the specimen than the harder steel.

All the serrations up to this time were such as to produce one vertical cut and a diagonally squeezed section on the other side (Figure I upper right face). Since the resin penetration seemed to be governed by the serrations, it was decided to determine the serrating action which contributed most to the acceptance of the fluid. Accordingly, cutters were arranged in a specific but irregular manner to produce a known pattern of cutting and squeezing action. Impregnation of samples having this irregular pattern showed that the contour of the diffused resin is quite similar to that of the serrating knife (Figure I). In other words, a squeezing action on the surface materially aids subsequent diffusion, and therefore a broad shallow serrating tool is to be desired.

B. Dimethylol Urea (D.M.U.)

Serrated samples were immersed in the resin solution for 6, 12, and 24 hour periods with diffusion periods of 24, 48, 72, and 96 hours (total 12 samples). These were then placed in a hot platen press and compressed from the original thickness of 0.9 inch to 0.75 inch with the final thickness held by steel stop blocks.

Fig. I. The Effect of Serrations on Surface Impregnations.
(Mag. 3X)

Examination of the twelve specimens showed no apparent difference in either soaking time or diffusing time, i.e., a six hour soak and twenty-four hour diffusion period produced a sample visually comparable to a twenty-four hour soak, ninety-six hour diffusion. The samples all had smooth, hard surfaces, but the degree of penetration in each sample could not be detected because of the similarity in color between the D.M.U. and wood.

Each of the samples were subjected to a drop surface moisture test with the water spot continually replenished as it disappeared. There was a slight raise in grain under these conditions, but it was definitely less than on a control specimen of untreated wood.

Because of a defect in the press, one of the above samples was heated a considerable time before being compressed to 0.75 inch. Upon examination it was found that this sample had a relatively low surface hardness. It was therefore decided to determine the effect of pressure upon the final cured products.

A set of D.M.U. soaked and diffused (24 hours - 24 hours) samples were cured at the same temperature for the same length of time but with pressure applied at various intervals of cure (Table I). A similar set of plain water soaked specimens was also prepared.

The results on the D.M.U. samples, tabulated in Table I, show that at constant temperature, time, and percentage compression, the compressed wood area is practically constant regardless of variance in method of applying pressure. It can also be seen that as the time of heating without pressure increases, this hardened compressed wood area moves from the surface towards the interior of the wood. This phenomenon, though also present in the water soaked samples, is more pronounced in the D.M.U. treated because of the curing action of the resin upon heating.

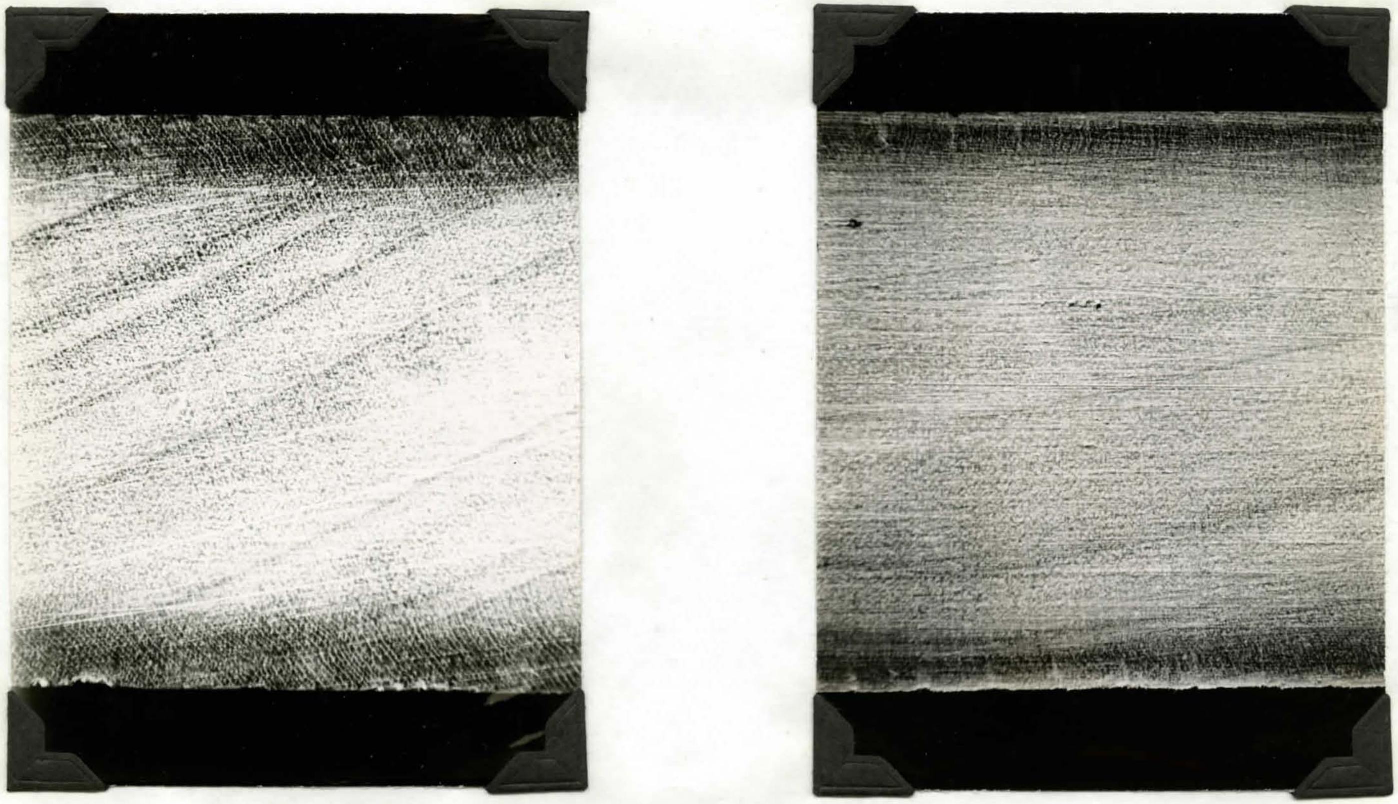
These results are shown pictorially in Figures 2, 3, 4, and 5, the compressed area being the dark portion having the wavy medullary rays. It is evident that the hardened compressed area is caused by a bonding during the procedure and is produced only in the section subjected to heat, pressure, and plasticizing agent simultaneously. Consequently for surface impregnation the pressure at final cure should be applied immediately and quickly to insure a hardened surface and soft core.

TABLE I. - PRESSURE CURING OF IMPREGNATED WOODS.

D.M.U. Treated Yellow Poplar

Method of Compressing	Results
Ia. Quickly pressed by 300°F. platens to 0.75 inch stop blocks, pressure and heat retained for 1/2 hour, cooled to 200°F. in press.	The sample showed a hardened outside edge 3/32 inch (approx.) with hard compressed wood characteristics (Figure 2a.).
Ib. Surfaces brought in contact with 300°F. platens for 5 minutes then pressure applied and sample finished as Ia.	The sample had a soft exterior with a harder compressed wood area beginning about 5/32 inch from the outside surfaces and extending almost to the center of the section. The serrations were open and unbonded contrary to conditions of Ia. (Figure 3a.).
Ic. Surfaces brought in contact with 300°F., platens for 10 minutes; then pressure applied, and sample finished as Ia.	The sample showed again the soft exterior whose area extended towards the center about 1/4 inch and then a hard section extending towards the center 3/32 inch (Figure 4a.).
Id. Surfaces brought in contact with 300°F. platens for 15 minutes; then pressure applied, and sample finished as Ia.	Comparable to Ic. except that the harder area had shifted to the center (Figure 5a).

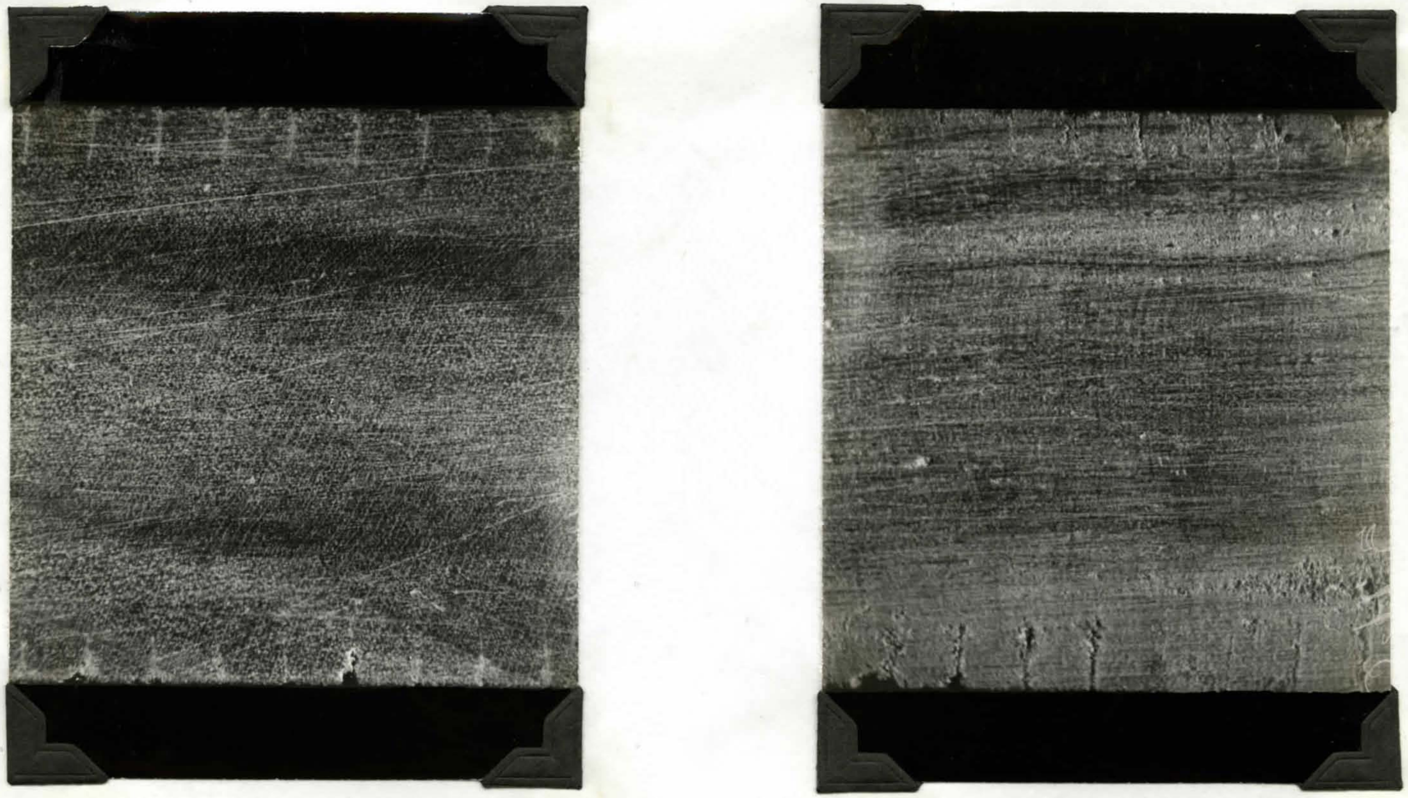
A similar set of plain water treated specimens was prepared. The results were similar but not so pronounced as can be seen in Figures 2b, 3b, 4b, and 5b.



a) D.M.U. Impregnated.

b) Water Soaked.

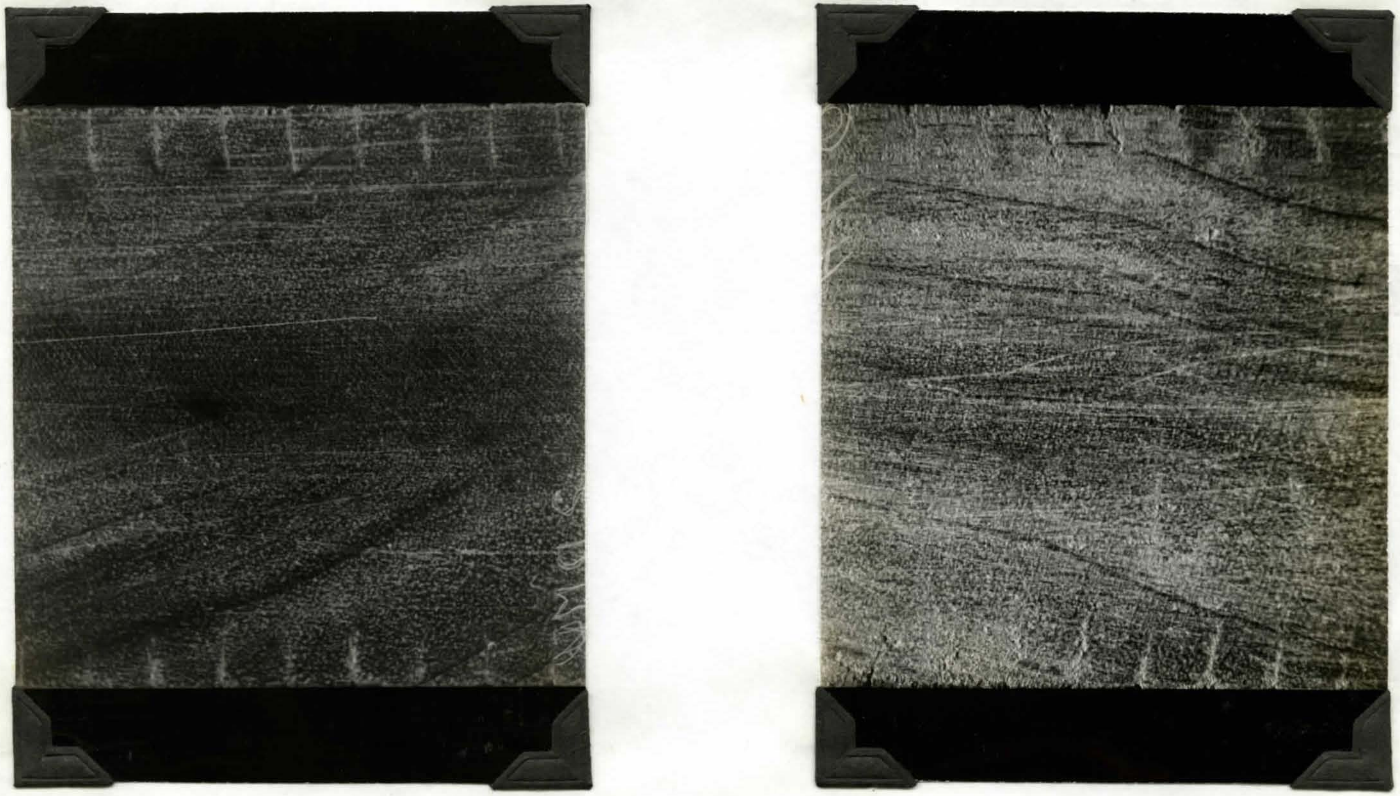
Fig. 2. Simultaneous Application of Pressure and Heat on Yellow Poplar. (Mag. 4X).



a) D.M.U. Impregnated.

b) Water Soaked.

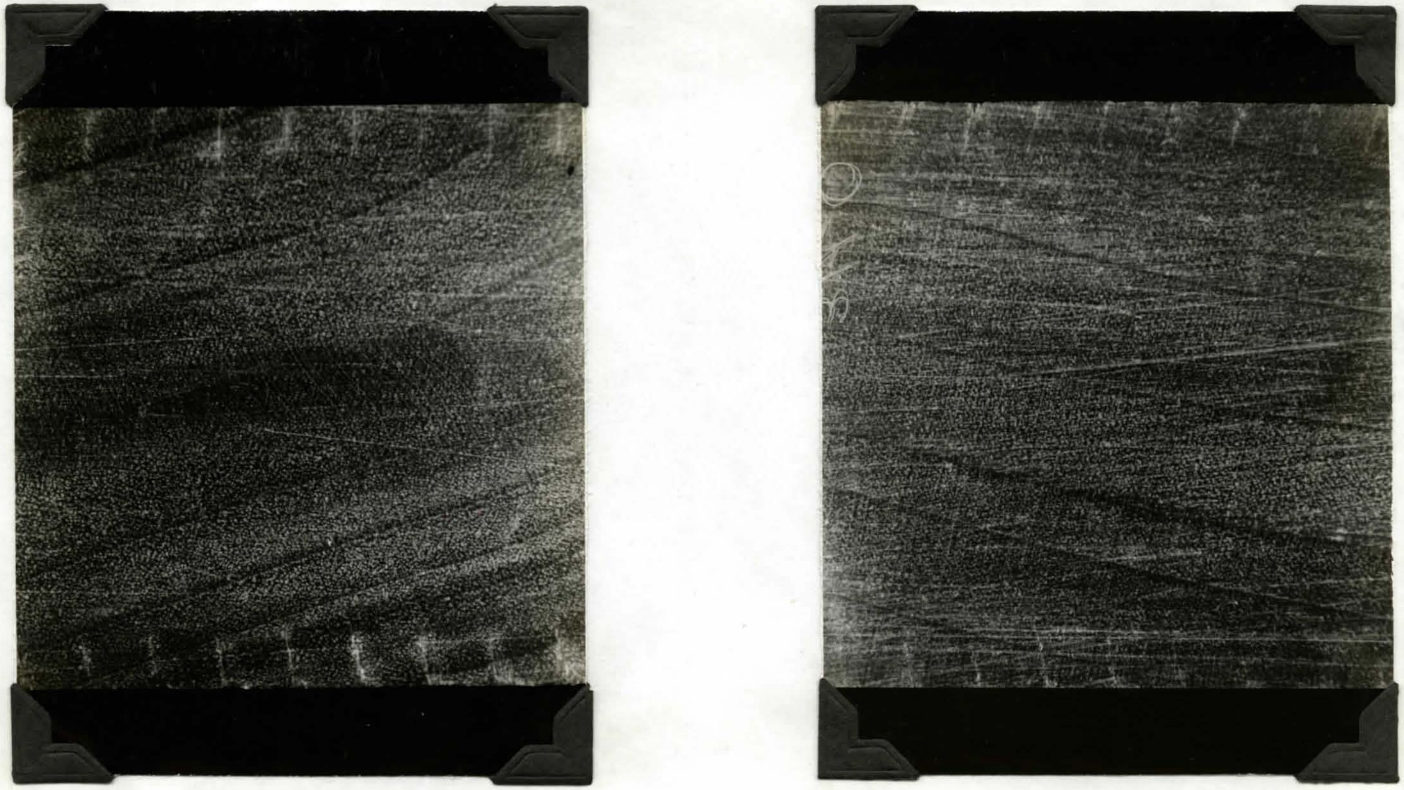
Fig. 3. Pressure Applied to Yellow Poplar After 5 Minutes Heating (Mag. 4X).



a) D.M.U. Impregnated.

b) Water Soaked.

Fig. 4. Pressure Applied to Yellow Poplar After 10 Minutes Heating (Mag. 4X).



a) D.M.U. Impregnated.

b) Water Soaked.

Fig. 5. Pressure Applied to Yellow Poplar After 15 Minutes Heating (Mag. 4X).

B. HYDROSTATIC PRESSURE

APPARATUS:

A steel pressure cylinder (six inches inside diameter and twenty-four and one half inches high) with pressure gauge, pneumatic pressure connections, and a stainless steel bucket, was used in the impregnation of the wood samples.

MATERIALS:

Yellow poplar (4 x 4 x 9 inches).

Amberlite PR23, a powdered phenolic type resin (30 parts by weight) plus water (70 parts by weight). Total solid 30 percent.

Permatex No. 2 used as an end sealer.

PROCEDURE:

Wood samples were placed in the bottom of the stainless steel bucket and immersed in the impregnating agent. A pneumatic pressure was then applied and after a pre-determined time released suddenly. The samples were then air dried. All curing was done at 300°F. - half hour compressed from 0.9 to 0.75 inch.

DATA AND RESULTS:

A sample (containing all sapwood) subjected to impregnation under 85 psi. for one-half hour was found to be thoroughly impregnated. The time was cut down to 5 minutes, but there was still some end penetration extending the length of the piece. Penetration from the faces extended to an average of 1/16 inch deep though it was not uniform. Side penetration was negligible. Final cure produced hard surfaces about 1/20 inch and left the rest of the wood, including that which had been treated by longitudinal penetration, soft.

Since wood is more susceptible to longitudinal penetration than tangential or radial, the high hydrostatic pressure accelerated this end penetration without greatly affecting the other two.

It was therefore decided to seal off the ends of a sample with Permatex No. 2 and subject it to the same conditions as the last sample; i.e., immersion in resin under 85 psi. for 5 minutes. The result was a product having no end diffusion but uniformly impregnated faces 3/32 inch thick. Final curing produced an excellent surface impregnated product that had hard surfaces, each approximately 1/10 inch thick and a soft core. The successful results were effected on poplar containing all sapwood. It was then decided to determine the penetration in the heartwood. A sample having a plain heartwood surface and another containing a serrated heartwood surface were subjected to pressure impregnation of 85 psi. for five minutes. Both samples were end sealed before treatment. No penetration occurred in the plain heartwood surface, but a uniform surface penetration 1/8 inch thick occurred in the serrated heartwood.

Additional tests necessary to confirm these successful results had to be carried out using PR-60 resin as the manufacture of PR-23 was stopped. However since the PR-60 did not impart any color to the wood upon impregnation, an attempt was made to find a suitable dye.

The following chemicals were tested in a PR-50 solution (30% solids).

