FURTHER STUDIES TOWARD THE PREVENTION OF BROWN STAIN IN

SUGAR PINE LUMBER

Thesis by

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Since this report is a continuation of the work described by Mr. Steinour in his thesis,[A] and rightly should accompany that Thesis, the reader is referred directly to it for a description of the nature of the problem, the existing knowledge pertaining to it before Mr. Steinour started his work, and the facts concerning the stain and means of preventing it that he discovered. The experimental method he developed for making small scale kiln drying experiments was followed exactly in every detail, including the use of the same drying oven and instruments, and the same assumptions in calculating the data taken, so that the results described herein should be entirely comparable.

Schedule of Run Number 10. - As run number 8 was quite free of stain and number 9 showed more stain than one would like to have, even though it was not bad, it was planned to make the schedule of number 10 intermediate in severity with respect to temperature and humidity between the schedules of numbers 8 and 9. Since the schedules 8 and 9, however, were not greatly different, it is evident that number 10 is so much like the two of them that it should give results very similar to those of 8 and 9. There is one difference that may be important, namely, that the initial average moisture content was considerably higher than those of 8 and 9, which were 171 and 164 percent respectively (calculated as percent of dry weight) compared with 236 percent for number 10. Chart 10 shows the schedule graphically.
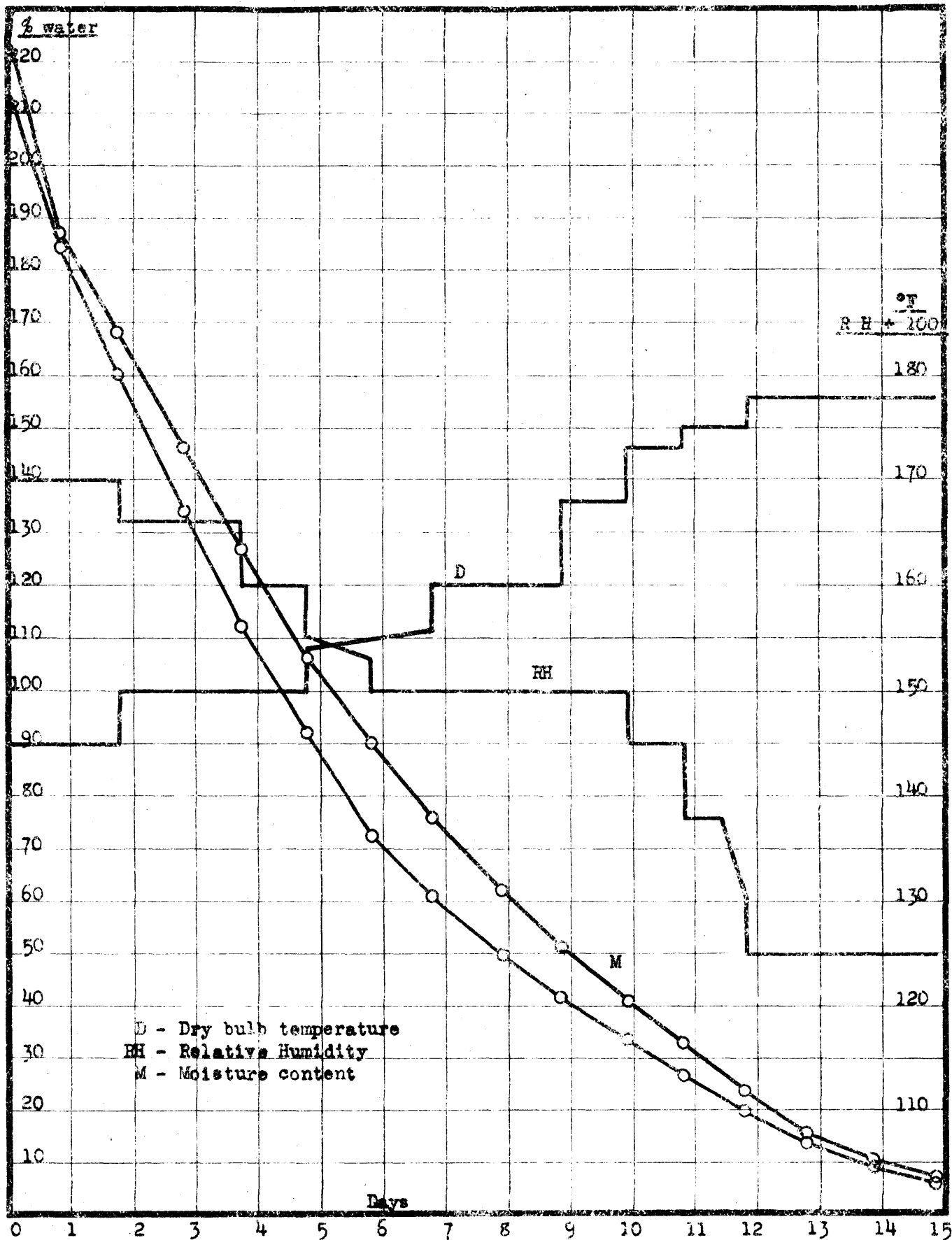
Chart 10 - Run No. 10

Initial moisture content of stock - Run 10
    Percent dry weight   Average   236
                                                          Range   209-255

Final moisture content at middle of boards
    Percent dry weight   Average   14
                                                          Range   9-22

Initial steaming at 100% relative humidity
    Time exclusive of that necessary to
        reach temperature - hours   2
    Temperature - °F   155
    °F above starting temperature of schedule   10

This run also left the wood in apparently good physical condition.

Warping was slight and there was no checking at the ends. About a quarter

of the pieces showed a tendency to bind on the saw. Compared to other runs

the case hardening shown by the stress sections (described in Steinour's

Thesis, p. 24) was moderate.

Staining in Run Number 10. - The stain developed in this run was

very bad. It was dark brown, very intense and deep. It was at least as

bad as in run 7. The stain was more intense in the heartwood and in the

pieces having high final moisture content.

Schedule of Runs Number 12 and 17. - This result (run 10) with a

schedule that was expected to give little or no stain showed very conclu-

sively the importance of the previous history of the wood under test. It

indicated also that possibly stock with very high initial moisture content,

such as was the stock for this run, is very much more difficult to handle

than wood with only moderate initial moisture content. With these facts

clearly in mind it was decided that a successful schedule would probably

be one which was designed to cause the stain that formed to be deposited

in the surface of the wood so that it would subsequently be removed when

the pieces were surfaced to finish sizes. If this could be successfully ac complished, then the very troublesome difficulty of preventing the production of stain would be eliminated because it would not matter then how much stain might develop if it could all be caused to deposit very near the surface of the rough boards. Since some effort had already been made to accomplish this end, it was evident that advantage must be taken of every possible means of bringing about the desired results. One would wish to make the sap come just as near the surface as it is possible to realize before it e- vaporates and changes to steam. Since both the brown stain and the substance from which it is derived have been shown to be sap-soluble, they would thus be deposited nearer the surface.

There are three factors that could be regulated to work together to bring about the transfusion of liquid water up to the surface; namely preventing case hardening, using as high a temperature as possible so that the fluidity of the sap will be high, and avoiding raising the temperature at the surface of the board once drying has started. The reader is referred to Appendix II for a detailed discussion of the reasons for so regulating these factors. In accordance with this purpose, the schedule shown in chart 12 was worked out. Runs 12 and 17 followed this schedule, and the moisture content curve in chart 12 shows the course of drying for the test boards of run 12. It will be noted that the temperature and humidity during the initial part of the run are very high. As drying progresses, the wet bulb temperature is decreased, in small decrements at first while the boards are wet, and in larger steps as the boards become dry. This causes an irregular curve for the dry bulb temperature, and such a procedure, it was hoped, would cause the temperature of the surface of the boards to

remain constant, or if it changed at all, to decrease but never rise. How well this was realized can be seen by reference to the experiment carried on in conjunction with run 17 and discussed in the part of this report in which surface and internal temperatures of a board during drying is treated. (See page 25.)

While the charge of boards to be used for run 12 were being steamed, an accident occurred. The boards had been heated up and the steaming period was almost over when it was discovered that the compressor which actuates the control and spray mechanism of the drying kiln was out of commission. It was thus necessary to defer starting the run until the next day. The kiln was shut up tight until then. The next day the temperature had fallen (from 185°) to 100°F (during 18 hours). Then 2 hours of steaming was repeated and the run started. In view of the findings by Mr. Steinour indicating that such a treatment would tend to produce brown stain, the results of this run were not accepted until another run just like it (omitting the excessive heating at first) had been made. That run was number 17, and in the following table and discussion it will be considered with run 12. The schedules are shown graphically in charts 11 and 12.

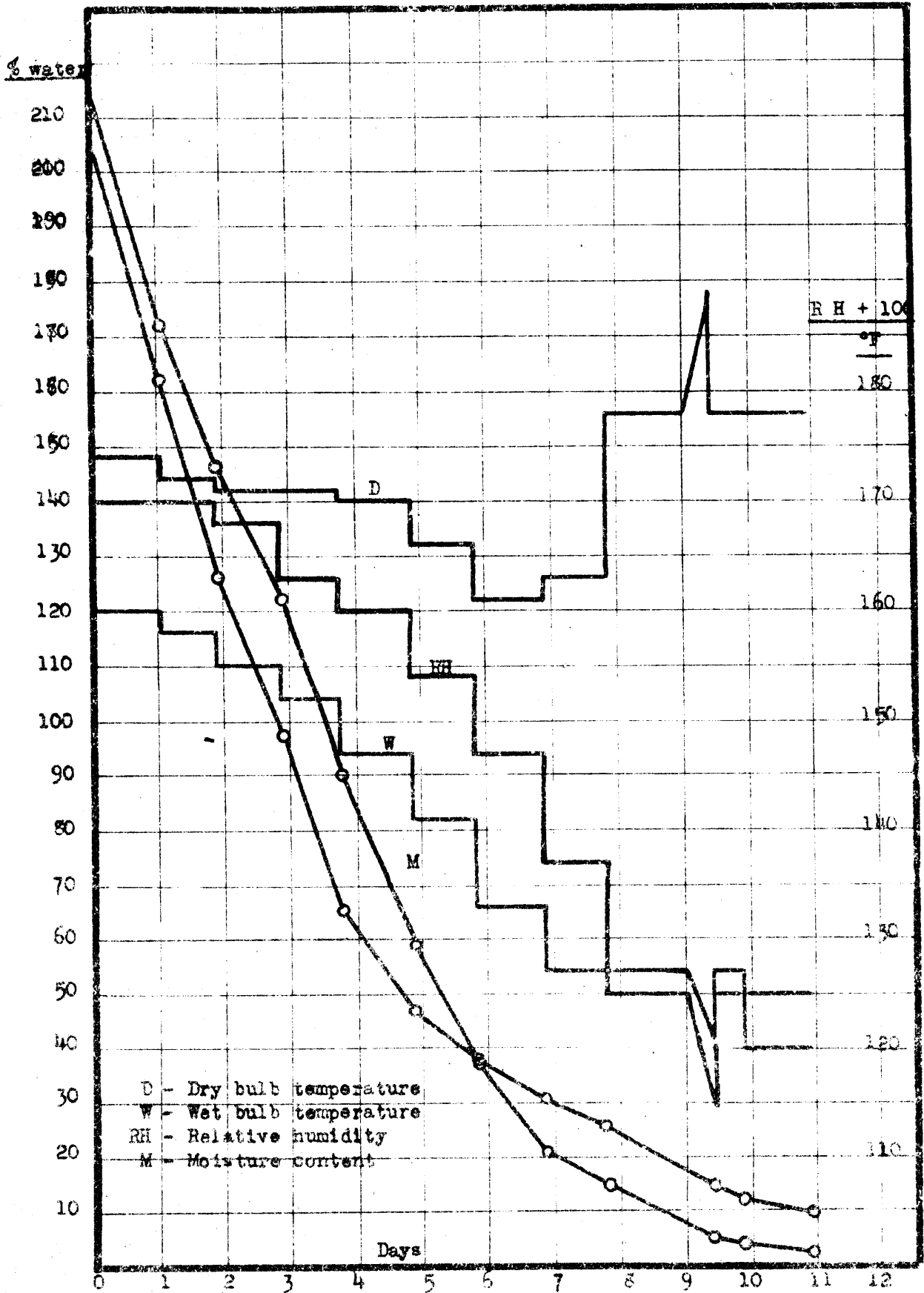|		12	17
Initial moisture content of stock			
Percent dry weight	Average	221	218
	Range	193-234	168-254
Final moisture content at middle of boards			
Percent dry weight	Average	10.1	8.75
	Range	4.6-20.1	5.7-10.7
Initial steaming at 100% relative humidity			
Time exclusive of that necessary to reach temperature - hours.		2	2
Temperature - °F.		185	185
°F above starting temp. of schedule		15	15

Chart 11 - Run No. 12
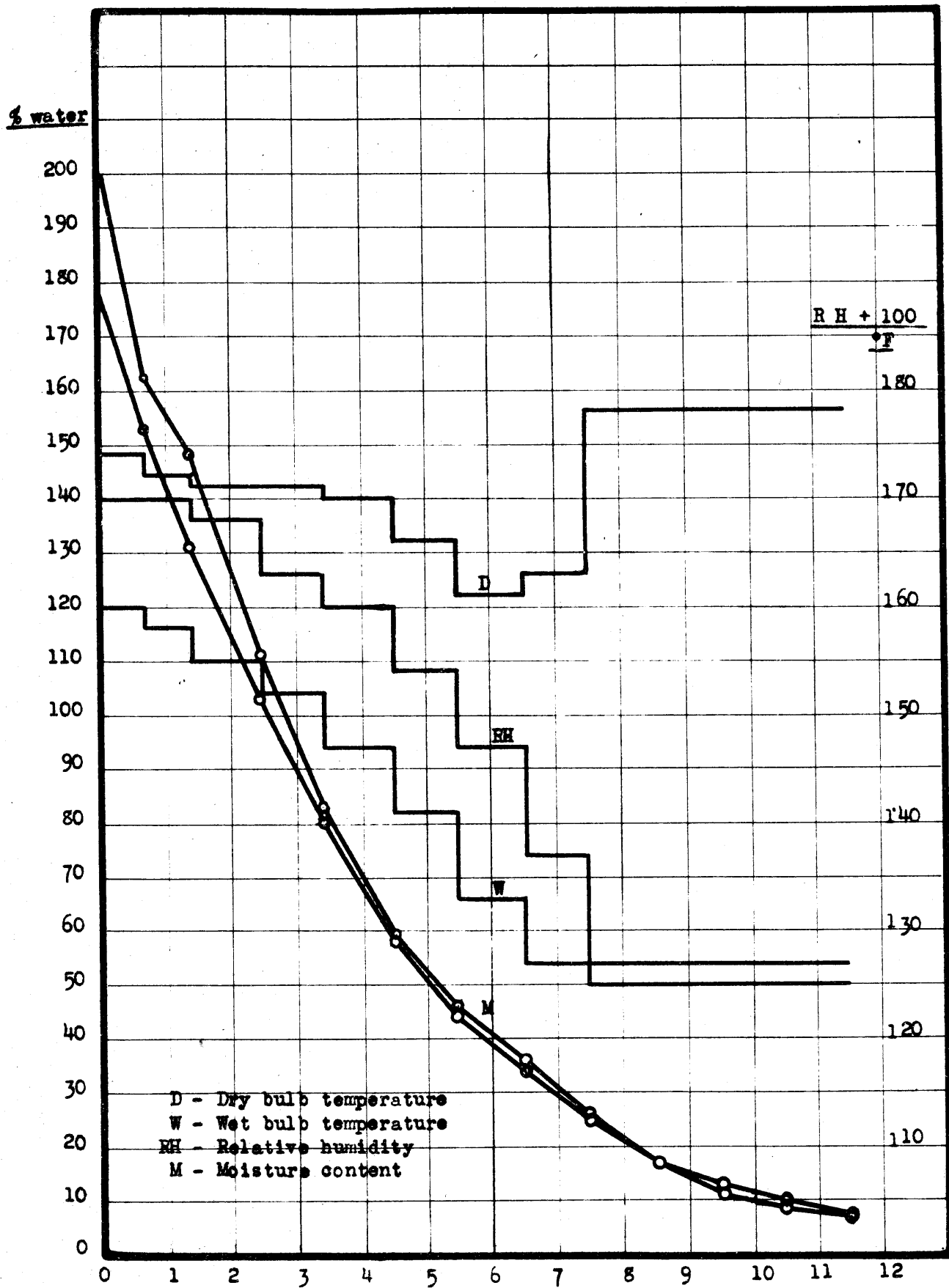
Chart 12 - Run No. 17

The physical condition of the wood from number 12 was apparently good. Only two pieces pinched the saw, and the slotted stress sections bent in much less than was customary with other runs. The wood of number 17, however, pinched the saw badly. The appearance and feel to the touch of this wood showed very strongly those characteristics that distinguish kiln dried wood from air dried wood.

Staining in Runs 12 and 17. - In all the runs of the experiments to be described in the first series of small scale kiln drying experiments with the exception of these two runs, 12 and 17, the rough boards have shown considerable stain on the surface as they came from the kiln. In these two runs, however, there was hardly a trace of stain on the surface. The color of the boards of run 12 was hardly altered at all by the drying, and the boards of run 17 were only yellowed a little. With the most careful examination only a few spots and streaks of very light stain were found on the surface of the boards of these two runs.

After the boards were surfaced to finish size, it was found that in both runs there was stain. It was of light intensity but penetrated deep into the wood. It occurred either in streaks or in diffuse patches, and largely in the heart wood. There was no real difference in the degree of staining between the two runs 12 and 17, so that the accidental over-heating in run 12 had no serious effect.

It turned out that these runs were a good check on each other and the results they gave were exactly the opposite of what was expected. It was expected that these boards would be badly stained on the surface and that the stain would not penetrate far, but as has been stated, the surface

was almost free of stain, and what little there was penetrated deeply and ruined the appearance of the finished lumber. It is evident then that the assumptions on which the original expectations were based were incorrect in some very important respect. This matter will be mentioned later in the report (Appendix II). There is one encouraging feature of this schedule, however, in that the total amount of stain produced in the boards was decidedly less than what had been produced before in other runs, and it is just possible that the high temperature treatment has a beneficial effect by killing enzymes that may be responsible for part of the series of changes that result in brown stain.