Carbon Black (2% by weight)
Lamp Black (2% by weight)
Aniline Blue (1 gm. per 2 liters)
Methylene Blue (1 gm. per 2 liters)
Methylene Hydrochloride (1 gm. per 2 liters)

The aniline blue, methylene blue, and methylene hydrochloride proved successful in giving the resin a green color which penetrated into the wood with the resin. However, upon curing the green color disappeared, and the resin became practically colorless again.

All the previous successful results were at 85 psi. The effect of varying this pressure was now determined. Four serrated poplar samples having only sapwood were end sealed, immersed in a PR-50 solution containing aniline blue (1 gm. per 2 liter), and subjected to 20, 40, 60, and 80 psi. respectively for 10 minutes.

The layers of impregnation varied from 0.08 to 0.15 inch in all four samples and no variations with pressure could be found. This indicates that in the short time of treatment the resin is easily diffused through the serrated wood surface - a depth of 0.06 to 0.07 inch - even at low pressures but that past the depth of serration the rate is too slow to show variation with pressure. A longer period of time to show this variation is not warranted since a depth of more than 0.15 inch is undesirable.

DISCUSSION:

The hydrostatic pressure method is an easy, quick, and effective way of surface impregnating sapwood provided that end diffusion can be prevented. However this method is of no use on wood containing heartwood surfaces unless they have been serrated. These serrations tend to make it possible to produce a more uniformly impregnated surface with little differentiation between heart and sapwoods.

The pressure and corresponding time vary with the different woods and resins; however on yellow poplar using PR-23, 85 psi. (gauge) for 5 minutes was satisfactory. In commercial practice the time may be too short and so a corresponding lower pressure and longer time may be substituted. A pressure of 20 psi. (gauge) for 10 minutes proved satisfactory on yellow poplar with PR-50.

C. WOOD COMPRESSION

APPARATUS:

A tin pan was used as a container for the wood and resin solution. A hydraulic press made by the Charles E. Francis Company (see Page 9) was used to apply pressure and flat steel bars of different lengths and widths were employed to transmit this pressure to various parts of the wood samples.

MATERIALS:

Yellow poplar, both plain and serrated, was used as test samples. The serrations were the conventional V shaped serrations .03 inch deep and 1/16 inch apart.

Amberlite PR 23 was used as impregnating agent.

PROCEDURE:

A sample was laid flat on a steel bar in the resin solution, and an identical bar was placed on its top surface directly above the bottom piece. This assembly was then placed between the platens of the press and pressure was applied to compress the wood to a definite thickness. After compression the pressure was released, but the wood was kept immersed in the solution for definite lengths of time. The samples were then air dried one day and sawed in two. All curing was done (after air drying) at 300°F. for a half hour at a pressure necessary to compress the wood from 0.9 inch to 0.75 inch.

DATA AND RESULTS:

A serrated sample (4 x 3-1/2 x 0.9 inches) was soaked 48 hours in water before being compressed in the resin solution to 0.5 inch. The sample was allowed to regain its original thickness before it was removed (24 hours). The penetration of resin was throughout the thickness; but it was very non uniform, and there was indication that a great amount of end diffusion took place. Because of the great amount of impregnation, one day air drying was not sufficient; and upon curing, the resin extruded almost completely leaving only a very thin surface layer.

A plain sample (4 x 3-1/2 x 0.9 inches) soaked only 1/2 hour in water before treatment gave similar results except that the penetration from the faces was negligible which showed conclusively that the resin had followed the fiber axis direction.

A serrated sample (4 x 3-1/2 x 0.9 inches) was compressed in solution to 0.75 inch. The results were similar to those of the other samples. The penetration was throughout but very non uniform. A second sample treated the same way but having its ends sealed (Permatex No. 2 - see Page 20) had end penetration of about 1 inch. Examination of the mid section showed that surface impregnation was not uniform, and varied from 0.0 to 1/8 inch in depth depending on its position with respect to the serration. The cross section resembled that of an atmospheric soaked sample; however, the diffusion from the serrations into the wood were more pronounced in the former.

Two serrated samples (8 x 1-1/2 x 0.9 inches) were placed between two flat iron bars of such lengths that when pressure was applied all but an inch from each end of the samples were compressed. They were compressed to .75 inch then released and allowed to soak for 5 minutes and 24 hours respectively. In both samples the longitudinal diffusion extended about 3/4 inch from each end, and because of rupture there were some parts in which penetration had extended laterally into the wood for about 1/4 inch. However the surface impregnation of the 24 hour sample was more uniform extending to a depth of 3/32 of an inch from each face, whereas the 5 minute sample had impregnated faces varying from 1/16 to 3/32 inch deep.

It has been shown that a sample 4 inches long compressed to 0.75 inch encounters end diffusion throughout. Also it was noted that compressing an 8 inch length in which an inch from each end was not subjected to pressure caused only 3/4 inch penetration from the ends. It was therefore decided to determine how far the end diffusion actually proceeded when the whole sample is subjected to compression.

Two serrated samples (6 x 1-1/2 x 0.9 inches) were compressed to 0.75 inch, released in solution, and allowed to soak 5 minutes and 24 hours respectively. The 5 minute sample had impregnated faces about 3/32 inch thick. Side penetration was less, and longitudinal was about 3/4 inch. The 24 hour sample showed slightly more uniform surface impregnation, but longitudinal penetration extended the whole length of the piece.

From these tests it can be seen that (1), a soaking period after treatment is necessary to insure proper surface impregnation; (2), this prolonged immersion causes a great amount of end diffusion; (3), a compression of 0.2" in 1" of wood thickness gives the necessary surface layer.

It was therefore decided to study more closely what happens at the surface subjected to pressure.

Two serrated samples (8 x 1-1/2 x 0.9 inches) were compressed to 0.75 inch only at their centers by means of flat bars above and below extending the width of the pieces and 1/2 inch of their lengths. One sample was soaked 5 minutes after compression and the other 24 hours. The 5 minute sample showed diffusion into the serrations throughout the piece, and at the area of compression a thin uniform layer of resin about 1/32 inch thick on each face. In the area of compression of the 24 hour sample a uniformly impregnated surface of 1/8 inch thick existed on each face. Upon examination of this area it was found that the resin had penetrated from the faces to a depth of 1/8 inch and then travelled longitudinally a small distance each way.

From these last tests there is indication that surface impregnating wood by a method involving actual compression of the wood in the resin is feasible under controlled conditions.

D. COMPARISON OF VARIOUS WOODS FOR SURFACE IMPREGNATION

This fourth part is divided into two sections:

A. Effect of Hydrostatic Pressure Impregnation on Various Woods.

B. Effect of the Three Impregnating Methods on Yellow Poplar and Black Gum.

All successful results reported using the hydrostatic pressure and the wood compression method were on PR 23 treated poplar having the conventional V shaped serrations. However, both the resin and type of serration were made unavailable before sufficient data could be accumulated.

It was therefore necessary to use another resin and a different kind of serration in carrying out this additional work. Amberlite PR 50 a liquid phenolic resin (30% solids) and V shaped serrations 1/16 inch deep and spaced 1/8 inch apart were chosen.

A. Effect of Hydrostatic Pressure Impregnation on Various Woods.

WOODS TESTED:

Black Gum - Containing both heartwood and sapwood.

Bass - Containing both heartwood and sapwood.

Aspen.

Cottonwood.

Both plain and serrated pieces of each species approximately 10 x 4 x 0.9 inches were tested.

PROCEDURE:

The wood samples were end sealed with Permatex No. 2 then immersed in the PR 60 resin under a pressure of 40 psi. for 10 minutes. Aniline blue was added to the resin (1 gm. per 2 liters) to impart a color to the wood. All samples were air dried 1 day and then cut perpendicular to the grain to observe the depth of penetration.

RESULTS:

Plain black gum showed no penetration in the heartwood and about 1/16 inch in the sapwood. The serrated sample showed uniform penetration of approximately 1/8 inch across both heartwood and sapwood.

Plain bass wood showed penetration as deep as 1/4 inch in both heartwood, and sapwood; however there was indication that the deep penetration was due partly or wholly to end diffusion indicating that the Permatex is either an inefficient end sealer for bass wood or some end grains were exposed on the faces. In the serrated sample the resin diffused into the serrations without much penetration into the sapwood and practically no penetration into the heartwood. However there was a slight amount of end penetration in the heartwood which extended the whole length of the sample.

Plain aspen had some penetration extending as deep as 1/8 inch, however most of it was unpenetrated. In the serrated sample resin diffused into the serrations but nothing more.

Plain cottonwood had very irregular penetrations of from 0 to 1/8 inch, but the serrated sample, although having a similar penetration, was much more evenly diffused.

DISCUSSION:

Though in all the species tested, the results of the serrated samples were more uniform, only the black gum emphasized the merits of serrations on heartwood and sapwood.

This wood seems to be very satisfactory for experimental work as its heart and sapwood are very distinguishable.

B. Effect of the Three Impregnating Methods on Yellow Poplar and Black Gum.

PROCEDURE:

A serrated and a plain sample of each wood containing both heartwood and sapwood were subjected to the following three tests:

1) Atmospheric immersion - 24 hours soak.

2) Hydrostatic pressure - soaked under 40 psi. pneumatic pressure for 10 minutes.

3) Wood compression - compressed in solution from 0.9 to 0.75 inch at the mid-section by flat steel bars 4 x 2 inches and then released and allowed to regain its original thickness before removing from solution.

All samples were end sealed with Permatex No. 2. After treatment they were air dried for one day, oven dried at a low temperature (110°F.) for a few hours, and then cut. A piece of each sample containing both heartwood and sapwood was then cured at 300°F. 1/2 hour, compressed from 0.9 to 0.75 inch.

DATA AND RESULTS:

Atmospheric immersion: Penetration in the sapwood of the plain poplar was non uniform but extended in parts to a depth of 3/16 of an inch. No diffusion took place in the heartwood. The serrated poplar had a more uniformly impregnated surface layer about 1/8 inch deep. Penetration into the heartwood occurred only in the serrations.

The diffusion in the plain black gum sample was negligible, and in the serrated piece diffusion occurred in the serrations but only slightly in the wood.

Hydrostatic Head: Penetration in the sapwood of the plain poplar was about 3/16 of an inch but absolutely zero in the heartwood. In the serrated sample the sapwood was completely impregnated, but the heartwood showed only diffusion into the serrations.

The diffusion in the plain black gum was irregular varying in the sapwood from 1/16 to 3/16 inch and the heartwood from 0. to 1/16 inch. The serrated sample, however, had an impregnated layer across the whole width varying from 1/16 to 1/8 inch and upon curing gave an excellent hard surface.

Wood Compression: Penetration at the area of contact in the sapwood of the plain poplar was slightly more than in the rest of the wood. However the heartwood showed no penetration. In the serrated sample, at the area of contact, impregnation of the sapwood extended to a depth of 3/32 of an inch; however the heartwood showed only diffusion in the serrations.

Slight penetration at the area of contact in the sapwood of the plain black gum was perceptible. However only diffusion into the serrations of both heartwood and sapwood occurred in the serrated sample. A serrated black gum specimen compressed to 0.5 inch instead of .75 was tried; and though penetration at the area of contact extended to a depth of 1/8 inch and tapered off towards the ends, its results were not considered successful. The reason for this was that in compressing the sample the steel bars tore the surface fibers, and it was because of these broken fiber ends that the apparent successful results were obtained.

DISCUSSION:

The results on the yellow poplar and PR 50 are erratic and not comparable to the work done using PR 23 resin. The large amount of diffusion at atmospheric pressure is more than has ever been encountered before. However the results on black gum and PR 50 substantiates all the work done using PR 23 except the wood compression. This latter method did not prove successful, but because the serrations were farther apart than in the previous work, the method cannot be disregarded without further study using the original serrations.

SUMMARY AND CONCLUSIONS

The success of atmospheric immersion is a function of the serrations on the wood surface. It has been shown that broad, shallow V shaped serrations placed close together are most favorable to surface impregnation.

The method of curing a surface impregnated product determines the final relative hardness of surface and core. If the pressure is applied quickly and instantaneously with the heat, a hard surface product with an uncompressed core will result.

Hydrostatic pressure provides an easy, quick way for surface impregnating sapwood and has proved successful on heartwood which has been serrated. A proper end sealer will prevent end diffusion. However it has been found that the presence of resin in the core does not affect the final hardness of the specimen provided the pressure is applied simultaneously with the heat during curing operations. This is true because a hardened surface is dependent upon the application of heat and pressure simultaneously. Only the surface is subjected to such conditions.

A hydrostatic pressure of 85 psi. applied for 5 minutes gives the necessary depth of penetration using Amberlite PR 23 on yellow poplar. And a pressure of 40 psi. applied for 10 minutes is suitable for Amberlite PR 50 on black gum.

Since very limited success has been made on the other two methods - atmospheric soak and wood compression - it is recommended that further study be made. Serrations having broad, shallow V shapes and located close together should be tried.

It is also advisable to accomplish the wood compression by passing the wood through rollers submerged in a rosin solution. Since this method would more closely resemble commercial plant operations the feasibility of the process could be determined more accurately.

II. GASEOUS IMPREGNATION OF WOOD

INTRODUCTION

Sapwood is the clearest and finest part of a tree. However because of its low resistance to fungi its uses are limited.

To increase its rot resistance it can be treated with liquid fungicides, but this necessitates drying and control of warping. It can also be treated with synthetic resins, such as the phenolic aldehyde type, which also increase the stability of the wood. However this requires not only drying but curing and is also expensive.

The object of this work has been to make preliminary investigations on an inexpensive gaseous impregnation method by which the fungicidal properties of sapwood could be improved. If the gas could be made to react with the constituents in the wood to form a non leachable toxic substance, the time and control of drying, which is necessary for liquid treatments, would be eliminated.

HISTORICAL

Much work has been done to improve the properties of wood. The United States Department of Agriculture, Forest Products Laboratory, has published many bulletins and papers on this subject. However an extensive library survey revealed that only liquid impregnation using various solutions and liquors has been investigated to any great extent. In fact only one paper could be found on the gaseous treatment. This was by Stamm and Hansen (9) of the Forest Products Laboratory who investigated the treatment of woods under high temperature and pressure with various reducing and oxidizing gases. They found that when oxygen, hydrogen, or air was heated with wood up to 165° - 205° C., the shrinking and swelling properties of the wood were reduced.

THEORETICAL

Wood (after debarking) is composed of sapwood and heartwood. Sapwood is that portion which still contains some living tissues and participates in the vital activities of the tree. As the tree continues to grow and increase in girth, all the living cells in some of the wood towards the inside die. This core of dead tissues in the stem is called heartwood.

As sapwood is transformed into heartwood, various organic compounds are formed. Substances of this nature infiltrate into cell walls and if copious in amount may even accumulate in cell cavities generally in the form of amorphous deposits (causing the color to darken). Because of this higher infiltration content, heartwood has greater density, greater rot resistance, and lesser permeability.

The theory on which liquid treatments are based is similar to that which nature uses in changing sapwood into heartwood, i.e., the impregnation of the cell walls and cavities with a substance which is toxic to fungi or which will react with the wood to become toxic. However for gaseous treatment the substance is not in substantial quantities to produce any effect unless it undergoes a chemical reaction with the constituents in the wood.

Since cellulose, the major constituent in wood, is very susceptible to decay, a reaction which would change its characteristics to a more toxic material would greatly increase the resistance of the material as a whole. If this could not be obtained, it is possible that a lignin compound could be produced.

EXPERIMENTAL

APPARATUS:

The test chamber was of steel construction, 6 inches inside diameter, 24.5 inches high, externally heated by a gas burner under a two inch base projection. This gas burner permitted reasonably direct heating of any substance to be gasified without direct contact of either heat or gas preferentially to one section of the treated specimen.

A Fred Carver hand operated press with manually controlled electrically heated platens was used to cure the samples.

MATERIALS:

Yellow Poplar - Three sizes were used, 8 inches long by 3 inches wide, and 0.75, 0.35, and 0.05 inch thick respectively.

Paraformaldehyde - Formaldehyde source.

Ammonium Carbonate - Ammonia and carbon dioxide source.

Dry Ice.

PROCEDURE:

The gas generating substance was placed in the bottom of the base projection, and the three sizes of samples stacked teepee fashion over so that fumes produced therein would act on all specimens similarly. The cylinder was then closed and heat was applied for a definite length of time after which the vessel was cooled, pressure released, and samples removed.

DATA AND RESULTS:

In the first tests with formaldehyde as the impregnating gas, 7 grams of paraformaldehyde per 100 grams of wood were placed in a test tube in the heating space; the cylinder was sealed and the pressure was slowly raised to 28 psi. by heating the paraformaldehyde. A temperature of about 150°F. was reached and maintained for two hours. After the sample was cooled, the pressure was released and the wood removed. Apparently condensed moisture had caused a stain on a portion of the wood, but otherwise there was no visible evidence of change.

The following two methods were used in an attempt to determine chemically the amount of formaldehyde absorbed or reacted:

1) The standard Hydrogen Peroxide Method for formaldehyde solutions. The solution used in testing was prepared by soaking the treated wood in a saturated potassium chlorate solution acidified with nitric acid.

2) The Potassium Dichromate Procedure. In this procedure approximately 5 grams of wood shavings are soaked in a solution of 50 ml. water, 5 ml. 3% potassium dichromate solution, and 1 ml. approximately 12 N. hydrochloric acid. This solution is then titrated using 0.1 N. sodium hydroxide with phenolphthalein indicator.

Both methods proved useless as the results were too erratic.

Further impregnation attempts were made using formaldehyde in the presence of nitric acid (3 ml. per 20 gm. of formaldehyde), and with nitric acid alone. A sample of wood was also run through the same treatment without an impregnant for control purposes. In these, tests weights were taken on the 0.75 inch thick sample, and with moisture content obtained prior and subsequent to impregnation, an attempt was made to weigh any gain.

It will be noted in Table II that there was an appreciable loss in weight of the wood when heated in the cylinder without an impregnant and that a loss was also found for the other two cases. It is noted, however, that the loss in the former case was greater than the latter although to only a small degree. This might indicate some absorption, but it cannot be considered significant without further proof.

Similar samples of wood were treated with a mixture of ammonia and carbon dioxide gas generated from ammonium carbonate. The procedure was similar to the formaldehyde treatment, but a pressure of 32 psi. (gauge) was reached. After it was cooled, the wood maintained a distinct ammoniacal odor. A segment was cut for use in compression tests, and the remainder was recharged into the container for treatment with carbon dioxide from dry ice. A pressure of 50 psi. (gauge) was realized but gradually decreased even with heating because a leak developed in the cylinder. The finished samples had no ammoniacal odor until cut in two. An odor was then detected from the center sections of the wood.

A series of tests was run on the formaldehyde impregnated wood and on the untreated wood to determine the nature of stabilization obtained by pressure and temperature. It was found that 385°F. ± 10°F. and 1000 psi. were the most satisfactory conditions, and subsequent

TABLE II. EFFECT OF GASEOUS IMPREGNATION ON YELLOW POPLAR.

Treatment	Formaldehyde with Nitric Acid	Nitric Acid	Control
Initial Weight	158.1 gm.	188.2 gm.	143.1 gm.
Moisture Content (%)	8.79	7.06	3.78
Dry Weight	144.2 gm.	174.9 gm.	137.9 gm.
*Final Weight	150.9 gm.	174.6 gm.	136.0 gm.
*Moisture Content (%)	5.94	3.41	2.75
*Dry Weight	142.0 gm.	168.7 gm.	132.0 gm.
Weight Gained (%)	-1.5	-3.6	-4.3

* Values taken after treatment.

tests were all made on these settings. With the formaldehyde treated wood, blisters and explosions occurred. This indicated the presence of unreacted or unstable products in the mass and were probably not caused by moisture content as no such occurrence was observed on wetter plain wood. The compression of the woods produced a smooth, dark brown surface, considerably harder than the original and of an average thickness of 0.32 inch from an original 0.75 inch. Rockwell "R" hardnesses run on the specimens were erratic and varied with the heartwood-sapwood structure beyond reasonable limits.

Samples of the treated and compressed wood were immersed in water for a week in an attempt to determine relative stability of the products.

The results tabulated in Table III show that in all cases the treated samples were more stable than the untreated wood. Although the formaldehyde-nitric acid treated specimen appeared best, the degree of increased dimensional stability was slight. All specimens showed a considerable fungus or mold growth on the wood and on the surface of the individual soaking baths. The species of the fungus or mold was not determined.

SUMMARY:

This preliminary investigation indicates that formaldehyde shows definite tendency towards action if catalized. However, the data are too meager for any positive conclusions.

It is recommended that a more definite means of testing treated samples be used such as an exposure test to wood destroying organisms.

TABLE III. - EFFECT OF WATER IMMERSION (1 WEEK) ON GASEOUS TREATED YELLOW POPLAR.

Treatment	Formaldehyde	Formaldehyde with Nitric Acid	Ammonium Carbonate	Ammonium Carbonate and Dry Ice	Control
Original Thickness	0.75 inch	0.76 inch	0.78 inch	0.76 inch	0.75 inch
Thickness After Compression	0.30 "	0.32 "	0.34 "	0.35 "	0.30 "
Thickness After Week Immersion	0.57 "	0.48 "	0.51 "	0.54 "	0.71 "

III. INVESTIGATIONS

ON SUBMARINE DECKING

INTRODUCTION

One of the most important uses of wood on American submarines is in construction of the superficial decking. Such a construction is subjected to severe hydrostatic pressure impacts caused by the descending or surfacing of the submarine, and is also subjected to decay encountered in sea water.