Schedules of Runs 13, 14, and 15. - After this result it hardly seemed reasonable to expect to find conditions that would be favorable at temperatures higher than what were used in the schedule of run 12, since the temperature was getting close to the upper limit of temperature that this wood can stand without injury.[a] Runs 13, 14, and 15 were then plan-ned to be something like runs 9 and 8, because it was thought that, al-though the results of 8 and 9 averaged together were not thoroughly satis-factory, these schedules were probably an improvement over previously us-ed schedules, and should be further tested. Also some experiments[b] could be carried out that might give interesting information about the mechanism of the development of the stain, i.e., in run 13 half of the

[a] Experience of the Sugar Pine Lumber Company has shown that temperatures higher than 180°F will cause deterioration of this wood.

[b] Refer to last part of report, page 24 for discussion.

boards were steamed before they were surfaced to finish size and in runs
14 and 15, half of the boards were removed from the kiln about the middle
of the drying period, surfaced to 1 13/16 inches thickness, and examined.
They were then replaced in the kiln. The purpose of these experiments
was to learn the effect of steaming the lumber with respect to staining
and to get an idea, if possible, of when the stain develops during the
drying period. Charts 13, 14, and 15 show graphically the schedules of
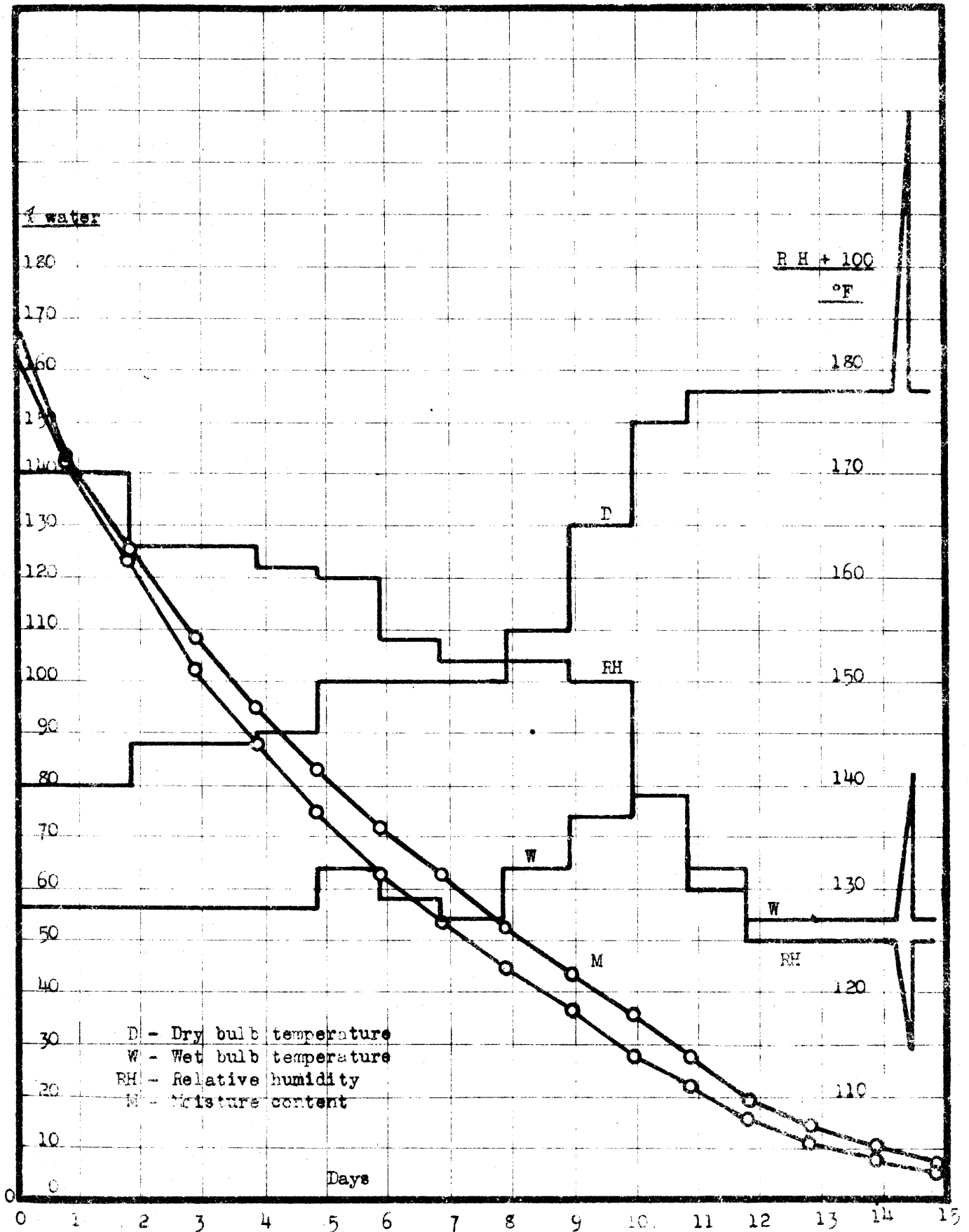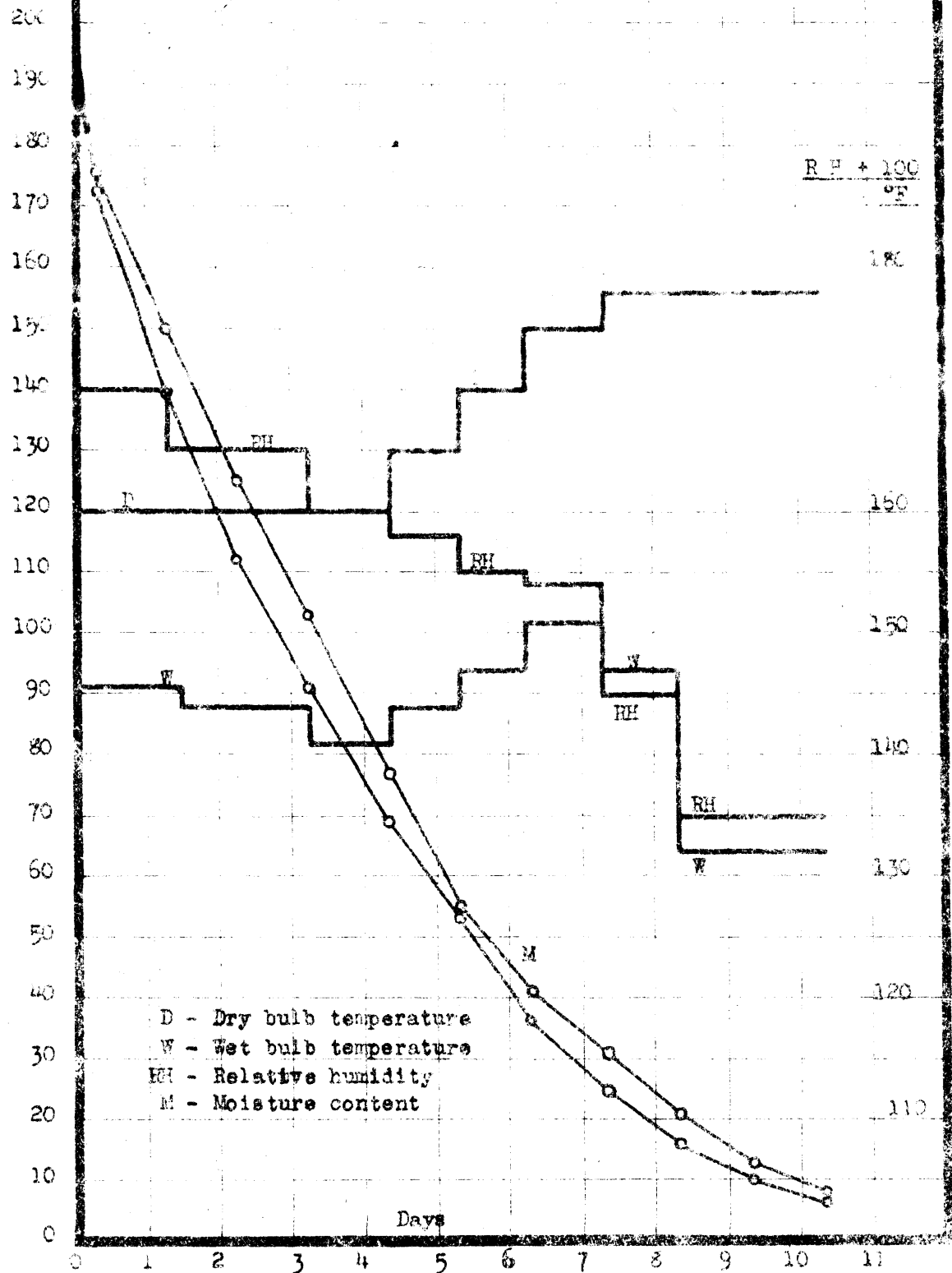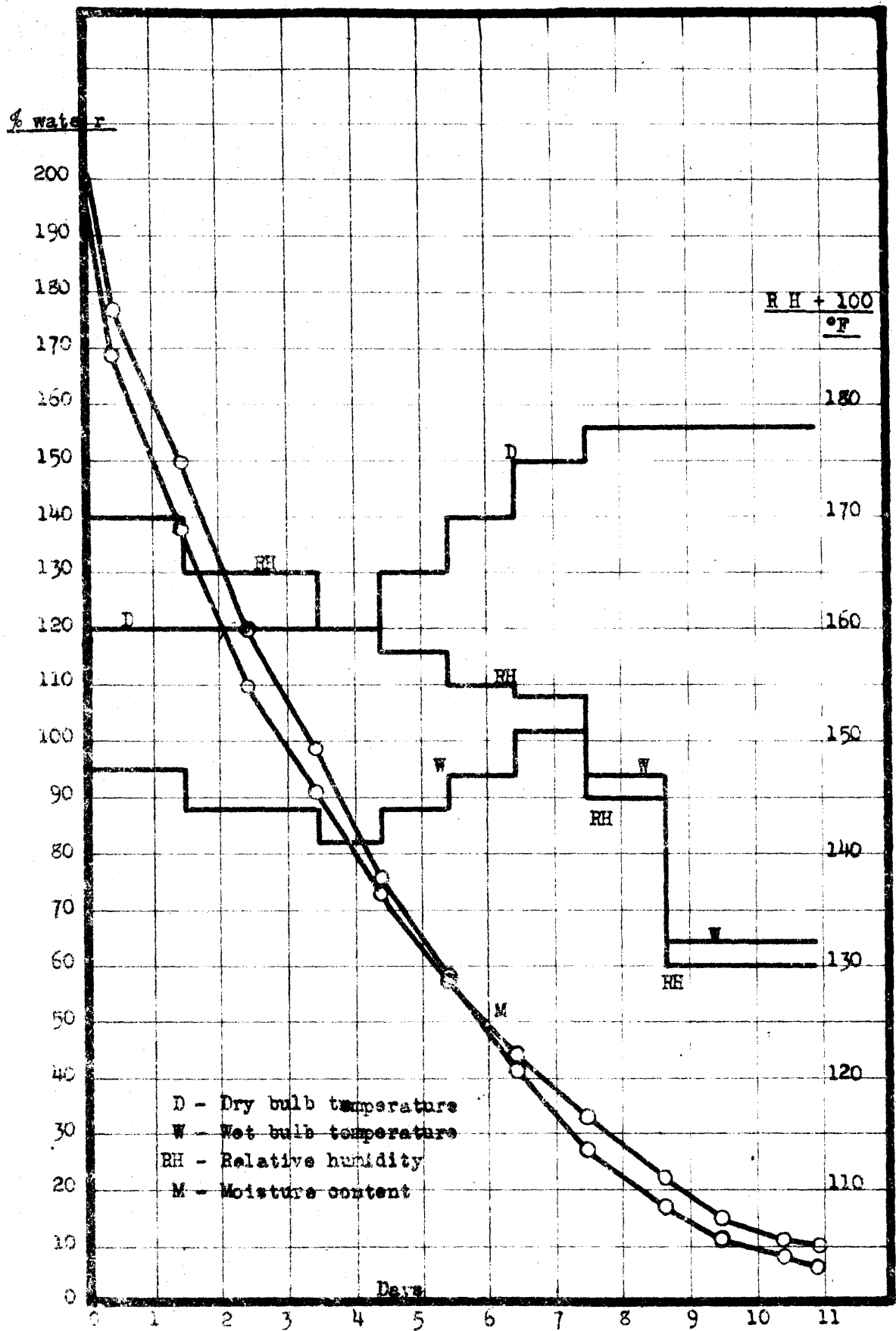these runs.

Chart 13 -- Run No. 13

Shart 14 - Run No. 14

Chart 15 - Run No. 15

		13	14	15
Initial moisture content of stock percent dry weight	Average	181	222	209
	Range	159-205	212-263	204-217
Final moisture content at middle of boards, percent dry weight	Average	12.6	9.9	10.9
	Range	9.5-17.6	5.1-20.6	8.2-12.5
Initial steaming at 100% relative humidity				
Time exclusive of that necessary to reach temperature. - Hours.		2	2	2
Temperature - °F.		155-160	155	175-180
°F above starting temperature of schedule		15-20	15	15-20

For runs 14 and 15 the drying data given above are based on tests made on only half the boards, since the half of the boards that were taken out at the middle of the drying period and surfaced could not be conveniently tested.

The physical condition of the wood resulting from these runs was moderately good, i.e., some of the boards showed a slight to moderate tendency to bind on the saw, and the stress sections showed a moderate tendency to bend in. The half of the boards of run 13 which were steamed were in somewhat better condition than the others. The fact that they were not in a great deal better condition than the rest of the boards is probably to be accounted for in the fact that while the charge in the kiln was cooling the flues were left open. We have since learned that this is very bad practice, because it lets the hot boards cool in an atmosphere of low humidity. Under these conditions the wood has a great tendency to dry and will become badly case hardened if it contains only a small amount of moisture at the start.

Staining in Runs 13, 14, and 15. - Runs 13 and 14 were in moderate to good condition with respect to stain. There were nine and ten boards

respectively in the two runs that were free of stain, and the remaining boards were lightly stained. The situation, however, was not as good for run 15, in which there were only four boards that were free of stain; the remaining boards were lightly to moderately stained. The operator at the planing mill in Pasadena made a poor job of surfacing this lot so that for many of the boards the cut was deep on one side and shallow on the other, making one side bright and clean and leaving the other considerably stained. Had the surfacing been more nearly equal on the two sides this run probably would have come out better. In run 13 there was some blue stain. This undoubtedly developed in transit between Pinedale and the laboratory.

Schedule of Run Number 16. - In order to compare the performance of our laboratory kiln with that of plant size kilns used in commercial practice, it was desired to make a run using stock of a size that is commonly run at Pinedale and of a quality that is commonly dired there without serious staining. Accordingly, a charge was made up of eighteen pieces (nine in a stack instead of seven) of six fourths stock designated "Shop and Better". By using more pieces and smaller stickers the same ratio of areas of free space to wood in the cross section of the air path was maintained and hence the air velocities were very nearly the same as those in our previous runs using eight fourth inch stock. This stock was, of course, much lighter in weight and brighter in color than the sinker stock that was always used in the previous runs. The drying schedule was planned to be one that would probably be used for such stock in commercial practice; so it would be possible to check the results against actual commercial experience. Chart 16 shows the schedule graphically.

Chart 16 - Run No. 16.
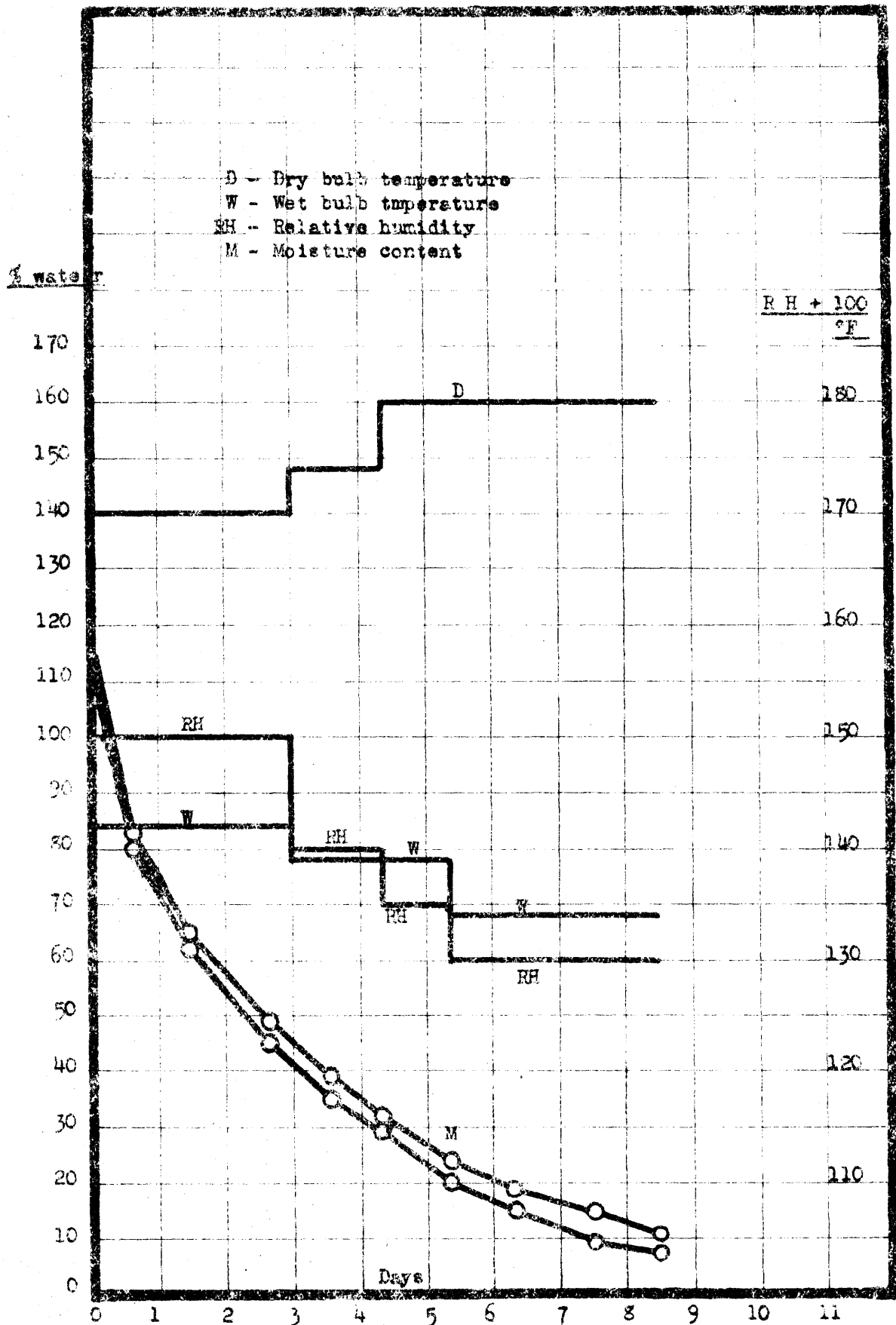
Initial moisture content of stock - Run 16
    percent dry weight   Average   72
                                              Range   54-116

Final moisture content at middle of boards
    percent dry weight   Average   6.3
                                                        5.1-11.7

Initial steaming at 100% relative humidity
    Time exclusive of that necessary to
        reach temperature - Hours.   1.5
    Temperature - °F.   180
    °F above starting temp. of schedule   10

The physical condition of this wood was good, as shown by absence of binding in the saw and only slight warping, although no stress sections were made because of the different thickness of the stock.