Therefore to be a suitable material the wood must have all the following properties:

a) Resistance to pressure impact

b) Resistance to decay

c) Dimensional stability

d) Wear resistance

e) Non-slipping surface especially when wet

The need for the first two properties has been mentioned. Dimensional stability insures tight fastenings, and wear resistance prolongs the working life of the deck. Since the deck will be used when wet, a non-slipping surface is necessary for the safety of the crew.

Teak wood has been found to be completely satisfactory, and no substitutes have ever been used. Because of the increased output of submarines in the past few years, however, the supply of teak has decreased to a critical point.

Impelled by this situation it has been the aim of this research to find a substitute which will have properties closely resembling teak wood.

HISTORICAL

In the past decade, because of the work of the Forest Products Laboratory, wood has begun to climb back to the important position it held before the perfection of metals and plastics. During this period many papers have been published on the improvement of the two main limitations of wood, namely, dimensional stability and decay resistance.

Stamm (1) discussed the effect of inorganic salts upon the swelling and shrinking of wood; however this method was not satisfactory, for the salts tended to leach out.

A more successful attempt to minimize shrinking and swelling of wood was made by Stamm and Hansen (2) by replacing the water with non-volatile materials. With the use of an intermediate solvent the water was displaced and such non-volatile materials as melted waxes, oils, and resins were diffused into the cell walls of the wood. Efficiencies as high as 80 per cent based on plain wood controls were realized.

In the cases mentioned, high efficiencies were achieved because of a very great decrease in the rate of absorption rather than a change in equilibrium moisture content. Stamm and Seborg (3), however, changed this equilibrium by forming synthetic resins within the fine capillary structure of the wood.

Improving dimensional stability by decreasing the water absorption also improved the rot resistance since moist wood is very susceptible to decay.

THEORETICAL

Wood is hygroscopic and, like all other fibrous materials, possesses the property of swelling and shrinking with change in humidity. Water is held in the wood in two ways: imbibed water in the walls of the wood cells, and free water in the cell cavities. When wood begins to dry, the free water leaves first followed by the imbibed water. The fiber saturation point is that condition when all the free water has departed but all imbibed water remains. Only below this point does wood shrink or swell upon change in moisture.

The use of a water repellant material such as wax or oil increases the dimensional stability of the wood since it forms a water resisting film on the cell walls. The use of a synthetic resin as an impregnating agent has been found to give better dimensional stability. In this method a low polymerized resin is diffused into the capillary structure of the wood and under increased temperature and pressure made to bind the fine wood structure into an infusible synthetic resin. Thus the hygroscopicity and corresponding shrinkage and swelling are decreased permanently by a chemical reaction.

EXPERIMENTAL

A. PRELIMINARY TESTS

To find a solution to this problem, some information of the type of wood failure encountered under actual conditions had to be acquired. Consequently a number of different woods were subjected to simulated sea conditions and their reactions noted.

APPARATUS:

A cylindrical pressure tank (8 inches inside diameter, 3 feet high) filled with 4 per cent salt water and having two valve connections one to an air compressor and one to the atmosphere were used as a testing chamber.

WOODS TESTED:

Mahogany

Maple

Yellow Pine

White Oak

Douglas Fir

Teak

PROCEDURE:

Submarines submerge to a maximum of 200 feet which corresponds to 88 psi. gauge, and their ascent is rapid being approximately 100 feet per minute. To test the wood species efficiently, it was necessary to simulate these conditions.

Samples were immersed in the salt water filled pressure cylinder and pressure (85 psi. gauge) applied for 17 hours followed by immediate release and 7 hours air drying at atmospheric pressure. The samples were exposed to 13 such cycles.

DATA AND RESULTS:

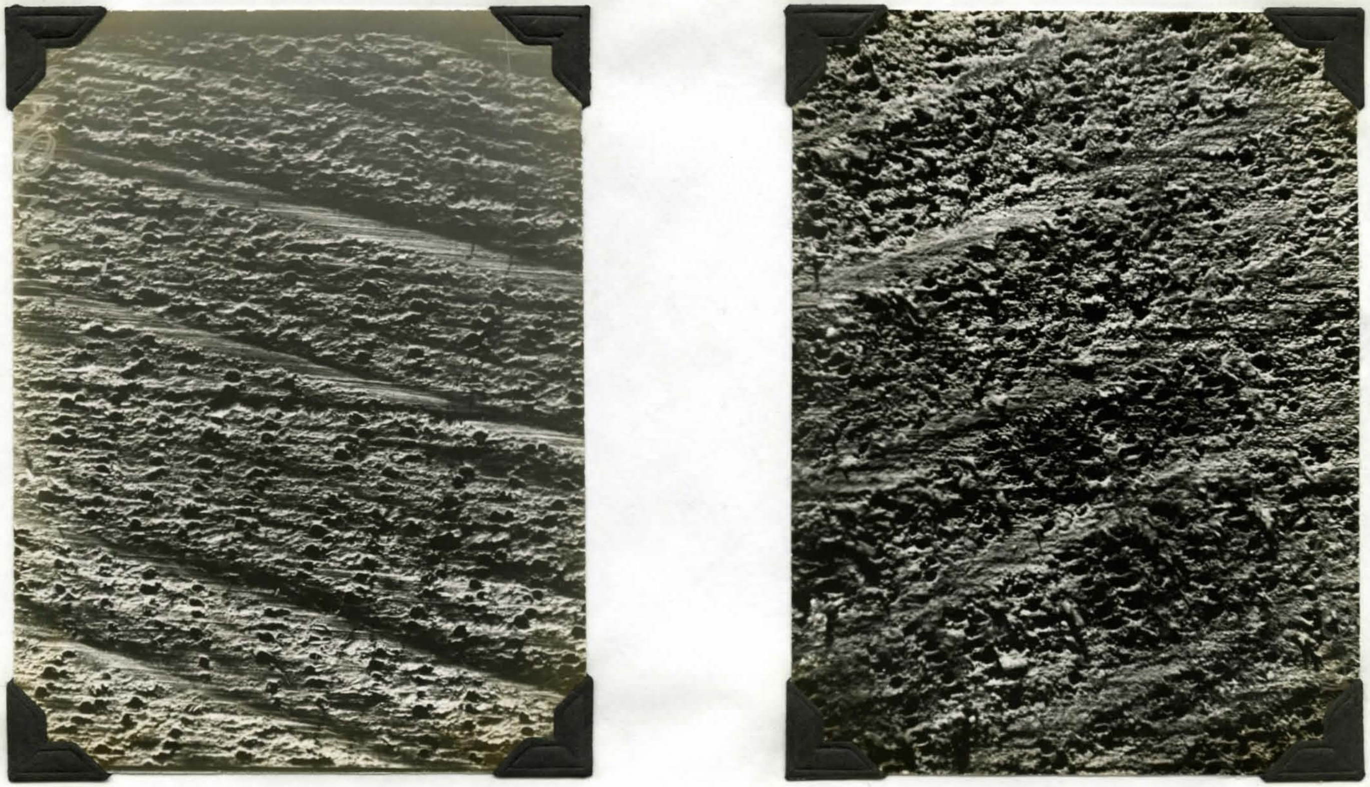
In the ring porous oak, pine, and teak, slight enlargement of the spring wood pores was perceptible. The photomicrographs of Figures 6, 7, and 8, showing the woods prior to cycling and after being cycled 9 times, illustrate this defect. Surface cracking of the medullary rays took place in the white oak (Figure 6b) and slight warping occurred in the maple after the first cycle, but did not increase. All the other untreated woods had no change except in weight and dimensions which are recorded in Table IV (also see Figures 9, 10, and 11). Inspection of the D.M.U. impregnated specimen indicated that it had undergone slight checking (Figure 12) and weight and dimension changes, but the compregnated specimens were severely checked, and delamination of the spring and summer woods had taken place (Figures 13 and 14).

DISCUSSION:

The results of the pressure cycles indicate that teak, on the basis of its comparatively small weight and dimension changes, is the most suitable material. Mahogany, though very porous to the salt water, showed very good dimensional stability and no structural defects. The yellow pine, douglas fir, maple, and impregnated pine do not compare favorably with the teak and mahogany because of higher dimensional increases. The structural failure of the white oak and the compregnated samples make them unsuited for the particular use.

TABLE IV. EFFECT OF SALT WATER PRESSURE CYCLES ON VARIOUS WOODS.

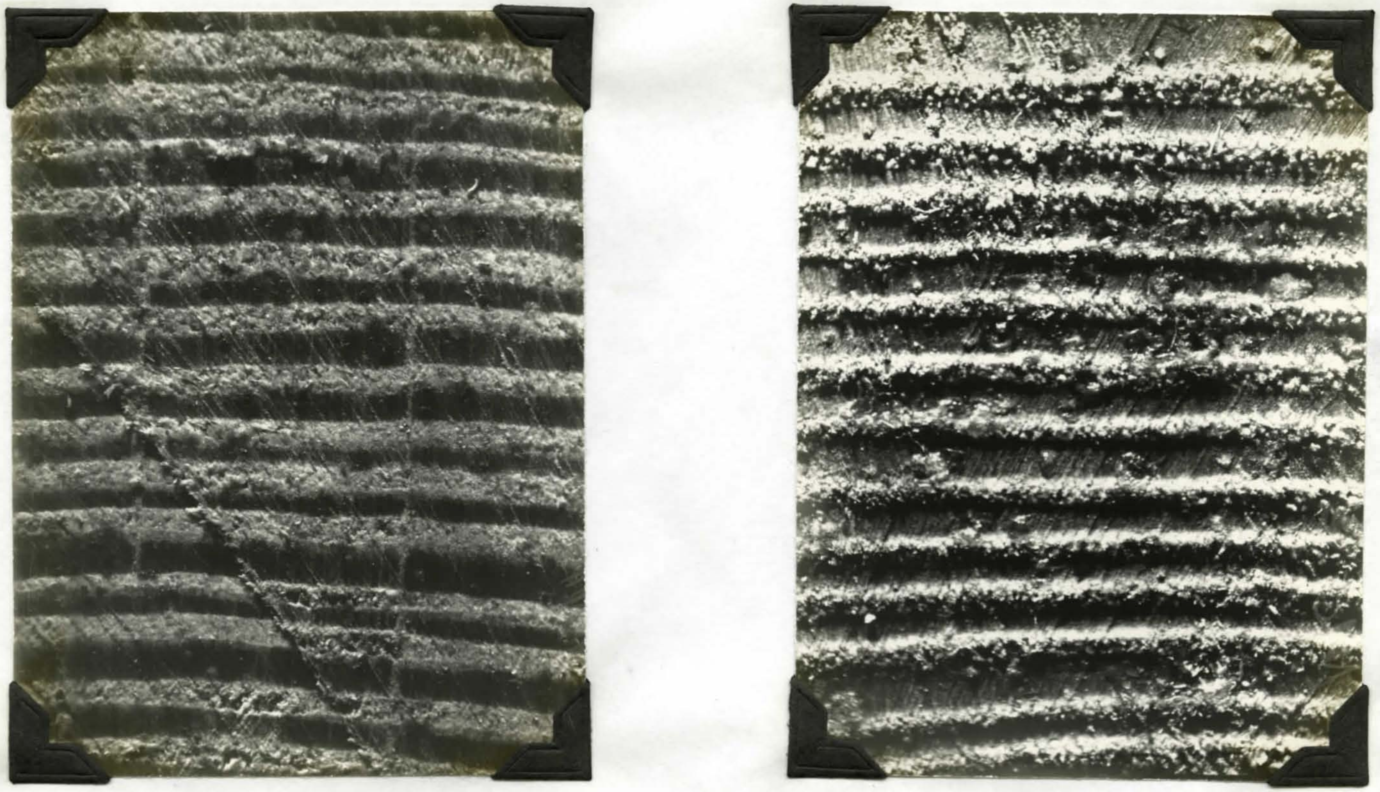
Specimen	Weight (Gm.)	Cross Section Dimensions (In.)	Weight (Gm.)	Weight Gain (%)	Cross Section Dimensions (In.)	Area Gain (%)
Mahogany	101.8	1.90 x 1.45	229.0	125.0	1.99 x 1.45	8.0
Maple	147.8	1.85 x 1.61	264.0	78.8	1.95 x 1.72	12.7
Yellow Pine	138.7	1.85 x 1.60	213.4	65.8	1.96 x 1.59	11.9
White Oak	127.8	2.21 x 0.94	194.0	52.4	2.37 x 0.98	11.5
Douglas Fir	54.2	1.95 x 0.75	120.3	122.0	2.16 x 0.79	15.8
Teak	68.5	1.95 x 0.76	108.0	57.6	1.99 x 0.79	7.4
D.M.U. Impregnated Yellow Pine	——	2.00 x 0.75	——	——	2.12 x 0.78	13.0
D.M.U. Compregnated Yellow Pine (25% Compressed)	——	2.00 x 0.70	——	——	2.20 x 0.72	11.3
D.M.U. Compregnated Yellow Pine (50% Compressed)	——	2.00 x 0.45	——	——	2.05 x 0.63	20.7



a) Original.

b) After 9 Salt Water Pressure Cycles.

Fig. 6. Cross Section of White Oak (Mag. 5X).



a) Original

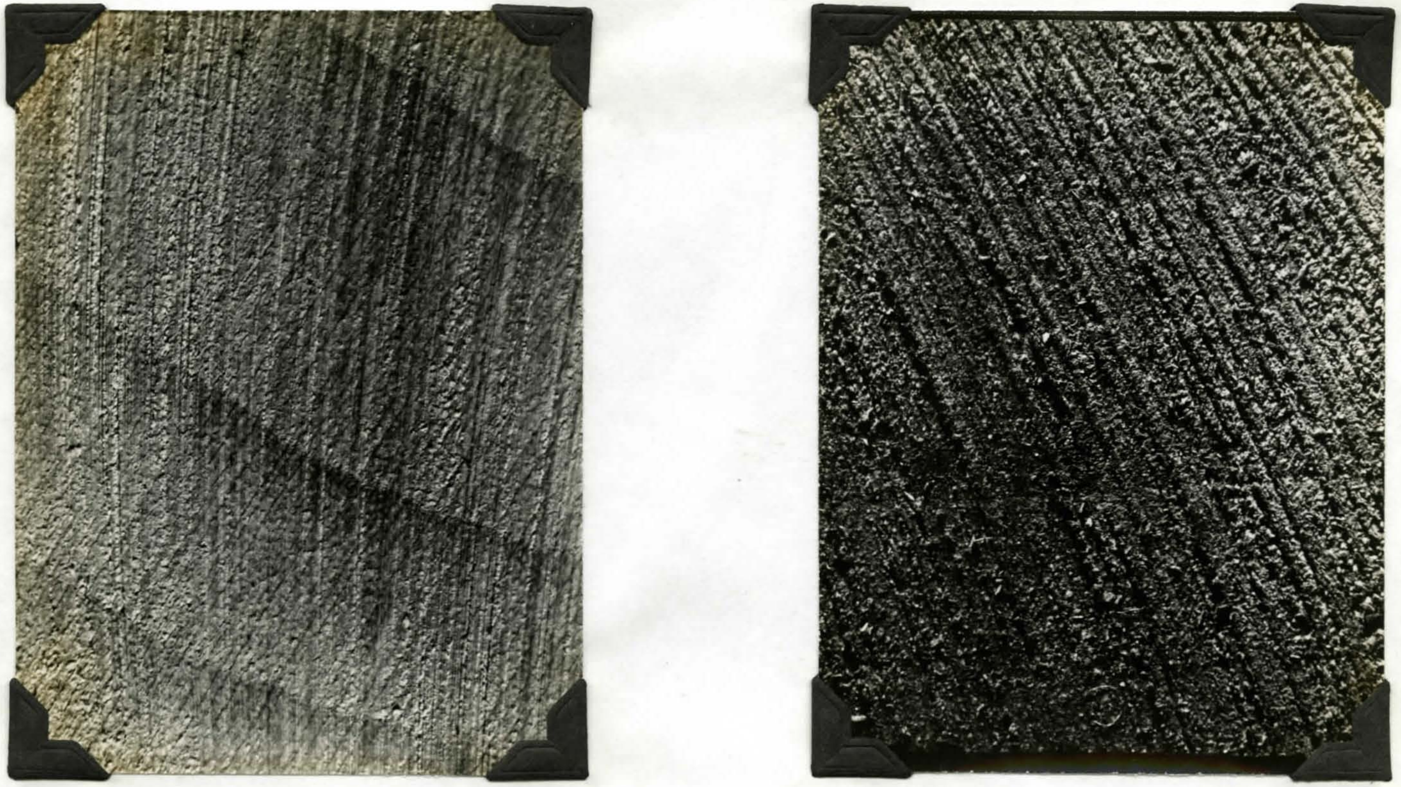
b) After 9 Salt Water Pressure Cycles.

Fig. 7. Cross Section of Yellow Pine (Mag. 5X).

a) Original

b) After 9 Salt Water Pressure Cycles.

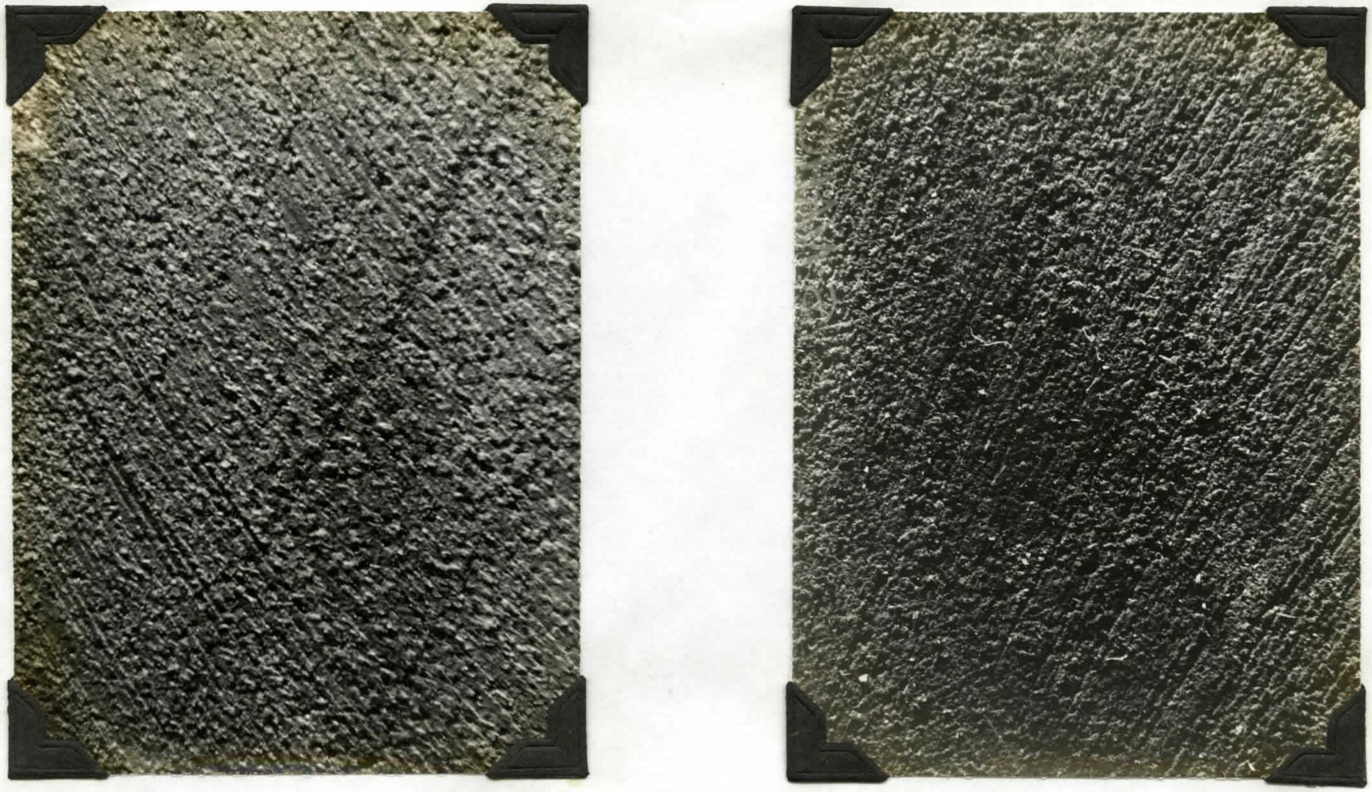
Fig. 8. Cross Section of Teak (Mag. 5X).



a) Original

b) After 9 Salt Water Pressure Cycles.

Fig. 9. Cross Section of Maple (Mag. 5X).



a) Original.

b) After 9 Salt Water Pressure Cycles.

Fig. 10. Cross Section of Mahogany (Mag. 5X).

a) Original.

b) After 9 Salt Water Pressure Cycles.

Fig. 11. Cross Section of Douglas Fir (Mag. 5X).

Fig. 12. Cross Section of D.M.U. Impregnated Yellow Pine After 9 Salt Water Pressure Cycles (Mag. 5X).

Fig. 13. Cross Section of D.M.U. Compregnated Yellow Pine (25% Compressed) After 9 Salt Water Pressure Cycles (Mag. 5 X).

Fig. 14. Cross Section of D.M.U. Compregnated Yellow Pine (50% Compressed) After 9 Salt Water Pressure Cycles (Mag. 5 X).