This schedule was completed in 204 hours or 8.5 days, which is in good agreement with experience at the mill in Pinedale. We may conclude, then, that results in regard to rate of drying obtained with our laboratore kiln could be satisfactorily reproduced in the large commercial kilns.

Staining in Run Number 16. - With the exception of one board which showed a slight streak of stain at the junction of the heart- and sap-wood and some streaks of stain associated with the knots there was no stain in this run. From nearly every knot there were two narrow streaks of light stain along the length of the grain. These streaks usually went all the way thru the board. The color was dark although the intensity was very light. Aside from these streaks the wood was very bright and excellent in appearance.

A NEW SERIES OF DRYING EXPERIMENTS

From the results of some small scale experiments designed to show the effect of cyanide (see Appendix I) on the browning of sugar pine it seemed very probable that it would be possible to dry timber in an atmosphere containing a small percentage of hydrocyanic acid gas and thus entirely avoid the formation of any brown substance. The results of the small scale experiments just mentioned, as well as several other facts recently learned about the effect of hydrocyanic acid on certain chemical reactions, such as those we think take place when wood turns brown, indicate that in the presence of hydrocyanic acid the chemical reaction which produces the brown stain would not take place at all. If this situation could be realized, then no attention whatever would have to be given to the previous history of the stock being dried, and a schedule which dried wood properly in the shortest possible time could be used. Accordingly, two runs, numbers 18 and 19, were made to test the effect of hydrocyanic acid under actual drying conditions. Since the technique of handling the very poisonous hydrocyanic acid gas was difficult, it was decided to dispense with the tests to find the initial and final moisture contents of the pieces. The operator had been able from experience to detect unusual conditions of moisture content during the process so that as long as no unusual conditions arose the desired information could be obtained from these runs without making the moisture tests.

Schedule of Run Number 18. - The boards for this run were stacked on a tight wooden platform with stickers between courses just as they

were usually stacked in the kiln. Then a gas-tight sheet iron box was
set down over the stack and the contact with the platform made tight. A
generator for producing hydrocyanic acid gas was then connected with the
compartment thus formed and set going, but it was soon evident that it
would not work properly. Some liquid hydrocyanic acid was then procured
and placed in the compartment in such a fashion that it would evaporate
and fill the chamber with gas. The boards were left in the gas over night.
Tests of the strength of the gas showed that the concentration of the
hydrocyanic acid gas became as high as 17% by volume. The next morning
they were placed in the oven and steamed and dried in the usual fashion.
The schedule was planned to be one of moderately high temperature and as
rapid as possible. Unfortunately the control mechanism failed to function
properly for a while early in the drying period and allowed the tempera-
ture to rise quite high. The schedule is shown graphically in chart 17;
the high jog in the temperature curves shows the period just mentioned
when the controls were out of order. The boards were a little lighter
than usual in this run indicating that the average initial moisture con-
tent was about 140%. The final moisture content was about 10%. Steaming
was carried on 1.5 hours at 170°F.

Arrangements had been made to convert the kiln to a condensing type
kiln which would permit closing the flues up tight so that the hydrocyanic
acid would be held inside. Shortly after steaming was completed, a sample
of the gas in the oven was analysed and contained 1.2% hydrocyanic acid by
volume. At the end of two days this value had fallen to 0.2% and at the
end of three days it was 0.02%. The fourth day there was less than 0.001%
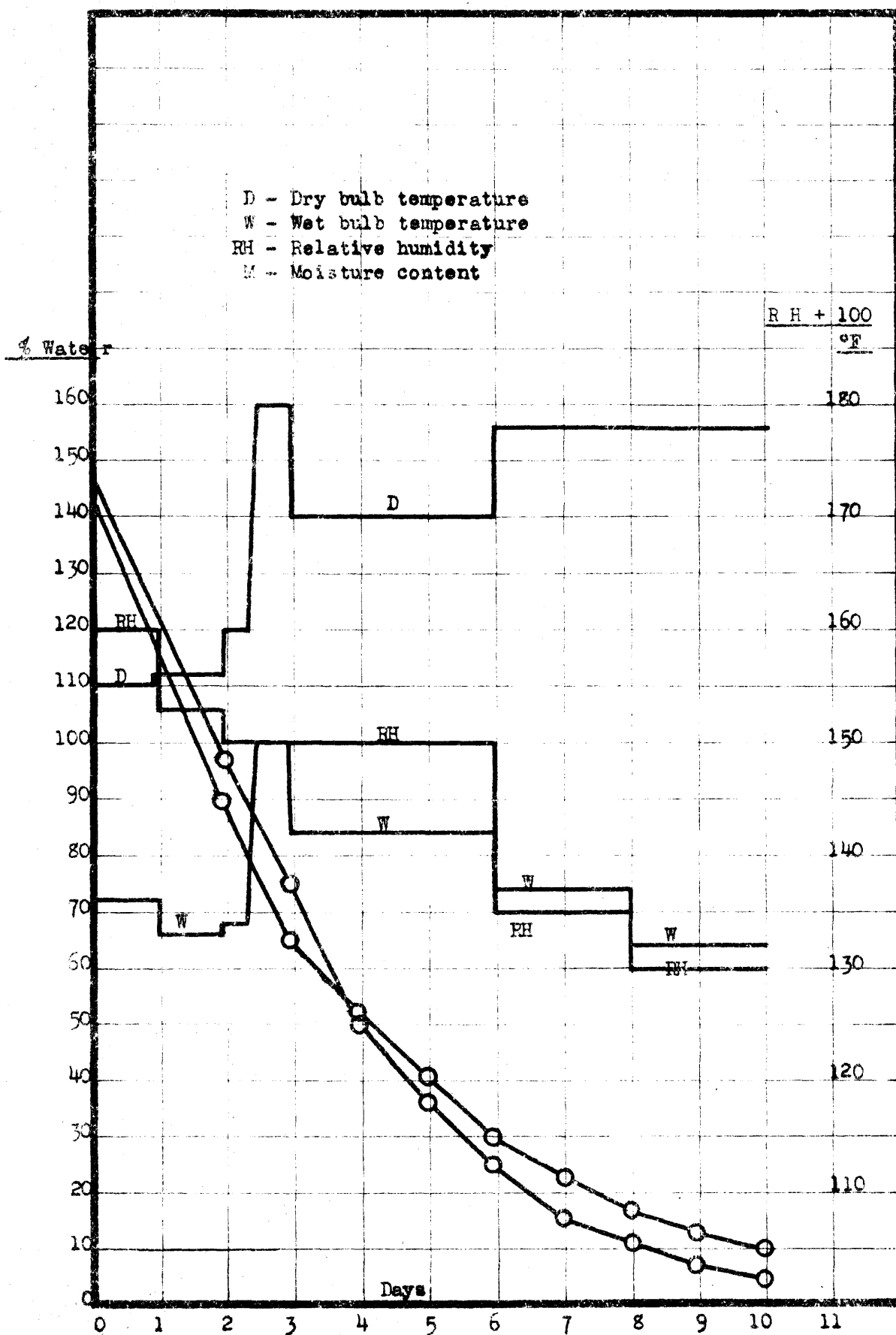hydrocyanic acid present.

Chart 17,- Run No. 18.

Staining in Run Number 18. - There were only four boards free of
stain. The others were quite badly stained, and two of them were the
most severely stained of any yet obtained in all this experimenting. All
of the wood was darkened a good deal, and the color of the stain was de-
cidedly different from any previously obtained. From these observations
it was concluded that the high temperatures reached in this run had caused
decomposition of the hydrocyanic acid, which itself, upon decomposing,
produces a dark brown substance. The concentration of the gas fell off
so rapidly, too, that very probably there was not enough of it to produce
the desired result.

Schedule in Run Number 19. - In accordance with the conclusions
concerning run 18, provision was made to feed hydrocyanic acid gas into
the kiln during the drying in order to keep the concentration of that
gas much higher than it had been in run 18, and the schedule of drying
was planned to maintain lower temperatures and lower humidities. In-
stead of pretreating in a separate compartment, as was done with the
boards of run 18, the boards for run 19 were stacked in the kiln and ex-
posed to hydrocyanic acid gas over night. Analysis showed the concentra-
tion of the gas to be about four percent by volume for the twelve hour
period. Then steam was led into the kiln in the usual fashion. Steam-
ing was carried on one hour at a temperature of 170-180°F. Chart 18
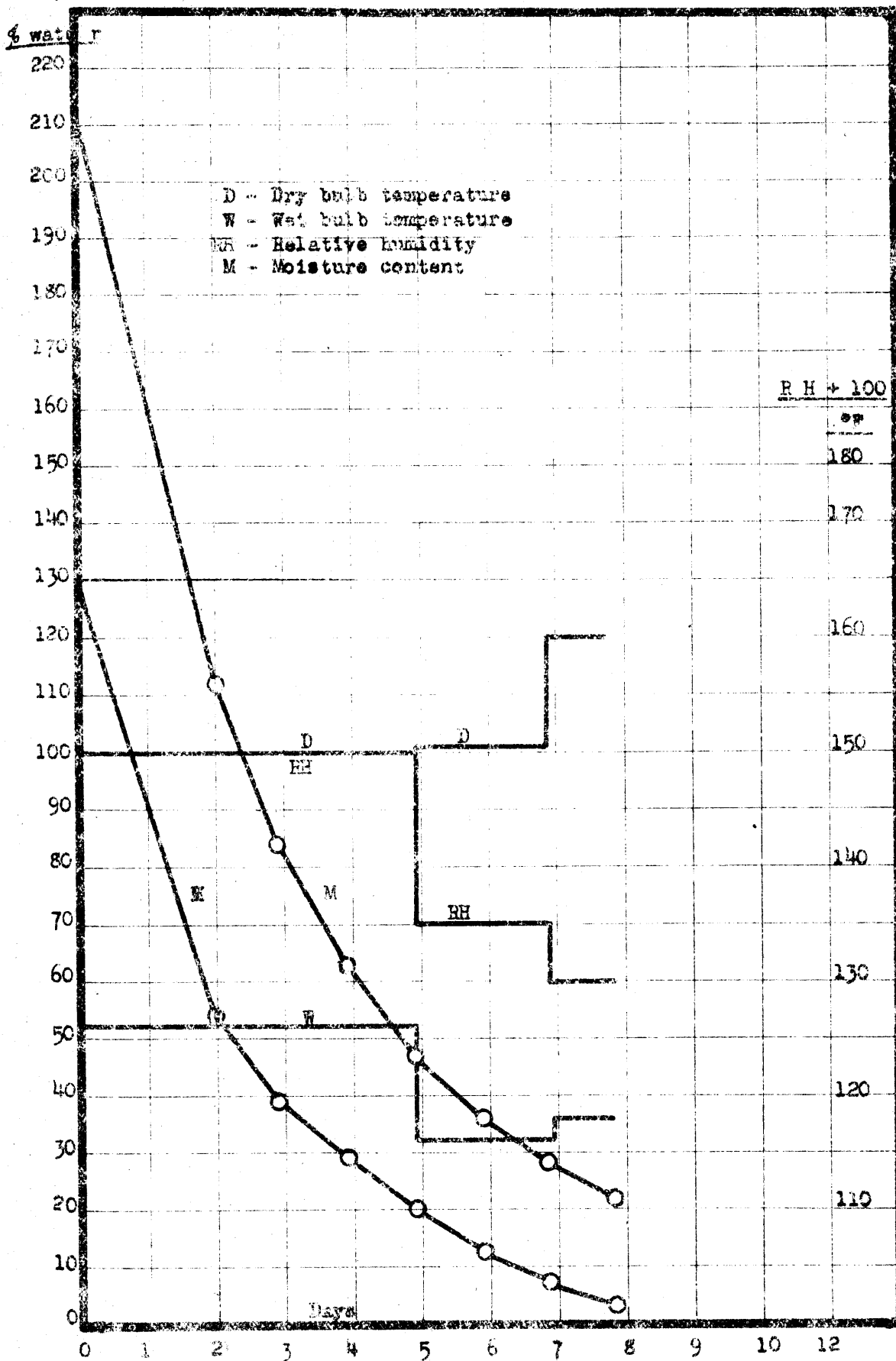shows the schedule that was followed.

Chart 18 - Run No. 19.

During the drying period the concentration of the hydrocyanic acid gas was followed by frequent analyses, and by adjusting the flow of the gas into the kiln, the concentration was held as near as possible at two percent by volume. There was some fluctuation from this desired value, so that occasionally the concentration became as low as one percent or as high as four percent. At the end of 165 hours, or after the moisture content of the heaviest pieces had dropped below thirty percent, the supply of hydrocyanic acid gas was shut off. Leakage from the kiln required that about three tenths of a pound of the gas per hour be fed in to maintain the desired concentration.

The stock for this run was a little lighter than usual, but since the results to be presently described turned out as they did, this condition made no difference.

Staining in Run 19. - During the drying period the pieces remained brighter in color than had been previously witnessed, but when they were removed and examined just prior to being surfaced, some stain was found. After surfacing to finish size there were only three pieces entirely free of stain. The other pieces were lightly stained and one was badly stained.

These two runs show quite clearly that under the conditions of drying the hydrocyanic acid has little or no effect in preventing the reaction that produces the brown stain. In the small scale experiments (see Appendix I) there must have been different conditions that were very important to the desired result.

EXPERIMENTS COLLATERAL WITH KILN DRYING EXPERIMENTS

Inspection of Pieces During the Drying Period. - During runs 14 and 15 (see pages 9-10) half of the boards were removed from the kiln at about the middle of the drying period(when average moisture content was about 50 %) and surfaced to finish size (1 13/16 inches). In run 14 the amount of stain observed in the pieces taken out at the end of the first half of the drying period was practically the same as that in the pieces taken out at the end of the whole period, but since there was very little stain developed in this run anyway, the result was indicisive and it was decided to try the same thing again in run 15. When the first batch of boards was taken out at the end of the first half of the run an interesting observation was made. The writer watched the pieces as they came out of the planer and only one piece showed any stain, but when the boards were hauled back to the laboratory and examined there, four of the seven pieces were found to have considerable stain. This stain was light, but sufficiently intense that it could not have been overlooked during the first examination at the planing mill. The time elapsed between the two examinations was about half an hour. Again, as in run 14, there was no certain difference between the amount of stain found at the end of the first half and at the end of the second half of the run.

On the basis of these observations, then, it follows that the damage is done to the lumber during the first half of the run, which is, of course, the reasonable thing to expect. The observations made while examining the first batch of pieces in run 15 tells us two interesting things. It substantiates in a decisive way the conclusion previously

made that the browning of sugar pine takes place in two stages, the
production of a colorless substance not at first present in the wood,
and then subsequently the oxidation of this in contact with air to form
a brown substance; and it shows that at a short distance under the sur-
face of the wood there may not be enough oxygen present to oxidize the
substances produced during the first stage of the browning process.