B. EXTENDED TESTS

From the preliminary tests it was shown that of the woods tested, only mahogany had dimensional stability comparable to teak. However, mahogany had very low surface wear resistance and very high water absorbency. Therefore to become a suitable teak wood substitute these undesirable characteristics had to be eliminated or lessened. An attempt to increase its surface wear resistance without decreasing dimensional stability was made by laminating hard maple veneers to mahogany cores. These samples were then treated with various impregnating agents to decrease their water absorbency, and then they were subjected to the pressure cycles. Mahogany and birch samples were also treated and subjected to this cycle.

APPARATUS:

A stainless steel bucket and a steel pressure cylinder (6 inches inside diameter, 24.5 inches high), externally heated by a gas burner under a 2 inch base projection, were used for impregnation. Tests were carried out in the pressure cylinder described in the preliminary tests.

IMPREGNATING AGENTS USED:

Copper Naphthenate - 16% solids (2:1 by vol. with mineral spirits)
Rez Sealer - (1:2 by vol. with mineral spirits)
Boiled Linseed Oil - acid refined (1:2 by vol. with turpentine)
Paraffin Oil
Tung Oil - raw (1:2 by vol. with mineral spirits)
Oleic Acid - (1:2 by vol. with turpentine)

WOODS TREATED:

Mahogany

Birch

Laminate - mahogany core (1 inch thick) with maple faces
(1/10 inch thick)

PROCEDURE:

Wood samples (approximately 4 x 3 x 1 inch) were placed in the bottom of the stainless steel bucket and immersed in the impregnating agent. The bucket was then lowered into the impregnating cylinder and held under a pressure of 85 psi. (gauge) for 5 hours with heat being applied for one of those hours. Then the pressure was slowly decreased to atmospheric in 17 hours. After being air dried for 2 days the specimens were subjected to the salt water pressure cycles, i.e., immersed in salt water under 85 psi. (gauge) for 17 hours followed by immediate release and 7 hours air drying at atmospheric pressure. Each sample was subjected to these cycles until no further weight and dimension increase could be detected. Controls of the three woods were also run.

DATA AND RESULTS:

Controls: The untreated mahogany, birch, and laminate (composed mainly of mahogany) showed a greater affinity for salt water than teak as can be seen by Figure 15. However dimensional stability of the mahogany and laminate compared favorably with teak (Figure 25). This was in close agreement with the results of the preliminary tests.

Table V shows the percentage pickup of the various woods upon impregnation. The pickup of the tung oil samples was considerably less than the others.

Appearance: All treated birch samples surface checked upon cycling. However this did not occur in the birch control or any of the other samples. A white waxy substance extruded from the oleic acid treated woods after each cycle. The copper naphthenate also exuded after each cycle causing the surface to be sticky. The rest of the treated samples were slightly oily resembling teak wood.

Weight Changes: The impregnating treatment greatly reduced the hygroscopicity of the woods and in all cases lowered the maximum values below that of teak. Figures 16, 17, and 18, based on the weight of wood just prior to the first cycle, illustrate this reduction. The tung and linseed oil appeared to give the more consistantly good results in decreasing this hygroscopicity. Comparison of the water absorbing properties of the individual woods treated with the same agent (Figures 19, 20, 21, 22, 23, and 24) shows no appreciable difference among the three.

Dimensional Changes: Discounting the treated birch samples because of their checks, all the impregnating agents but the oleic acid imparted improved dimensional stability to the woods. The bar graph of Figure 25 compares cross sectional area increases of the various treated samples to those of their controls. Mahogany, inherently a stable wood, showed the best stability in all but the paraffin oil treated. Dimensional stability of the control laminate, though not so good as mahogany,

TABLE V. - PER CENT WEIGHT INCREASE UPON IMPREGNATION.*

Impregnating Agent	Mahogany	Birch	Laminate
Copper Naphthenate	36.7	38.9	—
Rez Sealer	25.2	33.0	—
Linseed Oil	41.1	42.0	34.0
Paraffin Oil	56.2	58.8	31.5
Tung Oil	9.0	19.0	9.5
Oleic Acid	49.0	47.0	45.0

* Weight Increase Based on Original Weight Prior to Impregnation.

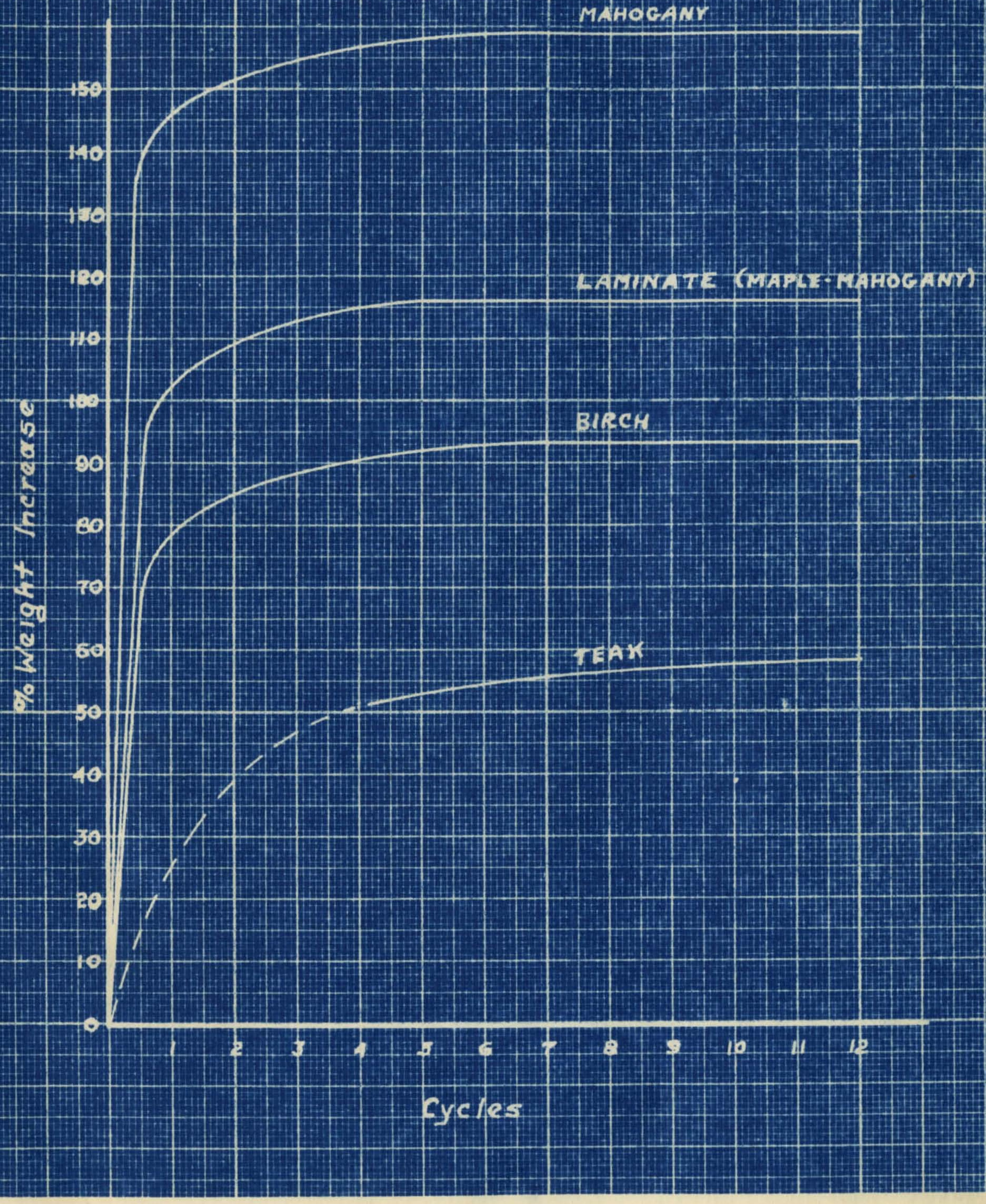


Fig. 15   Weight Increase of Wood During Pressure Cycles in Salt Water.

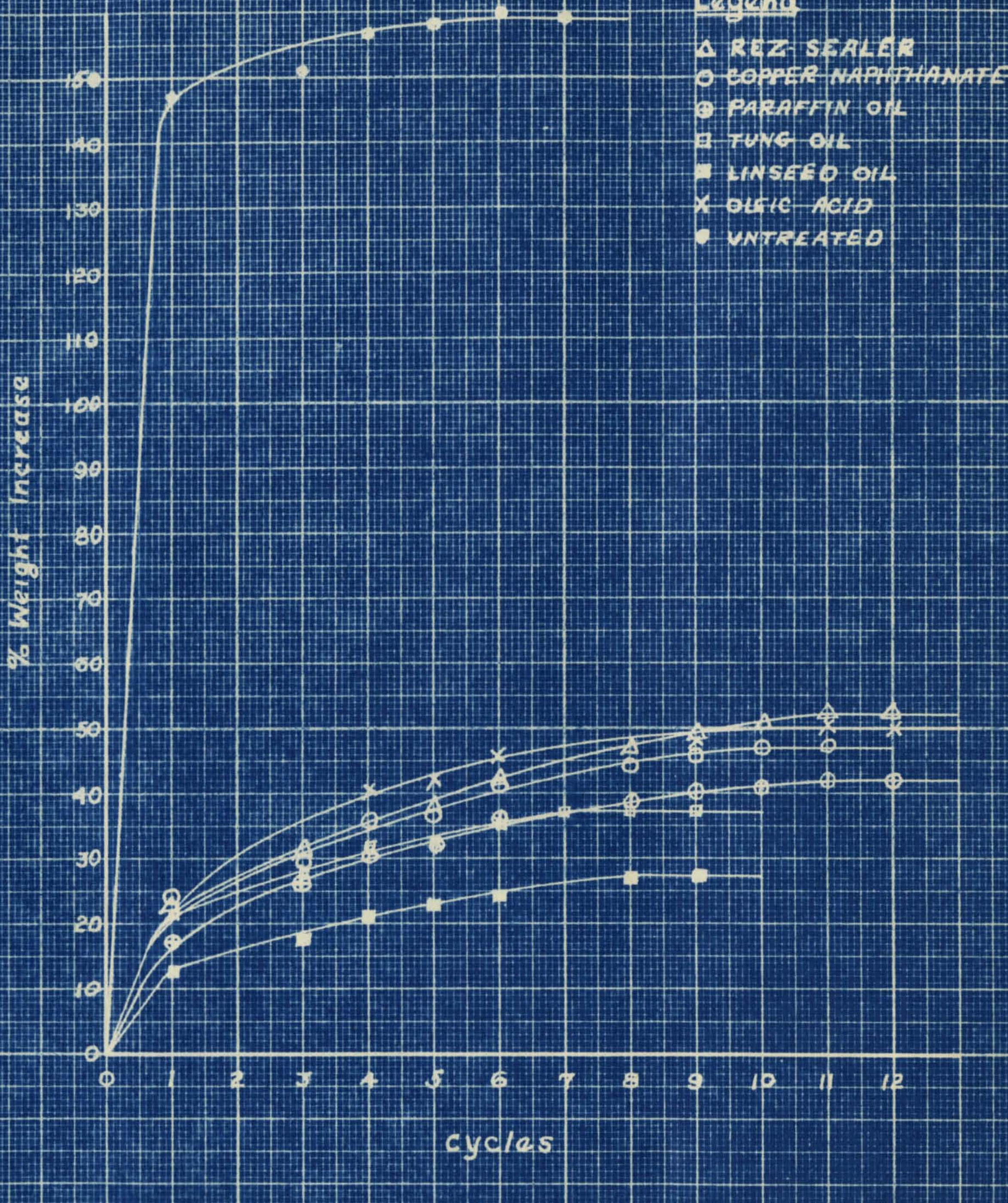


Fig. 16 Weight Increase of Treated Mahogany During Pressure Cycles in Salt Water.

compared favorably with teak, and all its treated samples showed still further stability. The tung, linseed, and paraffin oils and the Res Sealer showed the best results in reducing dimensional changes. The copper naphthenate, though increasing the stability of mahogany, gave the surface a very sticky coating making it undesirable.

A rubber coated wood sample was also subjected to the pressure cycles. However, after 6 cycles it developed surface blisters indicating the rupture of the wood-rubber bond.

SUMMARY:

The oleic acid and the copper naphthenate proved unsatisfactory as impregnating agents since they had a tendency to leach out upon subjection to the pressure cycles.

However, all the other impregnating agents tested, particularly the tung and linseed oils, imparted such stability of dimensional and weight changes to the mahogany and laminate that in every case these two woods proved equal or superior to teak wood.

Because of structural failure, both the birch wood and the rubber coated wood proved unsatisfactory for this particular use.

It is recommended that the mahogany-maple laminate be tried as a teak wood substitute on submarine decking. This product, when treated, had better dimensional stability and water repellency than teak, and unlike plain mahogany it has a hard wear resistant surface.

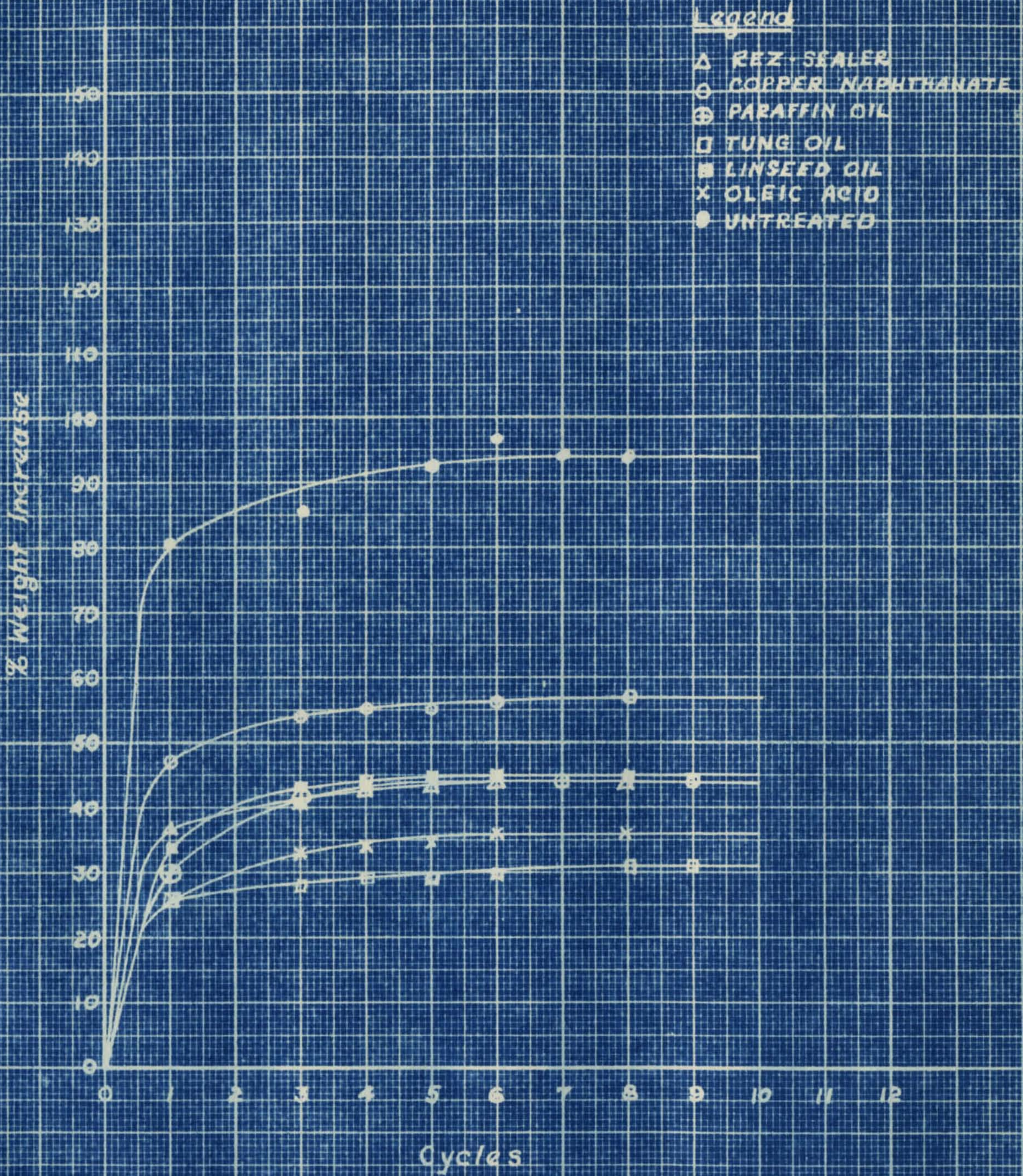


Fig. 17 Weight Increase of Treated Birch During Pressure Cycles in Salt Water.

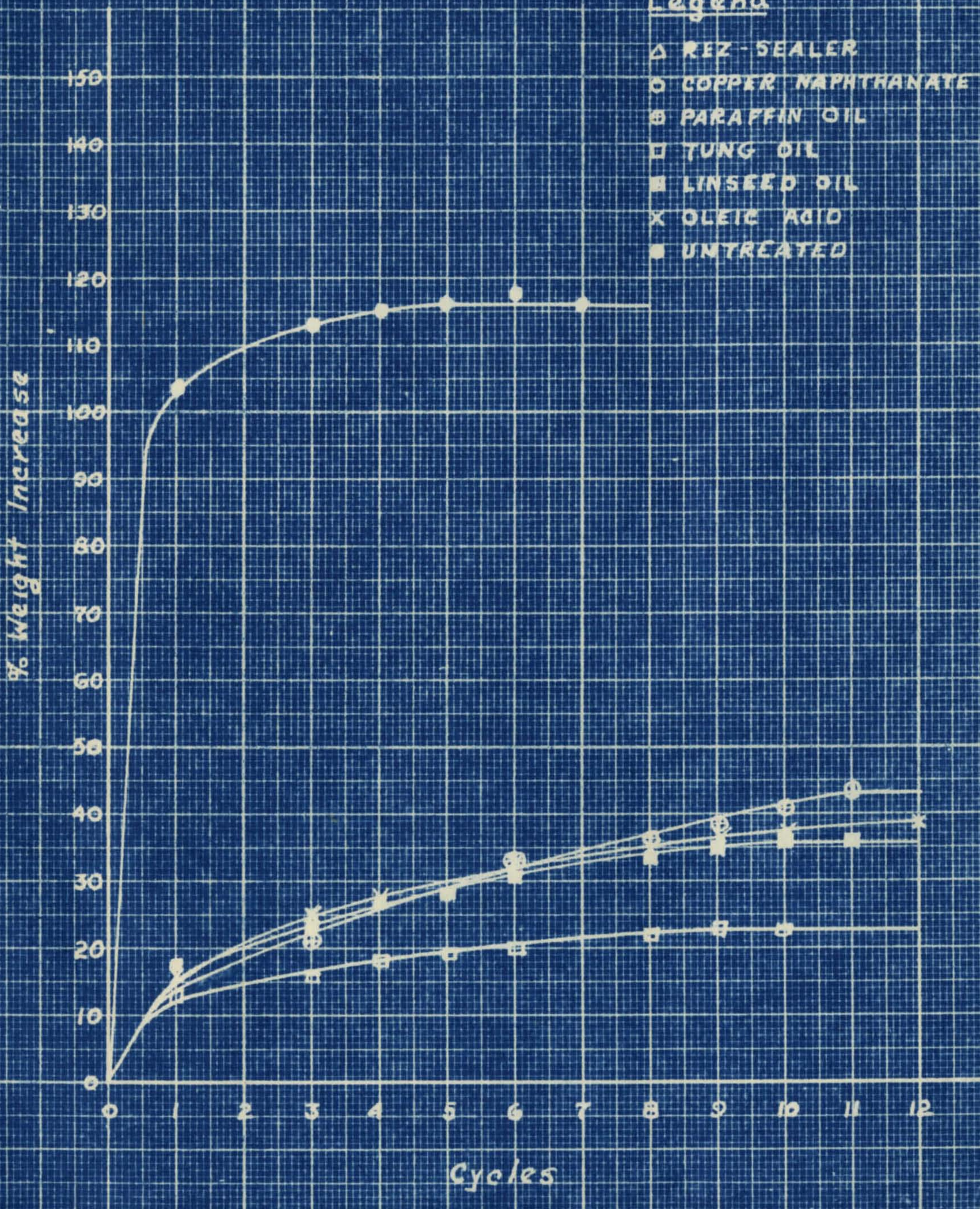


Fig. 18 Weight Increase of Treated Laminate (Maple Faces, Mahogany Core) During Pressure Cycles in Salt Water.