Surface and Internal Temperatures of a Board. - Before starting
run 17 (see page 5) two copper-constantan thermo-couples were prepared
and arranged so that the temperatures of the surface and of the middle
of one of the boards could be determined while the board was being
steamed and dried. One of these thermo-elements was thrust into a
small groove made in the surface of the board with a sharp instrument
and the fibers of the wood thus torn up were carefully pressed down over
the element. The temperature of the surface of the board should then be
quite accurately given by this element. Then a hole was bored midway be-
tween the upper and lower surfaces of the board from and perpendicular to
one edge to a depth of five inches with a 3/64-inch drill. The other el-
ement was thrust into this hole, which located it midway between the ends,
and one inch from the midpoint between the edges (the board was two inches
thick, twleve inches wide and forty-two inches long). The thermo-element
on the surface was directly opposite the element in the middle of the
board. "Cold junction" temperature was room temperature and read on a
mercury glass thermometer. A Leeds Northrup Potentiometer Indicator was
used to determine the electromotive force set up by the thermo-elements
and from a calibration curve for the elements the temperatures correspond-
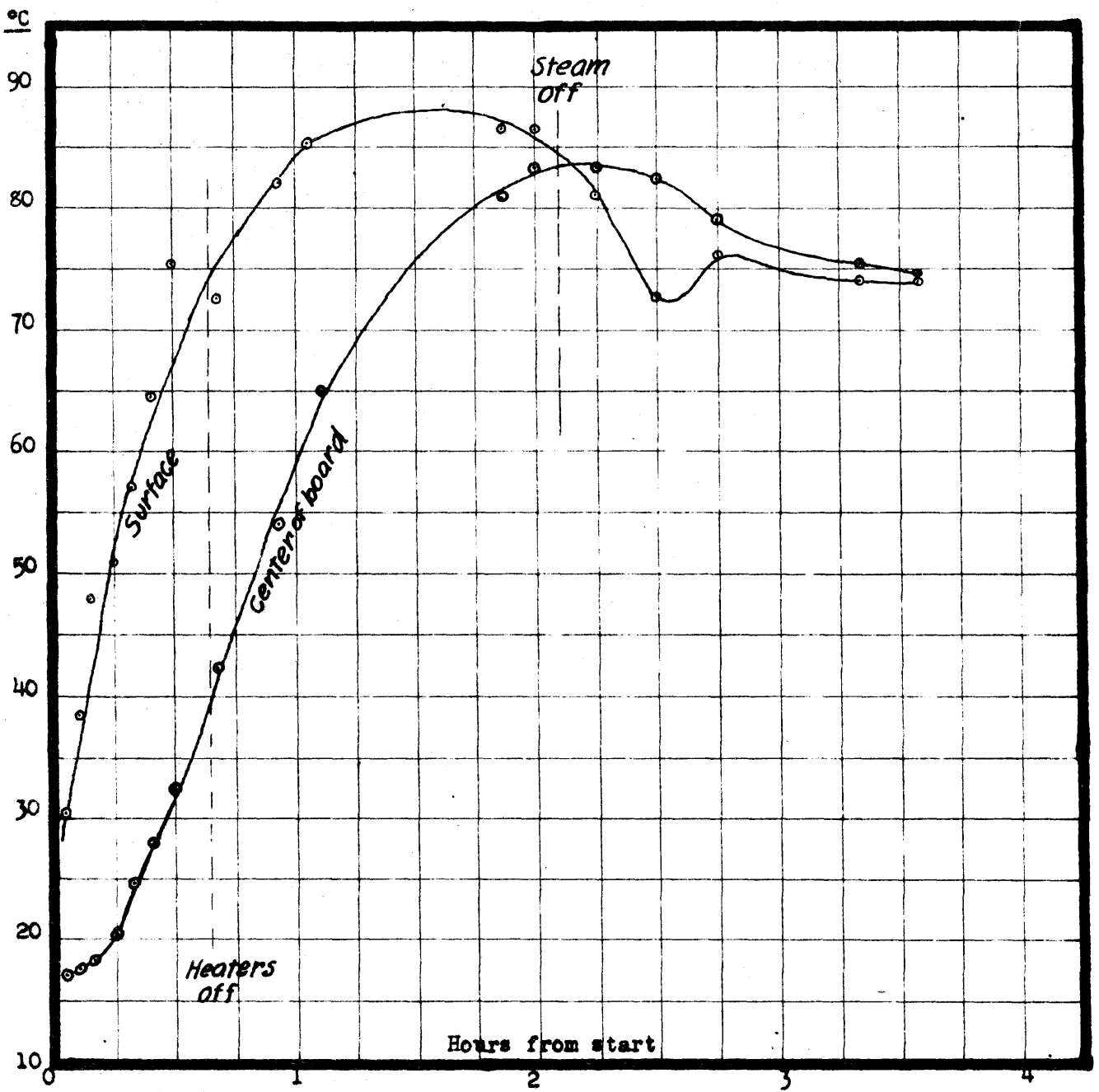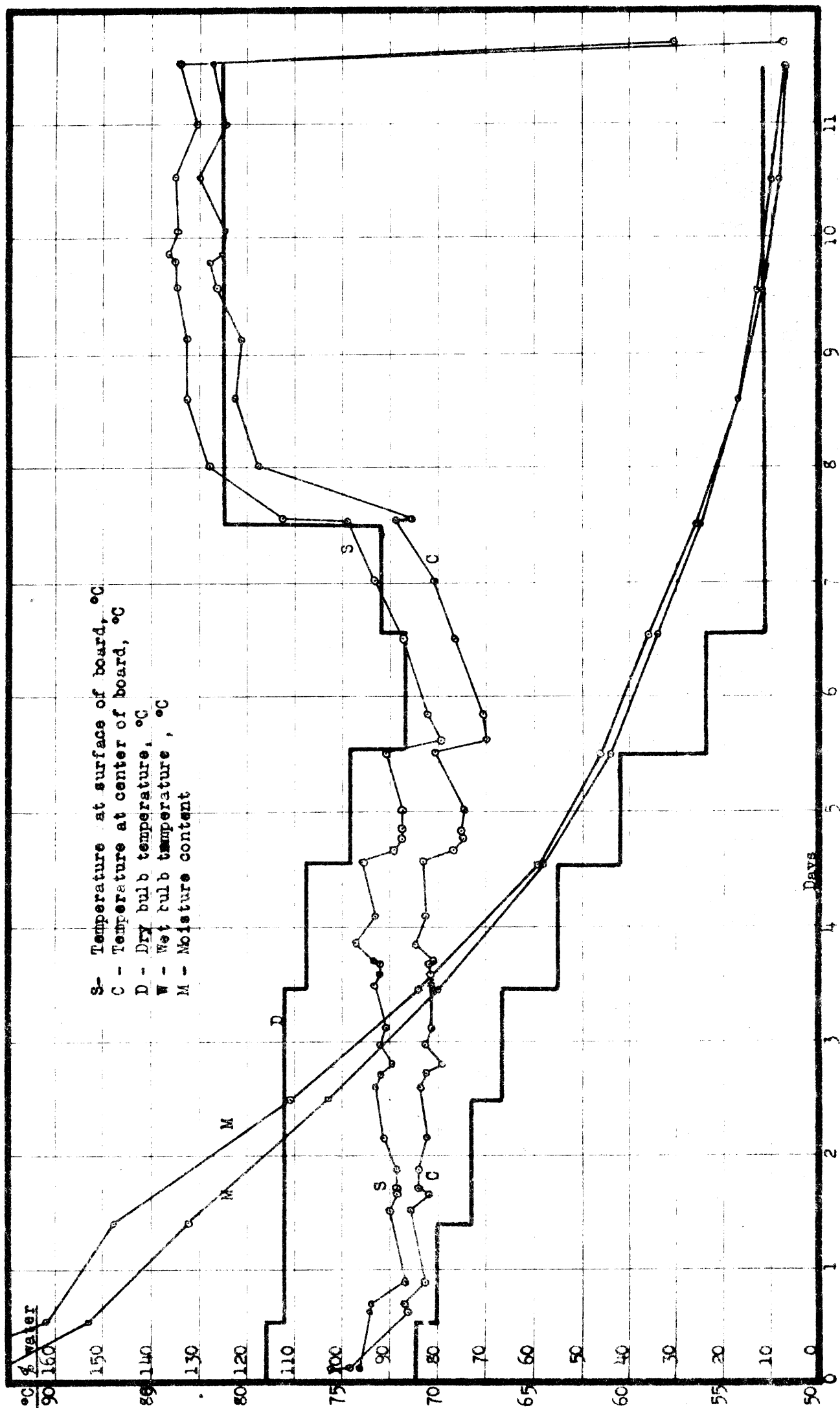ing to electromotive-force readings were obtained.

Chart 19

Chart 20

Legend:
S — Temperature at surface of board, °C
C — Temperature at center of board, °C
D — Dry bulb temperature, °C
W — Wet bulb temperature, °C
M — Moisture content

The accuracy of the temperature reading was probably well within one degree centigrade. Care was taken to avoid conditions that would develop parasitic electromotive forces in the system, and since one degree centigrade corresponded to about 0.043 millivolts and it was easily possible to set the instrument and read it to within 0.02 millivolt, there should not have been any appreciable error.

The data for the readings taken during the steaming and drying periods are presented in two sets of curves, charts 19 and 20, which are drawn to somewhat different scales. The first of these sets of curves shows the temperatures during steaming and for a short time thereafter, and the second set of curves shows the temperatures during drying as well as the wet and dry bulb temperatures of the air.

In this run, as in all the others, the steam spray and all the electric heaters were turned full on at the start. Then at the end of about thirty-five minutes the thermometers of the kiln indicated that the desired temperature was reached; at this time the electric heaters were turned off as shown on the chart. Then the temperature was controlled as well as possible by manually operating the steam valve until the temperature within the board was found to be as high as desired. The steam was then turned off and the kiln was opened in order to remove the water condensed on the floor. The temperature and humidity were then regulated to the desired value for the start of the drying period.

It is interesting to note on these curves that although the whole board was at first heated thru to a high temperature and then allowed to cool down to the temperature of the drying schedule, when equilibrium of temperature was established during drying, the temperature of the middle

of the board was always a few degrees lower than that of the surface. Since this sort of thing would be possible only when temperature equilibrium is very quickly established, this fact is evidence that the thermal conductivity of wet wood, unlike dry wood, is very high. The reason for the temperature of the center of the board being lower than that of the surface of the board is that the moisture content of the surface is lower, and in order for it to be in equilibrium with the inner parts of the board with respect to vapor-pressure of the water it contains, its temperature must be slightly higher.

Examination of the first portions of the curves of Chart 19 brings out two rather interesting bits of information. In the first place the rapid change in the slope at the beginning of the curve for the middle of the board can hardly be accounted for entirely by the initial rapid change of the temperature difference. The following table shows that although the temperature difference was increased about two and a half fold, the slope increased almost six fold (from time = 3 minutes to time = 20 minutes).

Time after heat was turned on min.	Temp. dif. between middle and surface of board °C	Slope °C per hour
0	0	0
3	13.2	6
6	21.0	10
15	31.6	34
20	32.4	52
25	46.6	52
30	43.0	52
55	28.0	52

If heat conduction thru wet wood were as thru a homogeneous body, the slope (for small intervals of time) would be roughly proportional to the temperature difference. Since this evidently is not true, we must conclude that wet wood must be considered a heterogeneous body in heat conduction considerations. That is, wet wood does not conduct heat the way a brass rod would conduct when its end was heated, rather it is like a steam line when the boiler is fired up; a wave of heat travels from one place to another, heating any part of the line very quickly as is passes.

Secondly, during the heating of this board a steady state was established as is shown from the straight sections of the curves between fifteen and thirty minutes after the start of the heating. It will be noticed that the slopes of the two curves in this region are not greatly different, which is further evidence that the heat conductivity of wet wood is relatively great. This can be seen qualitatively by considering that if the heat conductivity of this material were infinite, the two curves would be parallel and not quite as steep, and if it were zero, the curve for the temperatures at the center of the board would be horizontal, and the one for the temperatures at the surface would be almost vertical.