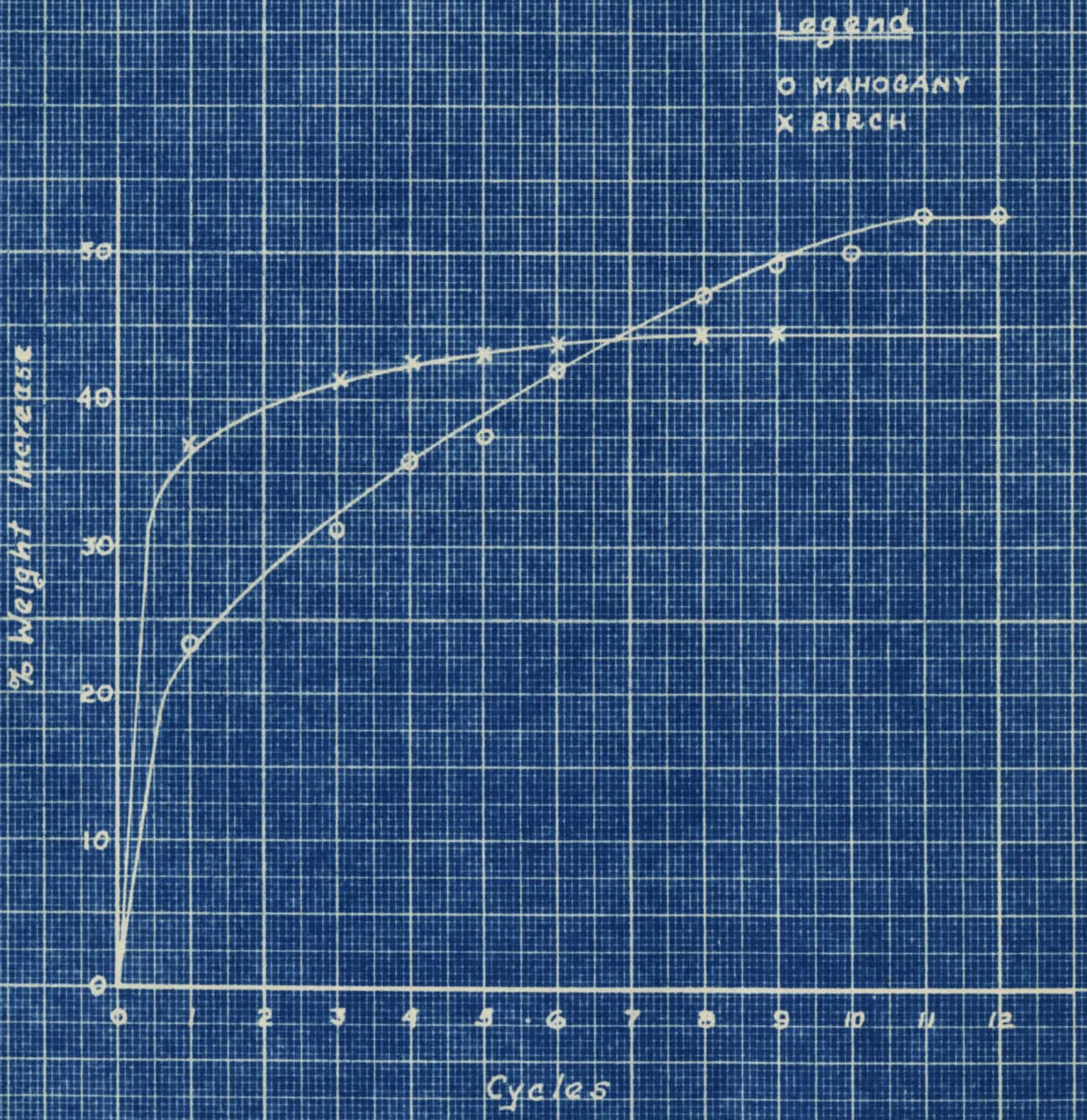


Fig. 19 Effect of Species on Weight Increase of Rez Sealer Impregnated Woods.

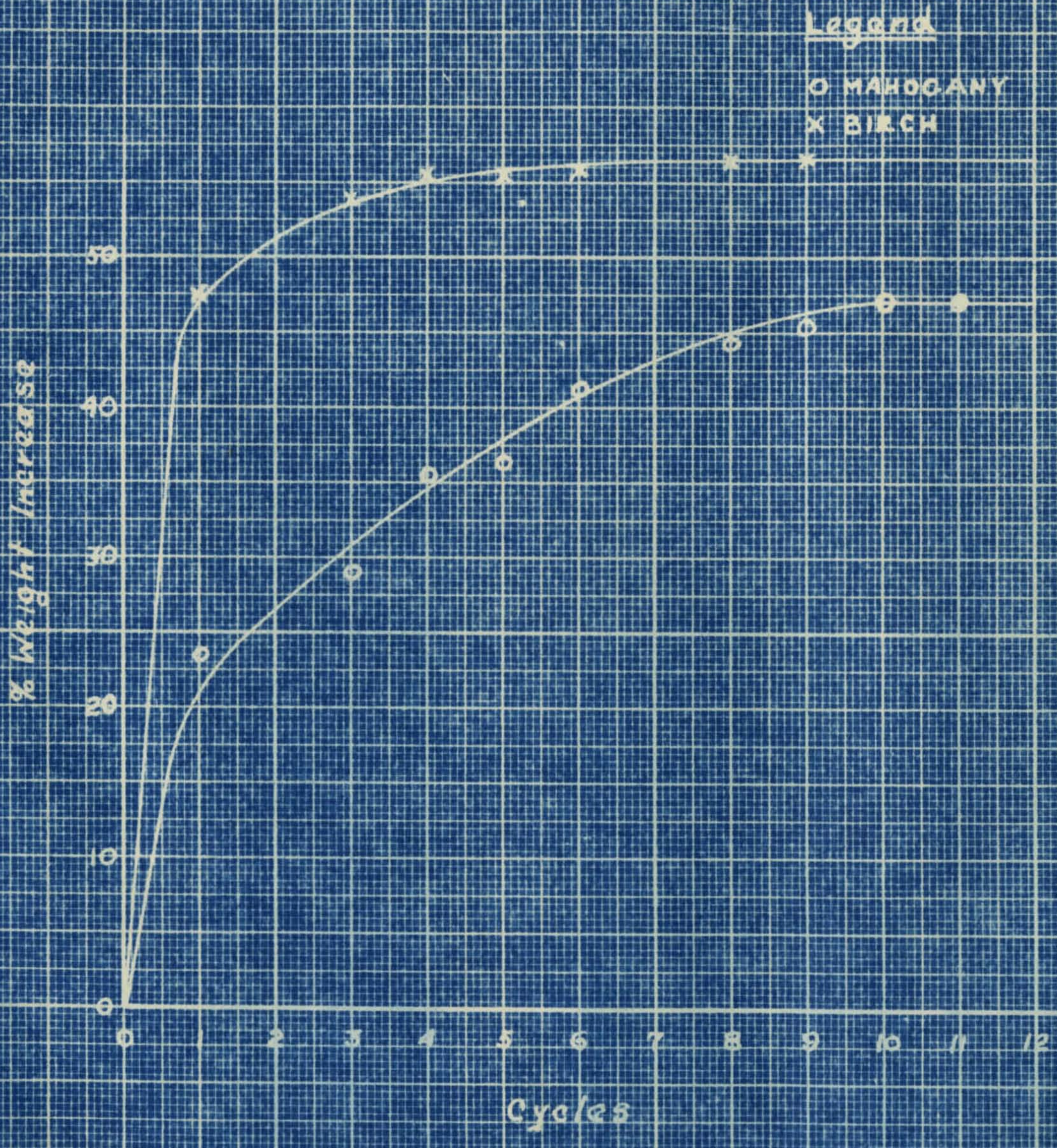


Fig. 20 Effect of Species on Weight Increase of Copper Naphthenate Impregnated Woods.

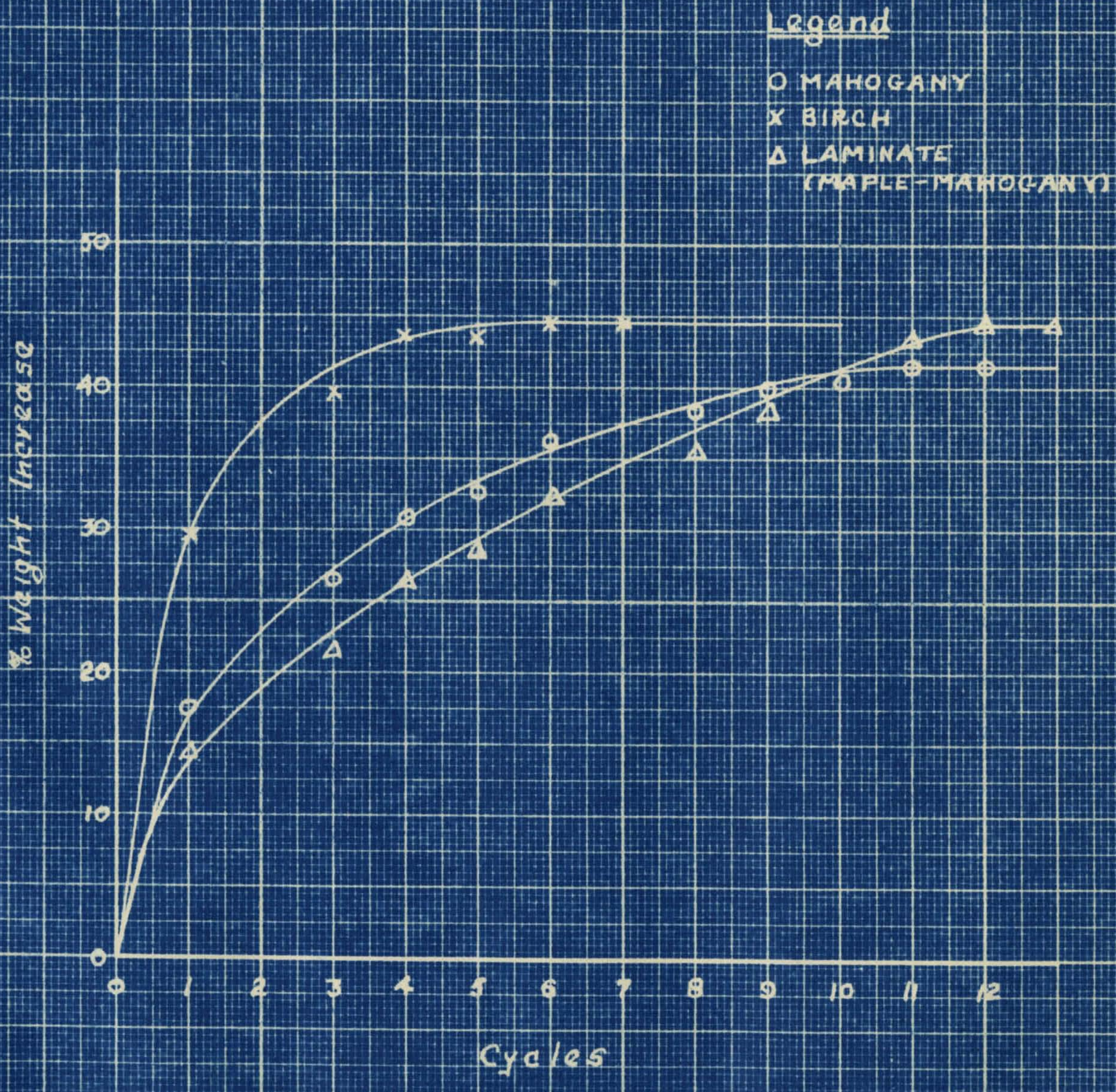


Fig. 21 Effect of Species on Weight Increase of Paraffin Oil Impregnated Woods.

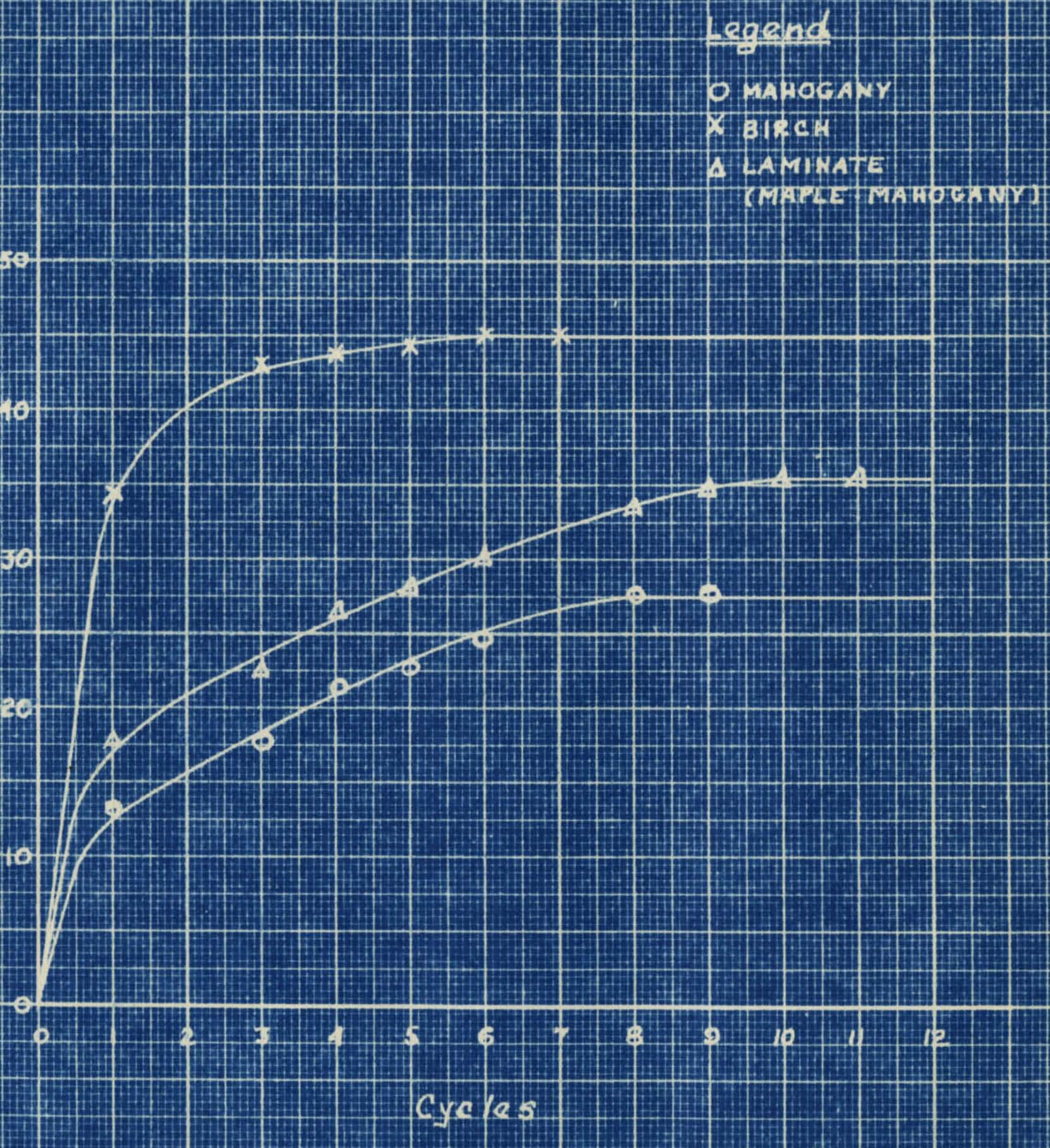


Fig. 22 Effect of Species on Weight Increase of Linseed Oil Impregnated Woods.

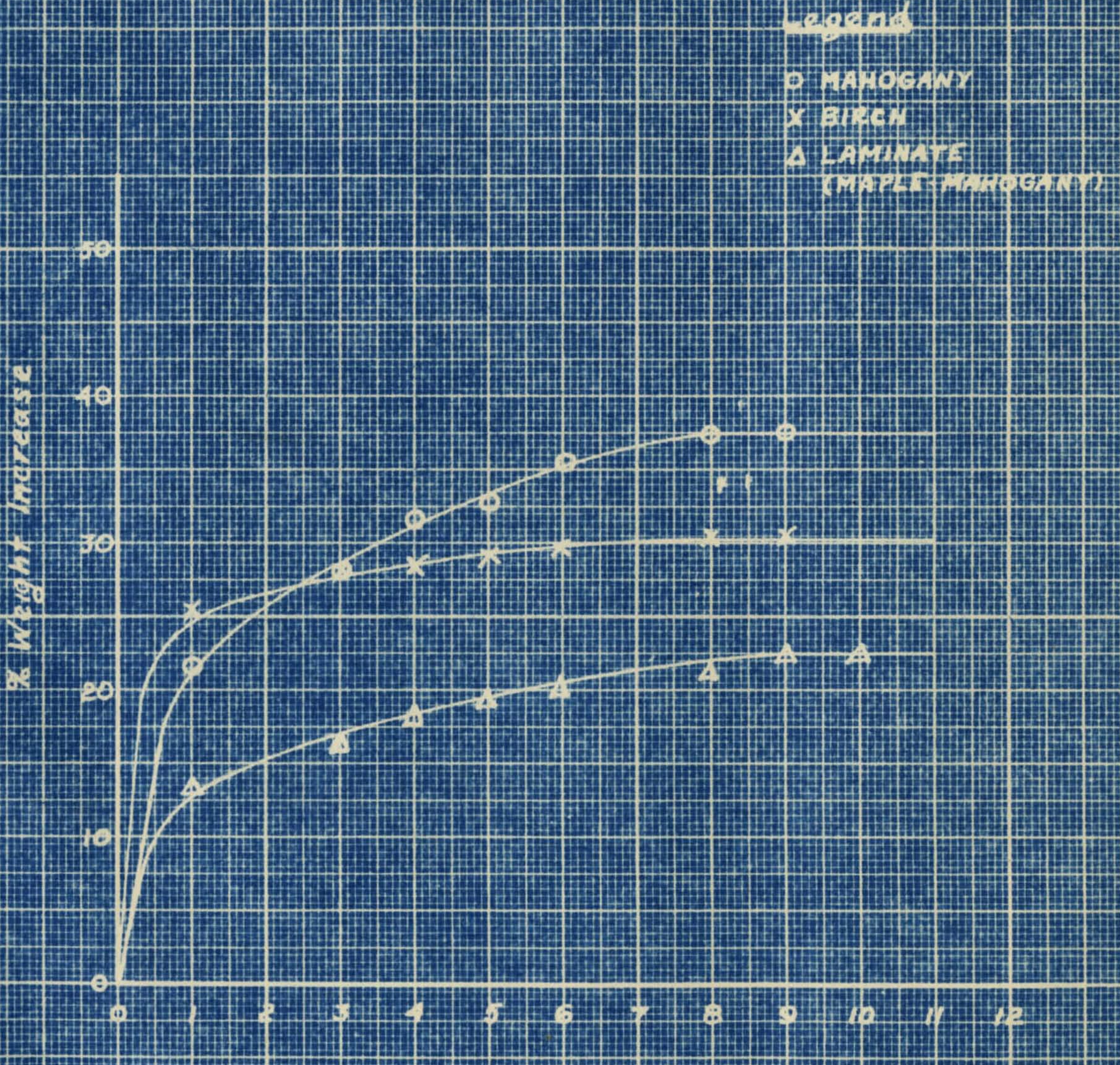


Fig. 23 Effect of Species on Weight Increase of Tung Oil Impregnated Woods.

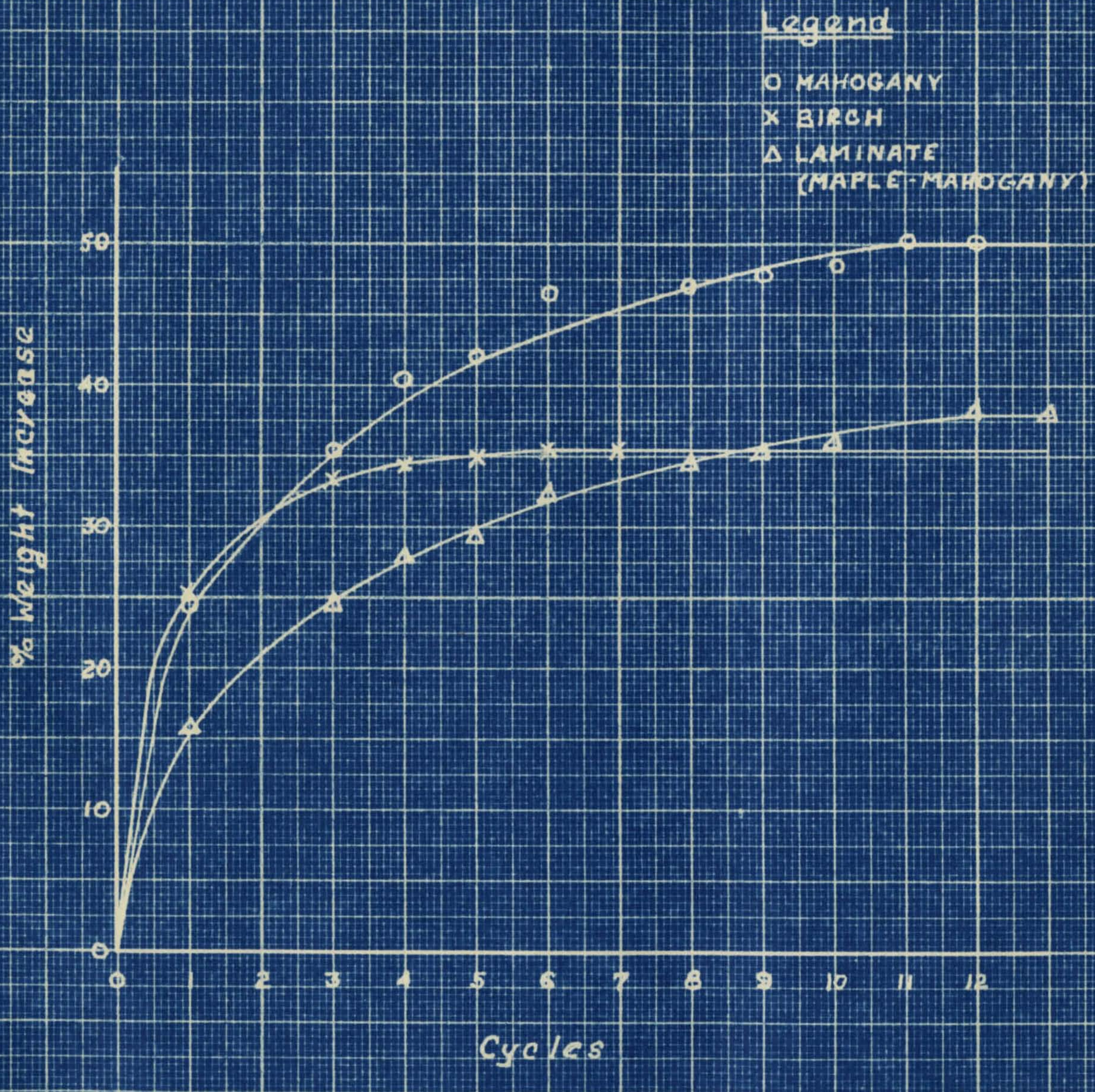


Fig. 24 Effect of Species on Weight Increase of Oleic Acid Impregnated Woods.

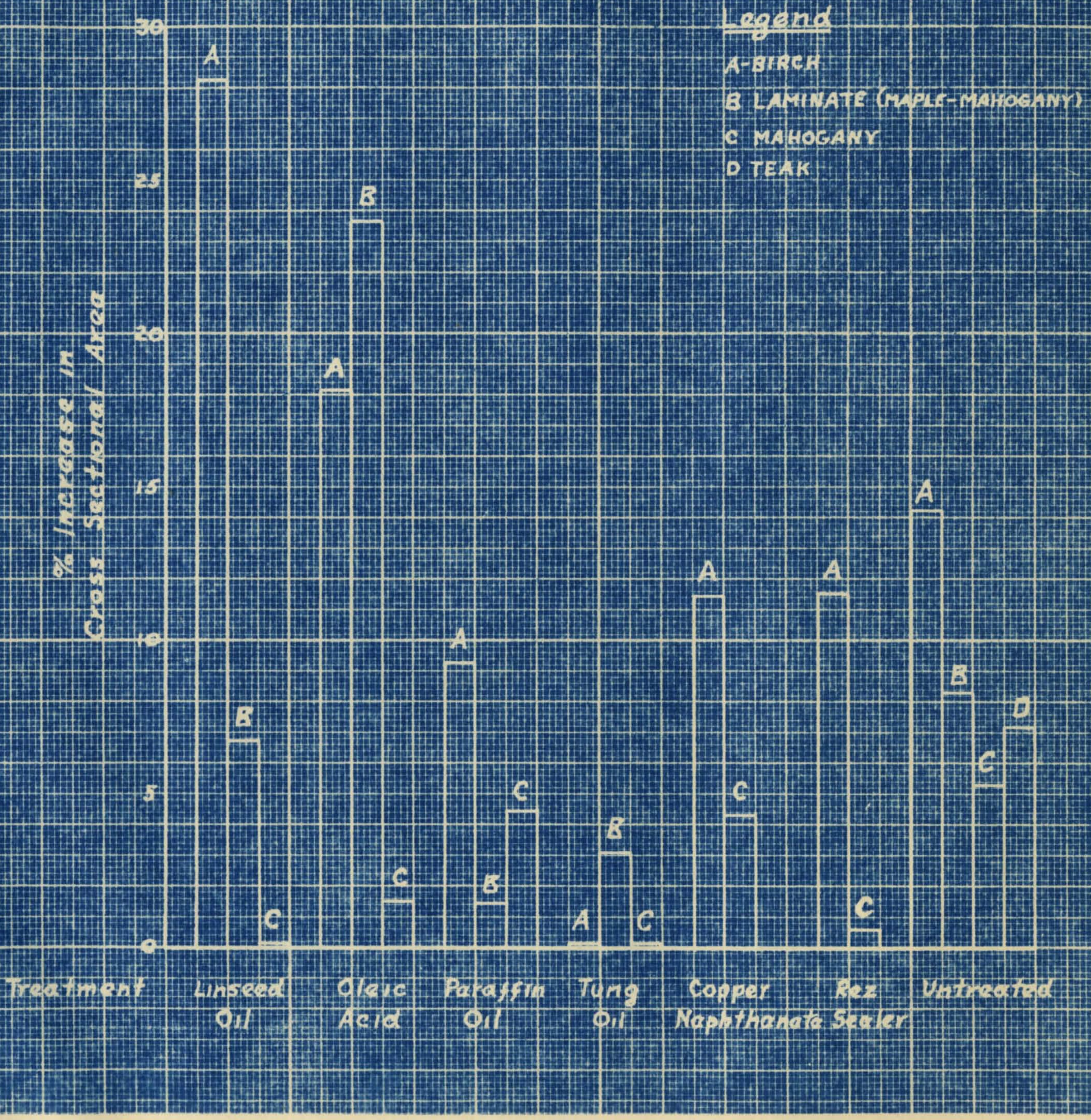


Fig. 25 Final Dimensional Changes of Impregnated Woods After Pressure Cycles in Salt Water.

IV. INVESTIGATIONS

OF MARINE ADHESIVES

INTRODUCTION

The most satisfactory adhesives used in the manufacture of wood laminates for marine use are synthetic resins of the phenolic aldehyde type. Since these adhesives are cured at elevated temperatures and pressures to insure proper bonding, their optimum curing conditions must be determined.

The purpose of this work was three fold: A) To determine the optimum curing conditions of a number of marine adhesives using a standard acetone extraction procedure; B) To investigate the substitution of an X-ray diffraction procedure for the acetone extraction method; C) To determine the pot life of an adhesive.

A. Determination of Optimum Curing Conditions of Marine Adhesives. - Acetone Extraction Procedure.

Many new glues of the phenolic-aldehyde type have been put on the market since the beginning of World War II. However before being used in production, the manufacturer carries out various tests on the adhesive to determine its suitability for the particular use.

In cooperation with Gamble Brothers, Inc., makers of laminated ship timbers, acetone extractions were carried out to determine the optimum curing temperatures and times on a number of resin adhesives.

B. Determination of Optimum Curing Conditions - X-ray Diffraction Procedure.

Such procedures as the acetone extraction for determining the cure of resin adhesives are long, tedious, and greatly dependent upon human accuracy. The procedures, moreover, cannot be applied to glued wood specimens but are confined to free films. Though not much is known of the nature of the glue bond, there is evidence indicating that free glue films are of a different nature from that of glue cured in contact with wood.

It was therefore the purpose of this X-ray diffraction study to eliminate the acetone extraction procedure and at the same time add to the evidence on the nature of the glue bond. Furthermore this procedure might provide a non-destructive method of determining the cure of glued wood specimens.

C. Determination of the Pot Life of Resin Adhesives - Viscosity of Mixed Cascophen LT-67 Adhesives.

The pot life of a resin adhesive decreases with increase in temperature. Therefore in the summer months extra measures must be taken to insure proper pot life.

Cascophen LT-67 (a neutral phenolic aldehyde type resin) mixed with 8 per cent M-18 (a paraformaldehyde base hardener), is a satisfactory marine adhesive, but it has a short pot life (2 hours at 80°F. It has been reported (8) that the use of FM-50 hardener (reported to contain ammonium sulfate), instead of M-18, increased the pot life of the resin to 70 hours at 80°F.

This section was undertaken to lengthen the pot life of Cascophen LT-67+M-18 while still retaining the M-18 hardener to insure curing and weathering characteristics.

HISTORICAL

Many attempts have been made to find a rapid, accurate test for determining the degree of cure of marine adhesives. Although actual service is the only sure test, some information can be gained by a number of procedures.

For some time the protective coating industry has used a solvent extraction procedure in following the polymerization of resin films. R.F. Blomquist (10) has investigated the use of a similar procedure in determining the cure of resin adhesives by acetone extraction. He has shown definite correlations between per cent extractibles and relative degree of cure when the glue is cured on a chemically inert surface.

Many X-ray studies have been made of synthetic resins and compounds of the types which are susceptible to polymerization. The course of acetylation of cellulose has been followed with X-ray photographs by Hess and Tregues (11).

Ellis (12) has presented X-ray diffraction patterns of a phenol-formaldehyde resin at 3 different stages of cure. These patterns indicated that as condensation proceeded the resin structure became more amorphous in nature. However other resins such as the phthalic glycerides have been shown through X-ray studies to approach the state of crystallinity as condensation proceeds.

Sacra (8) has determined the pot life of resin adhesives in terms of viscosity changes using a #4 Ford viscosity cup. He found that if the time for a flow of 50 ml. exceeded 400 seconds the glue was too viscous for satisfactory spreading.

THEORETICAL

The curing of a resin adhesive of the phenolic aldehyde type proceeds by the mechanism of condensation with the formation of 3 dimensional or space polymers of unknown size or completed structure. Acetone has the characteristic of disolving low and medium molecular weight polymers of this type. Therefore as the cure proceeds and less low molecular weight polymers are present the percent extractibles should decrease. This has been found to be partly true, i.e., the percent extractibles does decrease with cure; however, at final cure the value approaches a constant. This constant value varies with different glues and techniques of extracting.

Any two substances which are not identical in structure will give different X-ray pattern. It is upon this fact that the attempt to find a diffraction method of determining the cure of adhesives was based. As the curing of the adhesive proceeds, the X-ray pattern correspondingly changes, becoming more or less crystalline in nature depending upon the type of resin. If the change is predominant enough to tell unmistakingly how far the cure has proceeded it would be possible to shave a very small sample off the glue line and determine the cure without harming the finished glued wood products. Thus this method would eliminate a great amount of work and make it possible to test products without destruction.

Increase in condensation or cure of a resin is accompanied by increase in viscosity. Even at room temperature curing takes place. Thus an adhesive increases in viscosity upon standing, and its usefulness may be dependent on its pot life.

EXPERIMENTAL

A. ACETONE EXTRACTION OF GLUE FILMS

The use of acetone extraction of powdered glue films is made to determine the optimum curing conditions of the adhesive.

APPARATUS:

The main apparatus used was a battery of Soxhlet extraction units. Each unit consisted of a 400 ml. extraction flask, a syphon cup, Whatman extraction thimble, and a condenser cap. The syphon cup containing the extraction thimble was suspended by fine wire from the condenser cap which rested on the neck of the flask. The battery was in the form of a rectangular wooden box lined with asbestos paper, and fitted with a removable lid in which holes were cut to receive the extraction flasks. The flasks were placed in cylindrical metal reflectors which directed the heat to them from the 75 watt incandescent lamp heaters located on the bottom of the battery. Cooling water for the condensers was supplied through an iron pipe manifold, and the cooling system of the battery was connected in parallel.

Laboratory electric ovens were used to cure the glue films on glass plates. A standard mortar and pestle were used to hand powder the films to pass through a 48 mesh Tyler Standard Screen.

PROCEDURE:

The procedure consisted of preparing the adhesive, curing it on glass plates in ovens at prescribed temperatures and times, grinding the flakes, and extracting with acetone.

A Whatman filter paper was placed inside a Whatman extraction thimble and extracted with acetone in the extraction battery for 24 hours. The thimble was then dried at 110°C. in an electric oven for 1 hour and then placed immediately in a weighing bottle and weighed.

The adhesive was mixed according to the proportions and methods recommended by the company making each glue respectively. It was spread thinly on glass plates and cured according to prearranged schedule of temperatures and times. After curing, each plate was placed in a desiccator in a refrigerator which was held at 40°F. These glue flakes were then hand powdered by mortar and pestle to pass a 48 mesh Tyler Standard Screen and immediately replaced in the refrigerator. When all flakes were prepared, the powders were weighed into the soxhlet extraction thimbles and acetone extracted for 24 hours. The extracted glues and thimbles were then heated in a drying oven at 110°C. for 1 hour, placed in a weighing bottle, and weighed immediately. The loss in weight was recorded and calculated as percent acetone extractible on an initial weight basis. This procedure was standardized by Sacra and Williams (8).

ADHESIVES TESTED:

Durez 12688, a water soluble liquid phenolic resin (100 parts) plus Durez 12689 powdered hardener (20 parts) manufactured by Durez Plastics and Chemicals, Inc.

Bakelite XC-17613, a liquid phenolic resin (100 parts) plus Bakelite XK17618 powdered hardener (20 parts) manufactured by Bakelite Corporation.

Bakelite XC-17540, a powdered phenolic resin (100 parts) plus alcohol (60 parts) water (30 parts) and Bakelite XK-17545 a powdered hardener (15 parts) manufactured by Bakelite Corporation.

Plyophen 6000, a liquid phenolic resin (100 parts), containing approximately 60 per cent solids in an alcohol water solvent, plus Plyophen 6001 powdered hardener, (18 parts) a formaldehyde containing substance. Manufactured by Reichold Chemicals, Inc.

Cascophen RS-216, a liquid phenolic resin (100 parts) plus Cascophen FM-60 powdered hardener (15 parts) manufactured by the Casein Company of America.

Penacolite GS-1124 a liquid phenolic resin, (100 parts) plus Penacolite GS-1124 liquid hardener (25 parts) manufactured by the Pennsylvania Coal Products Company.

Lauxite PF-900, a liquid phenolic resin (100 parts) plus Lauxite PF-90C, a powdered hardener (17 parts) manufactured by I.F. Lauck, Inc.

DATA AND RESULTS:

The Durez glue flakes were dark maroon in color, hard, brittle, and had a burnt wood odor. The acetone after extraction had a rust color decreasing in intensity with increase in cure. Table VI and Figure 26 present the acetone extraction data of this adhesive, and it appears from the curve that a final extractive value of between 4 and 7 per cent is indicative of sufficient cure. This can be realized by a 120°F. cure of 6 hours or possibly a 100°F. cure of 6 to 24 hours.

The Bakelite XC-17613 glue flakes were brown in color, brittle, but not quite so hard or tough as the Durez glue. Except for the flake cured at 120°F.-24 hours, all had both a phenol and a formaldehyde color. This latter one had only a burnt wood odor which was probably caused by wood flour in the hardener. The 75°F. - 6 hour cured flake was too sticky to be pulverized, so it was torn into small pieces and extracted. Both the 6 hour and 24 hour flakes cured at 75°F. imparted a rust color to acetone. Table VI and Figure 27 indicate a relatively high final extractive value of 20 to 28 per cent. This value was reached at a 100°F. cure of 4 hours or more and was approximated also by a one hour 120°F. treatment. This indicates sensible agreement with the manufacturer's literature although it is doubtful if his values of less than 100°F. can be entirely accepted.

The Bakelite XC-17540 glue flakes were maroon in color and equal in hardness to Bakelite XC-17613. The 8 hour and 24 hour flakes cured at 160°F. and the 15 minutes flakes cured at 200°F. had formaldehyde odors. Both the 8 hour at 160°F. and the 15 minute at 200°F.

flakes imparted a cloudy color to the acetone upon extraction. The latter to a greater extent. The acetone extractible values for this adhesive (Table VII and Figure 28) bunched from 5 to 14 per cent on all specimens excepting the 15 minute at 200°F. sample (26.2 per cent). Although the end point is not completely established it appears that satisfactory cures may be obtained by 8 hours at 100°F. or 2 hours at 180°F. These values are in close agreement with the manufacturers recommendations.

The Plyophen 6000 glue flakes were dark maroon and, except for the 4 hour cure at 80°F. specimen, were hard and brittle. Since this latter one was too plastic to pulverize, it was shaved into small pieces and extracted. Table VIII and Figure 29 indicate a final extractive value of between 6 and 8 per cent. This can be realized by a 6 hour cure at 150°F. The high acetone extraction at 80°F. would not warrant curing the adhesive at this temperature.

The Cascophen RS-216 glue flakes were maroon and hard and brittle. The final extractive value appears (Table IX) to be about 24 per cent. Thus it appears that the cure can be attained at 150°F. in 4 hours or 120°F. in 6 to 24 hours.

Penacolite glue flakes were darker and slightly harder than the Cascophen RS-216; and in room temperature curing, it skinned over with the formation of a relatively wrinkled surface. This adhesive appears to reach a final acetone extraction value of between 12 and 16 per cent (Table X). This can be attained by a 4 hour cure at 150°F. or a 24 hour cure at 120°F.

The relatively high acetone extraction value of these last two glues are not necessarily indicative of poor glue bonding on wood, for they may be caused by the nature of the adhesive. However, as has been mentioned, at full cure the value should be constant.

The Lauxite PF-90C glue flakes were dark brown and all but the 4 and 6 hour cures at 80°F. were hard and brittle enough to pulverize. These last two were shaved into small pieces and extracted. However, upon extracting these two it was found that the small pieces had fused together to form a case hardened mass thereby hindering complete extraction. The low values shown in Table XI for the 4 and 6 hour cures at 80°F. bear out the conclusion of incomplete extraction. The plot of per cent extractible vs curing temperature of Figure 30, though not too consistent, indicates a final extractive value of between 0 and 3 per cent. This can be realized by a 6 hour cure at 120°F. or a 4 hour cure at 150°F. A 2 hour cure at 150°F. is questionable.

TABLE VI. - ACETONE EXTRACTION OF DUREZ 12688 AND BAKELITE XC 17613 ADHESIVES

Per Cent Extractible

Curing Temp.	Durez 12688		Bakelite XC 17613			
	6 hours	24 hours	1 hour	4 hours	6 hours	24 hours
75° F.	17.8	5.15			62.0	31.0
100° F.	7.76	6.46		21.5	23.5	
120° F.	6.62	3.81	26.3		26.8	19.9

TABLE VII. - ACETONE EXTRACTION OF BAKELITE XC 17540 ADHESIVE

Per Cent Extractible

Curing Temp.	1/4 hour	2 hours	6 hours	24 hours
160°F.	26.2		13.4	11.5
180°F.		13.9	10.2	5.62
200°F.		11.7	8.22	

TABLE VIII. - ACETONE EXTRACTION OF PLYOPHEN 6000 ADHESIVE

Curing Temp.	Per Cent Extractible 2 hours	4 hours	6 hours	24 hours
80°F.		24.8	16.0	11.8
120°F.	10.2	9.5	7.3	7.8
150°F.	8.6 7.6	10.0 2.6	8.2 4.1	

TABLE IX. - ACETONE EXTRACTION OF CASCOPHEN RS-216 ADHESIVE

Curing Temp.	Per Cent Extractible 4 hours	6 hours	24 hours
80°F.	30.8	29.5	26.6
120°F.	26.4	28.0	23.6
150°F.	24.7	24.5	

TABLE X. - ACETONE EXTRACTION OF PENACOLITE G.S. 1124 ADHESIVE

Curing Temp.	Per Cent Extractible		
	4 hours	6 hours	24 hours
80°F.	26.3	24.3	12.9
120°F.	27.0	20.6	16.1
150°F.	23.9	17.1	

TABLE XI. - ACETONE EXTRACTION OF LAUXITE PF-30-C ADHESIVE

Curing Temp.	Per Cent Extractible			
	2 hours	4 hours	6 hours	24 hours
80°F.		19.8*	10.0*	25.9
100°F.	9.07	11.69	7.69	3.16
120°F.	3.97	4.40	3.98	-0.21
150°F.	3.70	1.69	-1.60	

* Considered unreliable because of physical structure

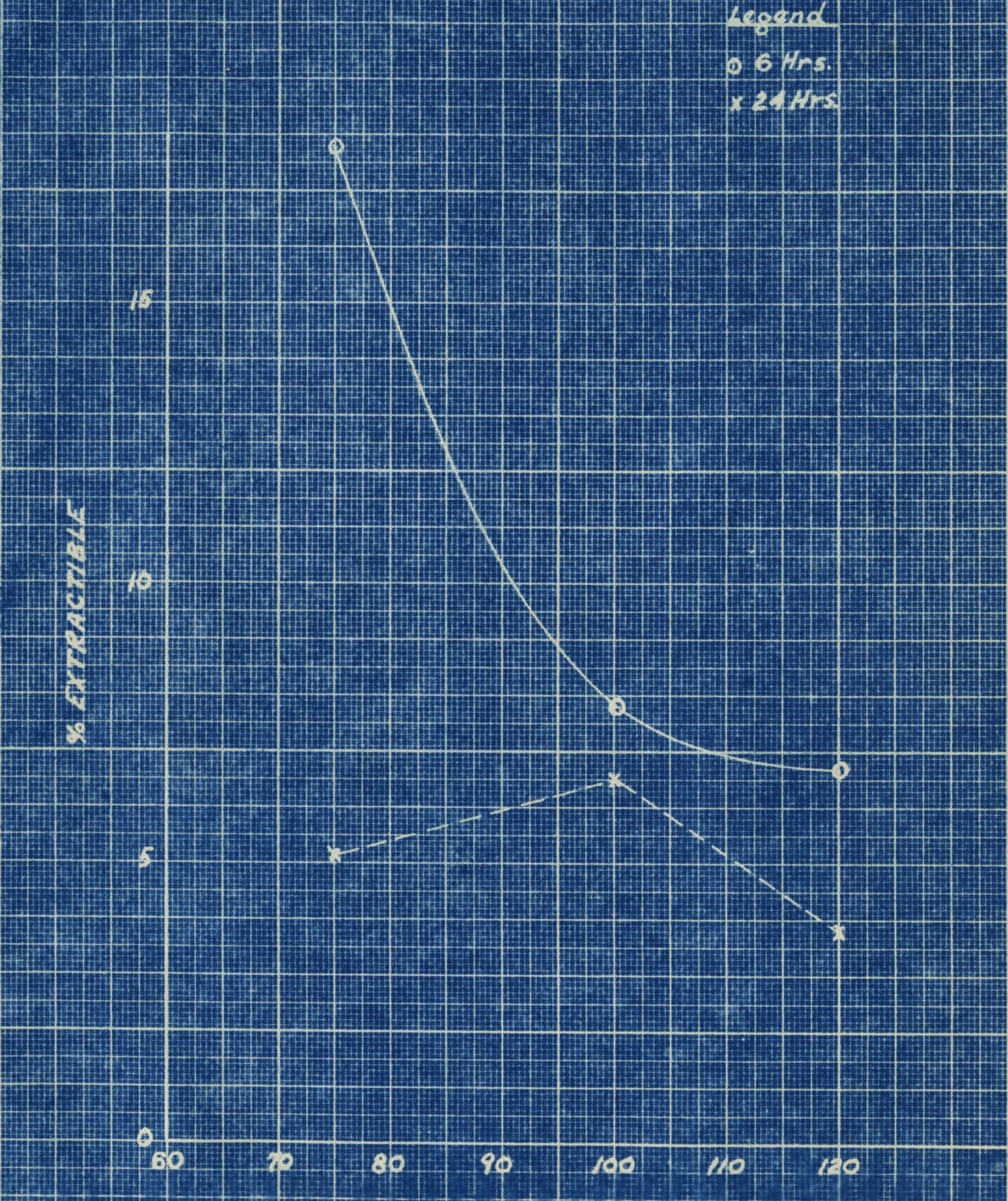


Fig. 26 Acetone Extraction of Durez Adhesive (#12688 Resin, #12689 Hardener).

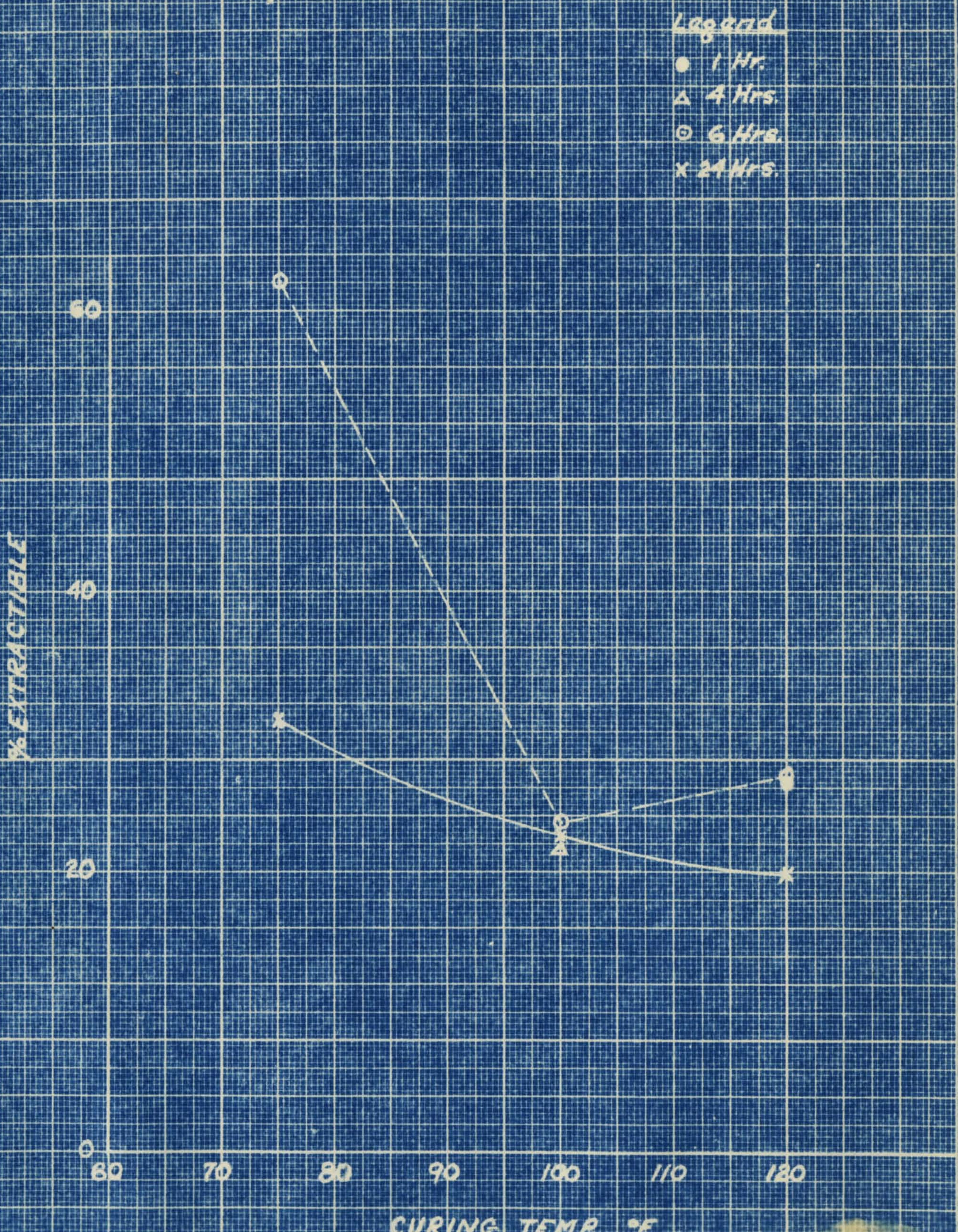


Fig. 27 Acetone Extraction of Bakelite Adhesive (XC 17613 Resin, XK 17618 Hardener)

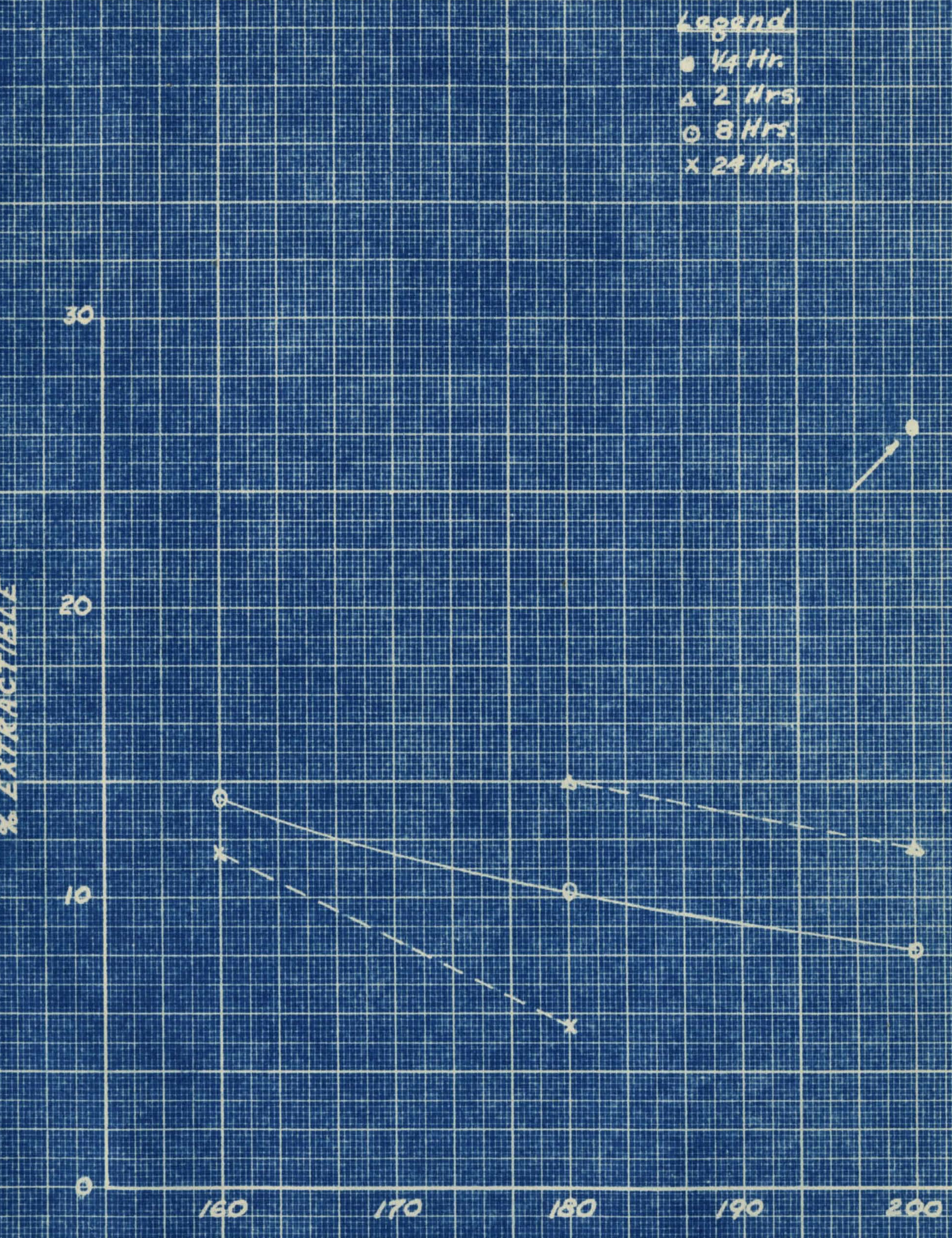


Fig. 28 Acetone Extraction of Bakelite Adhesive (XC 17540 Resin, XK 17545 Hardener).

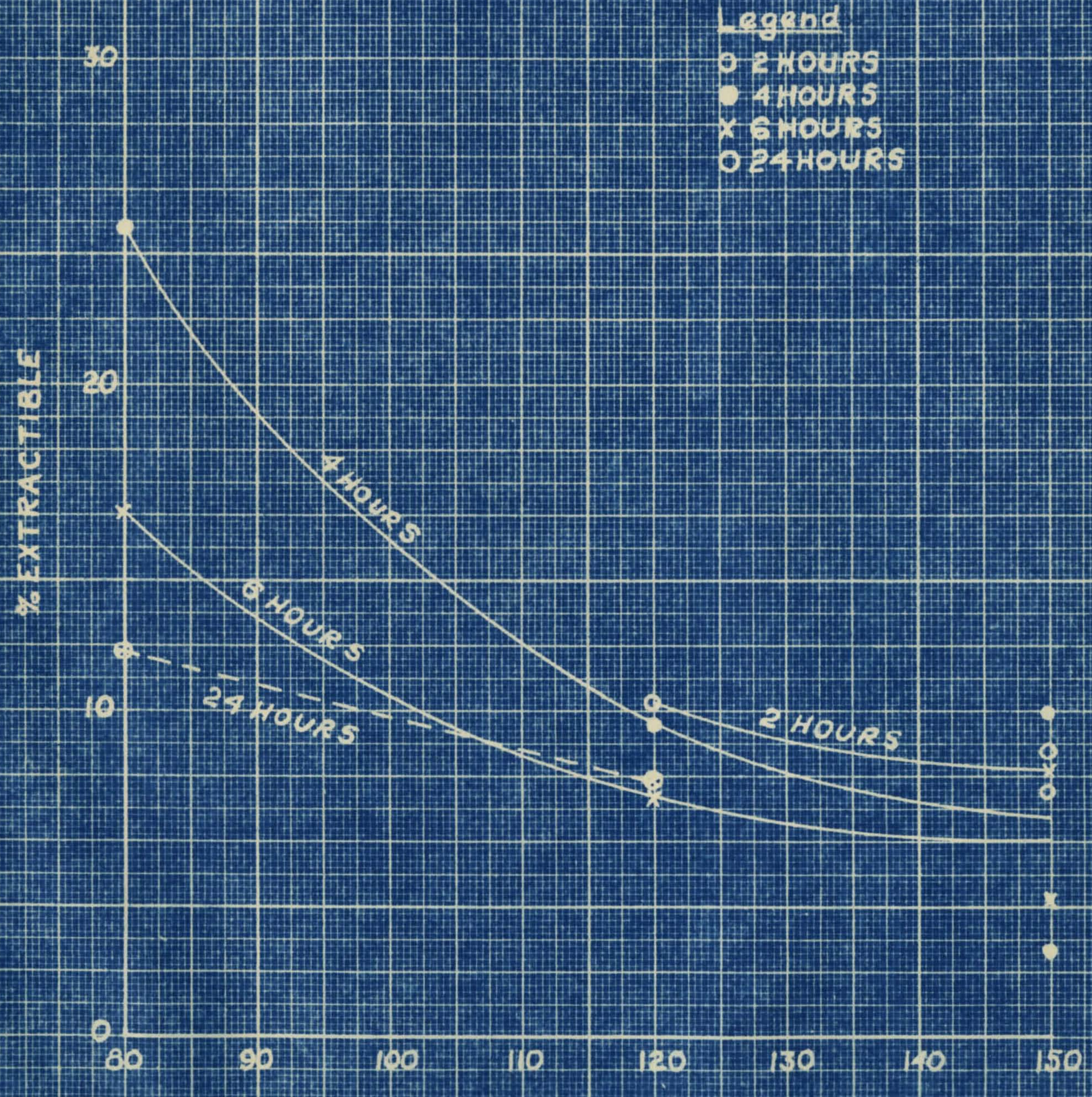


Fig. 29 Acetone Extraction of Plyophen Adhesive (#6000 Resin, #6001 Hardener).

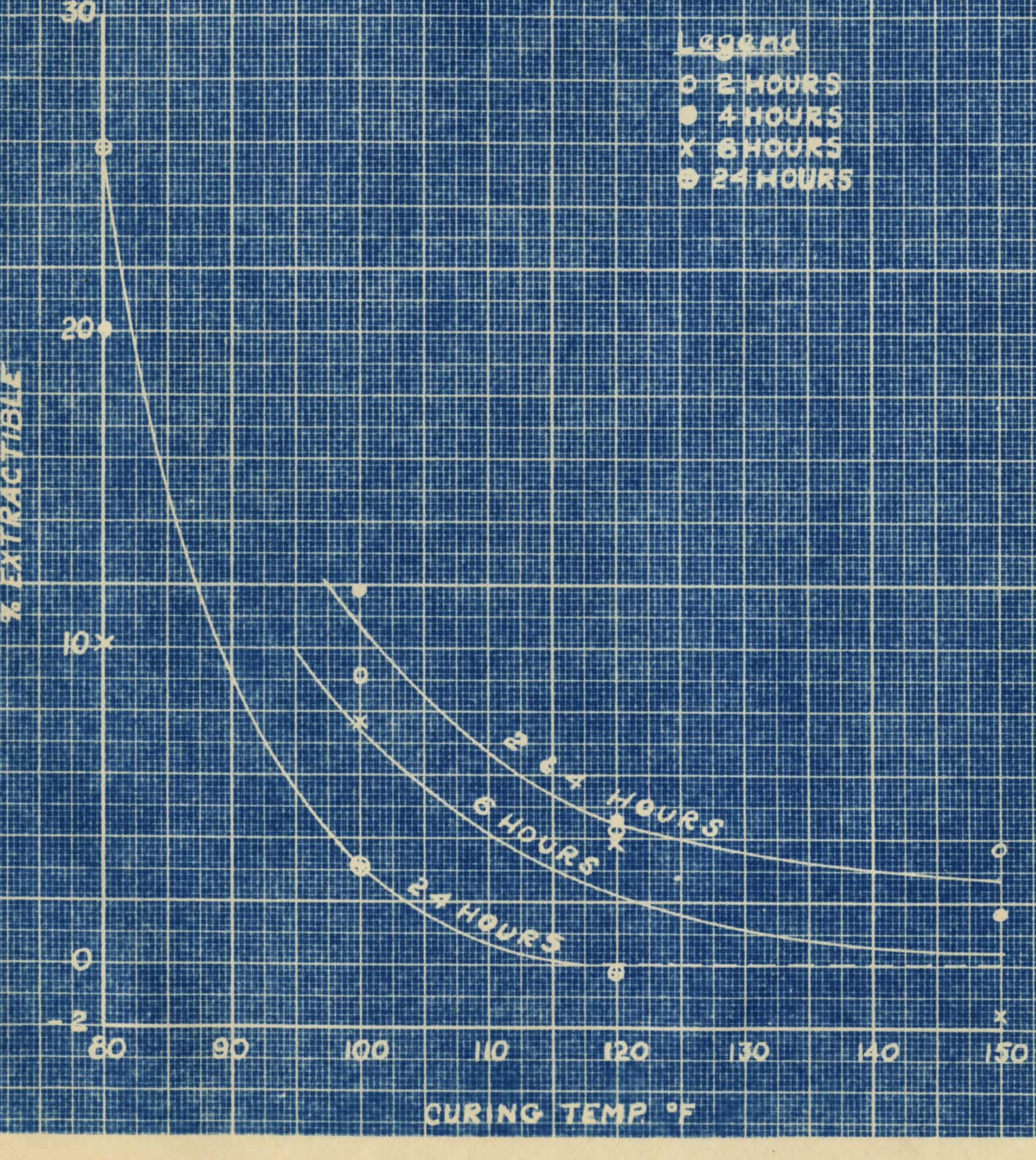


Fig. 30 Acetone Extraction of Lauxite Adhesive (PF90C Resin and Hardener).

B. X-RAY DIFFRACTION PROCEDURE

This section is a preliminary investigation of the use of an X-ray diffraction procedure for determining the cure of resin adhesives.

APPARATUS:

A Hayes Diffraction Unit employing characteristic K α radiation from an iron target tube and filtered with beryllium and manganese screens was used to X-ray the samples. A laboratory electric oven was used to cure the glue films on glass plates and heat the oak and cellulose.

MATERIALS TESTED:

Cascophen LT-67, a liquid phenolic resin plus 8 per cent M-18 hardener, a paraformaldehyde base catalyst. Manufactured by The Casein Company of America.

White Oak shaving approximately 1/32 of an inch in thickness.

α-Cellulose, commercial material approximately 95 per cent Cellulose.

PROCEDURE:

All radiographs except that of the uncured Cascophen LT-67 (Figure 31) were taken perpendicular to the fiber direction. In this case the adhesive was put on the head of a nail and placed in front of the filtering screens. The Laue diffraction method was used to take all X-rays except that in Figure 33 which used the powder method.

The samples X-rayed and the distance, time, voltage, and amperage used on each are given in Table XII.

TABLE XII. SPECIMENS X-RAYED AND THE CONDITIONS.

Specimen	Treatment	Distance from Plate (cm)	Time (hrs)	Kilo-Volts	Milli-amps	Figure No.
LT-67 Plain	Uncured	3	1.5	35	10	31
LT-67 - M-18	"	"	"	"	"	32
LT-67 - M-18	"	Powder Method	"	"	"	33
LT-67 - M-18	24 Hours at 25° C.	3	"	"	"	34
LT-67 - M-18	6 Hours at 100° C.	"	"	"	"	35
LT-67 - M-18	24 Hours at 120° C.	"	1.5	35	10	36
Oak Shavings	Uncured	5	4.5	"	"	37
Oak Shavings	24 Hours at 120° C.	"	"	"	"	38
Oak Shavings LT-67 and M-18	Uncured	"	"	"	"	39
Oak Shavings - LT-67 and M-18	24 Hours at 25° C.	3	1.5	"	"	40
Oak Shavings - LT-67 and M-18	6 Hours at 100° C.	"	"	35	10	41
Oak Shavings - LT-67 and M-18	24 Hours at 120° C.	5	4.5	"	"	42
α- Cellulose	Uncured	"	"	"	"	43
α- Cellulose	24 Hours at 120° C.	"	"	"	"	44
α- Cellulose - LT-67 and M-18	Uncured	"	"	"	"	45
α- Cellulose - LT-27 and M-18	24 Hours at 120° C.	5	4.5	35	10	46

DATA AND RESULTS:

Inspection of Figures 32, 34, 35, and 36 showing diffraction patterns of the Casoophen LT-67+M-18 adhesive at different stages of cure indicates that the amorphous resin becomes more crystalline as condensation proceeds. This is shown by the increase in intensity of the second smallest ring from a general fogginess in the uncured sample (Figure 32) to a defined ring in the cured films (Figure 36). The diffraction pattern of Casoophen LT-67 plain (Figure 31) shows 4 well defined rings, but the addition of the catalyst creates an amorphous pattern. Since the technique used in taking the X-ray of the Casoophen LT-67 plain differed from the others and the addition of the catalyst showed such a difference in structure, it may be probable that the technique used in taking the X-ray of Casoophen LT-67 plain was responsible for the change. However because of a breakdown in the diffraction unit another photograph of Casoophen LT-67 plain could not be taken.

Oak shavings showed four normal rings with a slight orientation which is shown as a bright band across the photograph of Figure 37. Upon heating the shaving at 120° F. for 24 hours the orientation increased, indicating a definite change in the wood structure (Figure 38).

The X-ray photographs of Casoophen LT-67+M-18 adhesive on oak shavings at different stages of cure (Figures 39, 40, 41, and 42) indicate that except for the rotation of the orientation band the pattern is essentially that of oak shavings alone under the same conditions. Thus, in this case, the curing of the adhesive on oak is masked by the wood.

Fig. 31. X-ray Diffraction Pattern of Uncured Cascophen LT-67 Adhesive.

Fig. 32. X-ray Diffraction Pattern of Cascophen LT-67 & M-18 Adhesive (Uncured).

Fig.33. X-ray Diffraction Pattern (Powder Method) of Cascophen LT-67 & M-18 Adhesive (Uncured).

Fig. 34. X-ray Diffraction Pattern of Cascophen LT-67 & M-18 Adhesive (24 Hours at 25° C.).

Fig. 35. X-ray Diffraction Pattern of Cascophen LT-67 & M-18 Adhesive (6 Hours at 100° C.).

Fig. 36. X-ray Diffraction Pattern of Cascophen LT-67 & M-18 Adhesive (24 Hours at 120° C.).

Fig. 37. X-ray Diffraction Pattern of Oak Shavings.

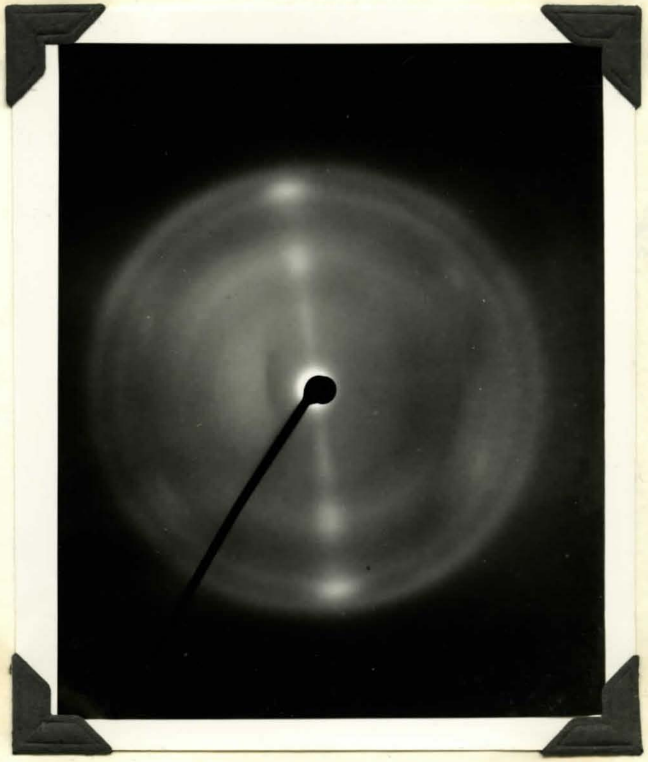


Fig. 38. X-ray Diffraction Pattern of Oak Shavings Heated 24 Hours at 120° C.

Fig. 39. X-ray Diffraction Pattern of Oak Shavings and Cascophen LT-67 & M-18 Adhesive (Uncured).

Fig. 40. X-ray Diffraction Pattern of Oak Shavings and Cascophen LT-67 & M-18 Adhesive (24 Hours at 25° C.)

Fig. 41. X-ray Diffraction Pattern of Oak Shavings and Cascophen LT-67 & M-18 Adhesive (6 Hours at 100° C.).

Fig. 42. X-ray Diffraction Pattern of Oak Shavings and Cascophen LT-67 & M-18 Adhesive (24 Hours at 120° C.).

Fig. 43. X-ray Diffraction Pattern of α- Cellulose.

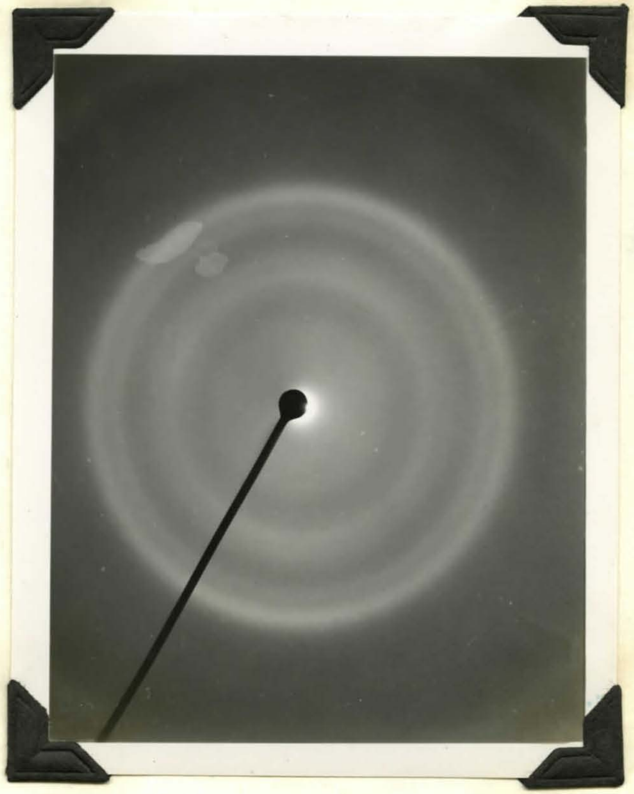


Fig. 44. X-ray Diffraction Pattern of α-Cellulose Heated 24 Hours at 120° C.

Fig. 45. X-ray Diffraction Pattern of α- Cellulose and Cascophen LT-67 & M-18 Adhesive (Uncured).

Fig. 46. X-ray Diffraction Pattern of α- Cellulose and Cascophen LT-67 & M-18 Adhesive (24 Hrs. at 120°C.).

The pictures of α-cellulose (Figures 43 and 44) show the same four normal rings as the oak. However, there is no preferred orientation as in the wood, and there is no indication of any change in the substance upon heating. Uncured glue on cellulose changes the pattern only by a slight increase in the intensity of the inner ring (Figure 45). Upon curing, the intensity of the outer three rings drops sharply, and the film (Figure 46) had some similarity to the glue sample cured on glass under the same conditions (Figure 36).

SUMMARY:

There is a definite difference in X-ray patterns between an uncured adhesive and adhesive cured on glass. However the results do not indicate a sufficiently sharp contrast between uncured and cured resins for its use as a reproducible control procedure.

When heated at elevated temperatures wood undergoes a structure change. However it appears that the α-cellulose is not the substance responsible for the change.

The glue does not appreciably affect the X-ray pattern of the wood. In fact, the curing of the adhesive is masked by the structure of the wood.

From the X-rays it can be seen that there is a difference in the nature of the glue when cured on glass and on oak shavings or α-cellulose.

C. VISCOSITY OF MIXED CASCOPHEN LT-67 ADHESIVES

This section was undertaken to increase the pot life of Cascophen LT-67+M-18 mixture by the addition of a small amount of FM-50.

APPARATUS:

The apparatus used in this determination was a #4 Ford cup, a Kodak timer, thermometer, and standard laboratory glassware.

MATERIALS:

Cascophen LT-67, a liquid phenolic resin. Manufactured by The Casein Company of America.

M-18, a powdered paraformaldehyde base catalyst.

FM-50, a powdered catalyst reported to contain ammonium sulfate.

PROCEDURE:

Samples approximately 250 ml. each were prepared of plain Cascophen LT-67 and Cascophen LT-67 plus 8 per cent of various mixtures of the two catalyst. The per cent is based on the weight of the pure resin. These samples were held at room temperature (87°F. ± 2°F.) in pyrex beakers covered with watch glasses for extended periods of time while viscosity tests were made at intervals. The viscosity measurements were made by observing the time in seconds required for 50 ml. of glue to flow through the orifice of a standard #4 Ford viscosity cup.

TABLE XIII. - VISCOSITY OF MIXED CASCOPHEN LT-67 ADHESIVES (Temp. 87°F.).

LT-67 Plain		LT-67 8% Old FM-50		LT-67 8% New FM-50	
Time of Set (Hrs)	Viscosity Seconds*	Time of Set (Hrs)	Viscosity Seconds*	Time of Set (Hrs)	Viscosity Seconds*
0	60	0.0	159	0.0	165
46	105	0.2	206	0.5	178
69	125	0.5	263	1.0	175
93	182	1.0	241	17.0	223
116	261	1.5	234	18.0	221
142	342	17.8	243	68.0	341
		69.3	410	91.0	440
		92.0	550	114.0	616
		115.0	610	138.0	950
		139.0	1051	144.0	830
		165.0	1320	164.0	1462

* Time of flow for 50 ml. through #4 Ford Cup.

TABLE XIII. - (Continued) VISCOSITY OF MIXED CASCOPHEN LT-67 ADHESIVES.

LT-67 8% M-18		LT-67 6% M-18 2% FM-50		LT-67 4% M-18 4% FM-50		LT-67 2% M-18 6% FM-50	
Time of Set (Hrs)	Viscosity Seconds*	Time of Set (Hrs)	Viscosity Seconds*	Time of Set (Hrs)	Viscosity Seconds*	Time of Set (Hrs)	Viscosity Seconds*
0.0	104	0.0	115	0.0	207	0.0	259
0.5	125	0.5	188	0.5	312	0.25	335
1.0	235	0.75	225	1.0	366	1.25	531
1.5	417	1.0	511	1.25	392	19.5	900
1.8	1024	1.5	622	1.5	454	25.0	960
		2.0	1356	3.75	1321		

* Time of flow for 50 ml. through #4 Ford Cup.

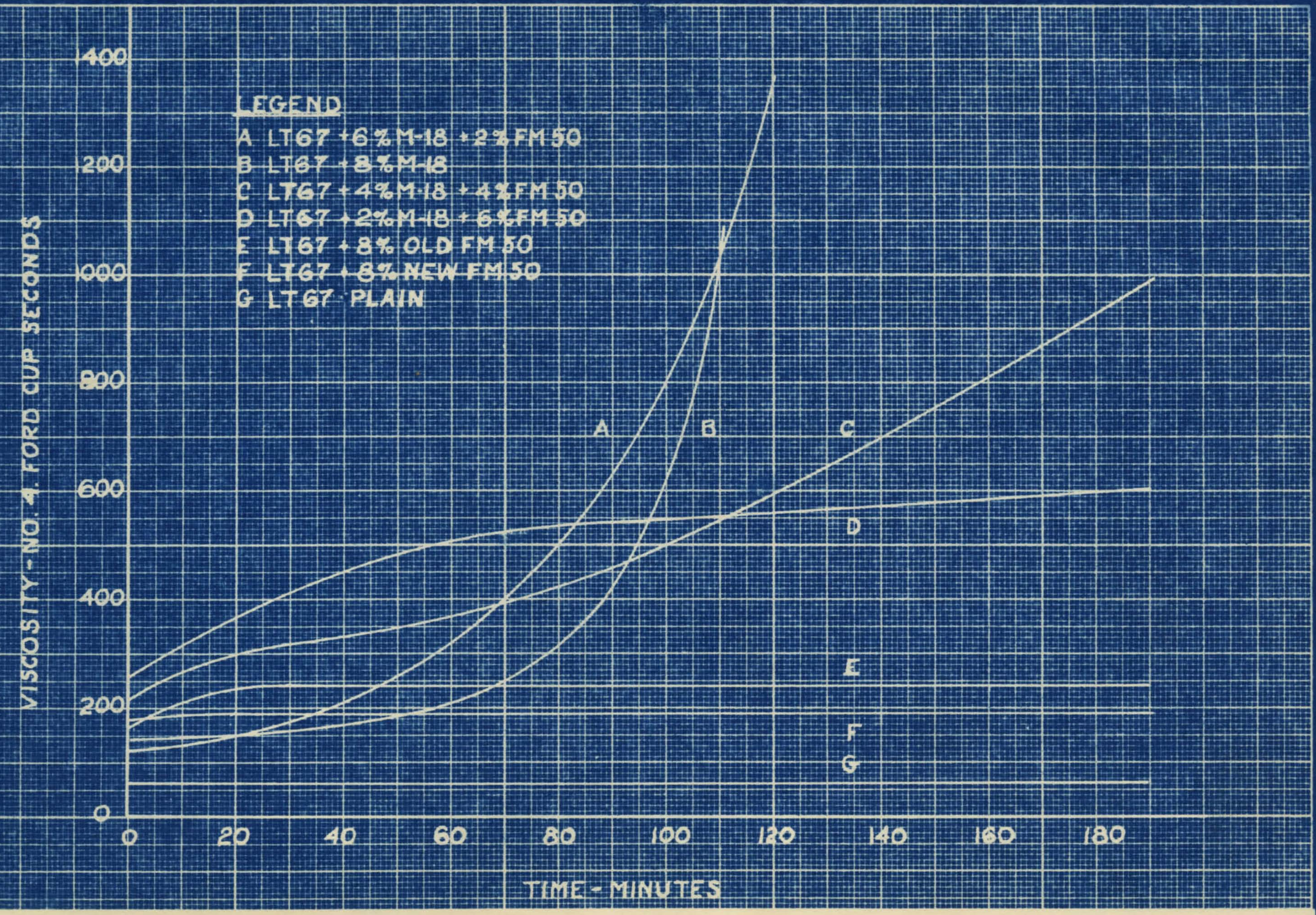


Fig. 47 Viscosity Changes of Mixed Cascophen LT-67 Adhesives at 87°F (50 Ml. thru #4 Ford Cup).

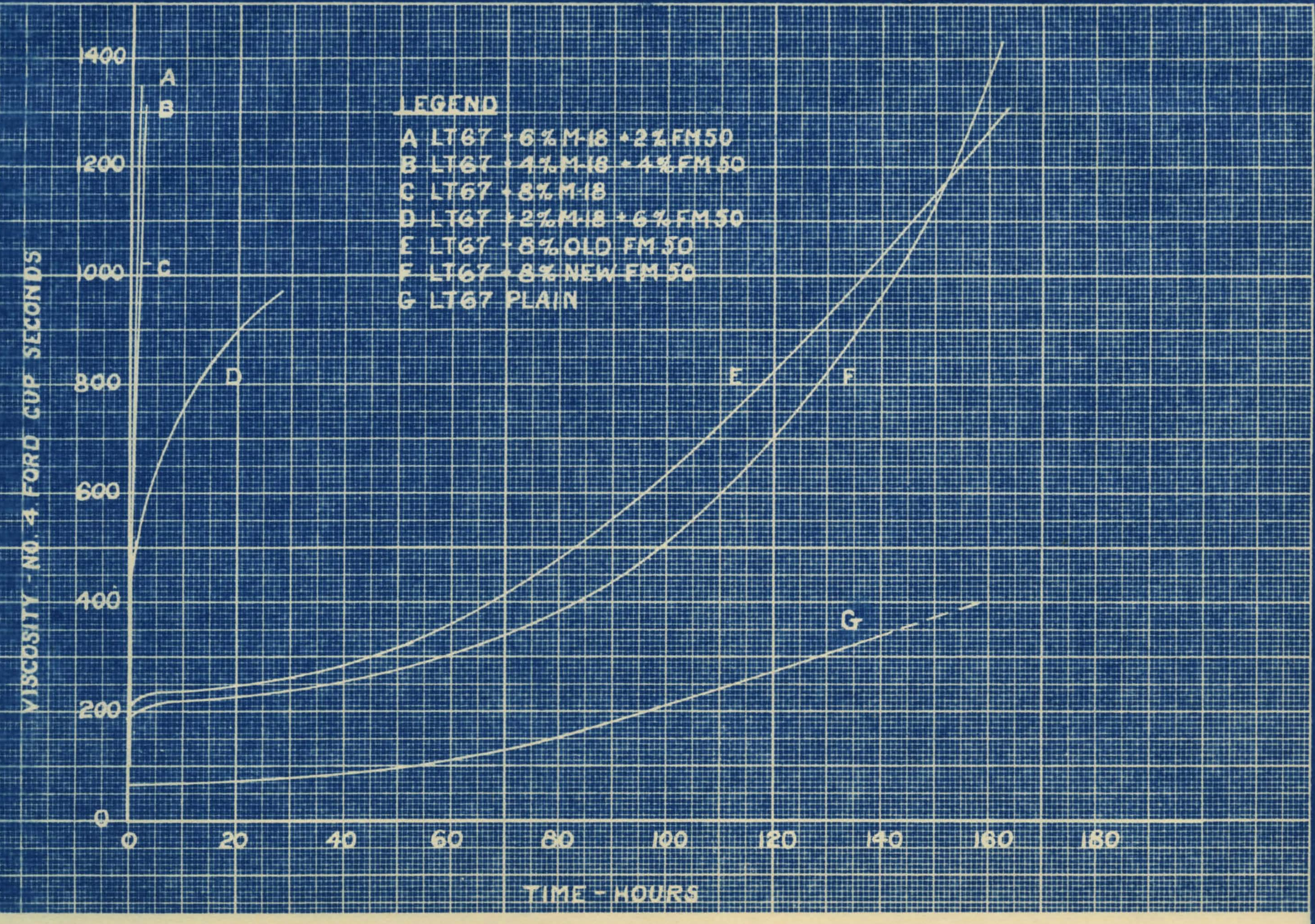


Fig. 48 Viscosity Changes of Mixed Cascophen LT-67 Adhesives at 87°F (50 Ml. thru #4 Ford Cup).

DATA AND RESULTS:

Table XII and Figures 47 and 48 present the viscosity data of the various mixtures. The data are also presented of an FM-50 which had been stored one year at room temperature.

It can be seen that the pot life of the adhesive is greatly lengthened by using FM-50 in place of M-18. However it is also evident that up to an hour and a half, and a viscosity reading of 500 seconds any mixture of FM-50 with M-18, tends merely to thicken the adhesive more than if only M-18 were present. The rate of increase in viscosity above this point is considerably slowed by the presence of FM-50. However it has been mentioned previously that 400 seconds is the desirable upper limit of usable viscosities; therefore it is evident that the presence of FM-50 with M-18 can only be harmful.

SUMMARY AND CONCLUSIONS

1. Acetone Extraction of Glue Films.

The recommended curing conditions of the adhesives are as follows:

Durez 12688 + 12689
100°F. - 24 hours
120°F. - 6 hours

Bakelite XC+17613 - XK+17618
100°F. - 4 hours
120°F. - 1 hour

Bakelite XC-17640 + XK-17648
160°F. - 8 hours
180°F. - 2 hours

Plyophen 6000 + 6001
120°F. - 6 hours
150°F. - 2 to 4 hours

Cascophen RS-216 + FM-60
120°F. - 24 hours
150°F. - 4 hours

Penacolite GS-1124
120°F. - 24 hours
150°F. - 4 hours

Lauxite PF-90C
100°F. - 24 hours
120°F. - 6 hours
150°F. - 4 hours

2. X-ray Diffraction Procedure.

The results of glues cured on glass indicate a change in structure as cure proceeds. However the X-ray patterns do not show sufficiently sharp contrast between uncured and cured resins to be used as a control procedure in place of the acetone extraction method.

The diffraction patterns of the glue on oak and α-cellulose give evidence that there is a difference in the nature of the glue when cured on glass and on wood.

The curing of the adhesives on wood is masked in the X-ray patterns by the wood. Therefore it seems from these preliminary tests that the method of testing the cure of glued wooden specimens by X-ray diffraction is of no use. However the data are too meager to dispose of the procedure without some further study.

3. Viscosity of Mixed Cascophen LT-67 Adhesive.

The addition of FM-60 to a Cascophen LT-67+M-18 mixture will not increase the pot life but will definitely shorten it.

LITERATURE CITED

LITERATURE CITED

(1) Stamm, A.J., J. Amer. Chem. Soc., 56, 1195 (1934).

(2) Stamm, A.J. and Hansen, L.A., Ind. Eng. Chem., 27, 1480 (1935).

(3) Stamm, A.J. and Seborg, R.M., Ind. Eng. Chem., 28, 1165 (1936).

(4) Stamm, A.J. and Seborg, R.M., Trans. A. I. Ch. E., 37, 385 (1941).

(5) Berliner, J.F.T., Chem. Ind., 54, 680 (1944).

(6) Stamm, A.J., Millett, M.A., and Seborg, R.M., Mech. Eng., 67, 25 (1945).

(7) Bailey, S.D., Grinsfelder, H., and Klein, L., Ind. Eng. Chem., 36, 252 (1944).

(8) Sacra, C.F., M. Ch.E. Thesis in Chemical Engineering, U. of Louisville (1944).

(9) Stamm, A.J. and Hansen, L.A., Ind. Eng. Chem., 29, 831 (1937).

(10) Blomquist, R.F., U.S. Dept. of Agric., Pub. No. 1352, Sept. (1943).

(11) Hess, K., and Trogus, Z., Physik. Chem., 15, 157 (1932).

(12) Ellis, C., "The Chemistry of Synthetic Resins", Vol. I, page 83-88, New York, Reinhold Publishing Corp., (1935).

X

ACKNOWLEDGEMENTS

The author wishes to acknowledge the kind assistance and helpful guidance of Dr. G.C. Williams who directed this research.

He also wishes to express his appreciation to Gamble Bros. whose fellowship in the Division of Industrial Research made this investigation possible and to Messrs. C.D. Dosker and Harold Moser who represented Gamble Bros. and whose advise and opinions have been exceedingly helpful.

VITA

Otto Joseph Miloti, Jr. was born in Louisville, Kentucky, on July 15, 1923, the son of Otto J. Miloti and Angela Talamo Miloti. He received his primary and secondary education from St. Francis of Assisi and St. Xavier High School respectively.

Mr. Miloti entered the University of Notre Dame in September, 1941, and received the degree of Bachelor of Science in Chemical Engineering in June, 1944.

He was awarded a Division of Industrial Research fellowship at the University of Louisville in July, 1944, and received the degree of Master of Chemical Engineering in October, 1945.

He was a member of the University of Notre Dame Student Chapter of the American Institute of Chemical Engineering and is now a junior member of the senior organization.