The board to which these data relate had a moisture content of almost exactly 200% at the start of the run, and the distance between the two thermo-elements at the surface and middle of the board was just one inch.

Further discussion of the assumptions and reasoning underlying planning of the schedules used for runs 12 and 17 will be found in Appendix II. Appendix I gives the data and some discussion of small scale

chemical experiments with wood and sap relating to the brown stain problem. Appendix III contains data and discussion of some experiments on moisture gradient during drying. This series of experiments (run 11) was suggested by Mr. Steinour's work given in Appendix B of his Thesis and was expressly planned to check experimentally his conclusions based on theoretical considerations.

Considerable difficulty was encountered during this work in preventing the corrosion of the inside lining of the drying oven that was used as a kiln. The lining was of galvanized iron, and the zinc coating continually made trouble by causing protective coatings to peal off. Several coatings were tried in the oven and some more were tested on small sheets under conditions that duplicated conditions of operation quite well.

Aluminum paint alone [a]	Quickly peeled off, especially where moisture condensed.
Asphaltum paint, dried at [b] room temp., covered with 2 coats aluminum paint	Gave fair results.
Bakelite enamel, 5 coats [a] baked	Excellent protection on iron, scaled badly from zinc.
Asphaltum paint, baked [b]	Best protection of any.
Duco lacquer [d]	Very poor protection.
Brolite lacquer [e]	Very poor protection, but better than Duco.

a) Sherwin Williams Aluminum Paint in varnish vehicle.
b) U.S. Varnish Company's Acid Proof Paint. (Hasbrauch, N.J.)
c) Black Enamel XH989 from Bakelite Corporation.
d) Duco clear spray lacquer.
e) Clear brush lacquer from Brown-Leithold Co., Los Angeles.

DISCUSSION OF DRYING SCHEDULE STUDIES

In the following few paragraphs an effort will be made to review in brief form all of the drying schedules tried and their results. It will be possible to speak of the results only in relative terms because of the fact that stain on small pieces such as were used in the laboratory kiln looks much different from the same degree and quantity on the large pieces handled in commercial practice. That is, remarks concerning stain may be consistent relative to different experimental runs but the same extent of staining in an experimental and a commercial run might, because of the above mentioned difficulty, be graded differently. Another thing that must be borne in mind is that especial effort was made at the mill to select for us the stock which most often gave them trouble with respect to stain. We have the feeling that the stock we have been receiving would stain always for them in large degree although there is some uncertainty about it. Thus, when a run comes out with only a small amount of stain, all other factors being the same, one may conclude that it is an improvement over existing commercial practice. One remembers also that a good deal of skill and judgement was necessary on the part of the man who selected the stock for us, for if he made a mistake and sent us a shipment of stock that had less tendency to stain than usual, or if he happened to find stock that was unusually bad, conclusions based alone on the results of drying it could not mean much. It is decidedly unfortunate that this particular factor, which is so very important, could not have been better known and controlled.

In the following table the characteristics of the schedule and the results with respect to staining are summarized in a word of phrase in each case. The temperatures of initial steaming are not included, because it seems there is no relation between steaming temperature and amount of stain. This is probably because the time that steaming lasted is negligible in comparison to the length of the schedule. The second column describes the dry bulb temperature at the start; the third column describes the humidity; the fourth describes somewhat the nature of the schedule; the fifth, the final humidity (final dry bulb temperatures were 178 or 180°F without exception); the sixth gives in a word the relative amount of stain in the surfaced boards; and the seventh, the amount of brown material produced in the boards (observed both before and after surfacing). In case the amount of stain reported in the sixth column is less than that reported in the seventh column the penetration was not deep, and where the reverse is true the penetration is deep.

No.	Temp. at start	Humidity at start	Description of Schedules Changes during drying	Final Humi.	Stain Surface	Stain Total
1	Very low,105°F	Low, 50%	Dry bulb continually raised, humidity lowered continuously.	8%	Light	Moderate
2	Very low, 93°	Moderate, 65%	Dry bulb continually raised, humidity dropped; both slowly at first	10%	Slight	Small
3	Very low, 105°	Moderate, 55%	Dry bulb raised slowly, then rapidly; humidity lowered continuously	10%	Light	Moderate
4	Low, 135°	High, 80%	Dry bulb lowered to 120°F; constant 6 days; raised to 175°F, humidity lowered continually, with 3 steaming periods.	10%	Light	Moderate
5	Low, 135°	High, 85%	Dry bulb raised slowly during 7 days, then rapidly; humidity lowered gradually	10%	Light	Moderate
6	Moderate,150°	High, 70%	Dry bulb constant; humidity lowered slowly, then rapidly.	30%	Light	Moderate to large
7	Moderate, 140°	High, 70%	Dry bulb raised slowly, then rapidly; humidity lowered slowly, then rapidly	13%	Heavy	Very large
8	Moderate, 140°	High, 70%	Dry bulb raised slowly, then rapidly; humidity lowered slowly, then rapidly	25%	Slight	Small
9	High, 160°	High, 70%	Dry bulb constant, then raised rapidly; humidity lowered slowly, then rapidly	25%	Moderate	Moderate
10	Moderate, 145°	High, 70%	Dry bulb constant, then raised gradually; humidity constant, then lowered slowly.	25%	Heavy	Very large

No.	Temp. at start	Humidity at start	Description of Schedules Changes during drying	Final Humi.	Stain Surface	Stain Total
12 17	High, 174° "	High, 70% "	Dry bulb lowered slowly, then raised rapidly; humidity lowered slowly, then rapidly; surface temperature constant.	30%	Light	Small
13	Moderate, 140°	High, 70%	Same as 7, 8.		Moderate to light	Moderate
14	High, 160°	High, 70%	Same as 9.		Moderate to light	Moderate
15	High 160°	High, 70%	Same as 9, 14.		Moderate to light	Moderate
16	High(6/4) 170°	Low, 50%	Dry bulb constant, then raised; humidity lowered gradually.	30%	Slight	Very Small
18*	Moderate, 155°	Moderate,60%	Dry bulb raised rapidly; humidity lowered gradually	30%	Moderate	Small
19*	Moderate, 150°	Low, 50%	Dry bulb constant, then raised to 160°; humidity constant, then lowered	30%	Moderate	Small

* Dried in an atmosphere containing hydrocyanic acid.

In reviewing the above table, there are two factors the operation of which can be observed separately, first the relation of the type of schedule to the depth of penetration, and second the relation of the amount of coloring matter (last column) produced to the type of schedule. The first five runs, which started out at low temperatures, showed strikingly shallower penetration than the runs that followed. Runs 12 and 17 showed the deepest average penetration of stain and were the ones having the highest temperature at the start. See Appendix II for a more detailed discussion of this matter. If runs 7, 8, and 10 are not considered because they had unusual histories previous to their being dried, it will be found that the second factor worked in just the opposite way from the first one mentioned above. That is, runs starting at a low or even moderate temperature develop a larger amount of stain during drying (not taking into account where it is deposited) than those that start out at a high temperature and maintain it for some time. Although the relationship is not very striking, a careful examination of the more detailed descriptions of the staining given in the part of the report where the individual runs are described will bring it out.

From the first relationship noted in the preceding paragraph it is evident that the schedule designed especially to avoid deep penetration of the stain (runs 12 and 17) actually accomplished just the opposite effect (see Appendix III). It was based on an incorrect assumption about the mechanism of evaporation. In runs which produced conditions that this schedule was designed to avoid, then, one would expect relatively less penetration, which we find to be true as in the first five runs.

The reason this fact was overlooked is that in these runs a large amount of stain was produced, and thus the effect was masked. Schedules like these were used in commercial practice and found to be unsuccessful, undoubtedly for the same reason.

The second relationship must mean that there is some organic enzyme (b) present in the wood which greatly aids the production of brown stain and which is not destroyed by low temperatures, or even the highest temperatures encountered in permissible schedules unless these temperatures persist a long time. Then, too, a fact that is often overlooked is that the temperature of a wet board is only slightly above the wet bulb temperature, and not until after the board becomes dry and the damage has already been done does it approach the dry bulb temperature. Few schedules, then, have temperatures high enough and for a sufficient length of time that one would expect enzymes to be killed. It is an unfortunate circumstance that a schedule which would naturally cut down the amount of stain produced (like Number 12) and incidentally also give good physical condition is just the kind that will give the maximum penetration.

In conclusion, then, the writer suggests that it might be possible for the kiln operator to decrease the loss due to stain, although it would probably be impossible to eliminate it entirely, by using schedules which would allow considerable high temperature treatment at the start, in order to kill enzymes, and by arranging the schedule so that the surface temperature of the board would rise quite rapidly and over quite a range during the first two thirds of the schedule. These conditions are, of course, incompatible unless something like the following is done: steam at a high

temperature such as 180°F (82.5°C) long enough that all the boards are
actually heated thru for considerable length of time, as for eight hours
(or a shorter time if a higher temperature is used), then allow to cool
adiabatically in cool air of low humidity followed by a low-temperature
low-humidity drying schedule, during which the wood is occasionally steam-
ed. Following each steaming period the wood should be adiabatically cool-
ed to such a temperature as will follow right along the low-temperature
low-humidity schedule.

SUMMARY

1. Further drying schedules were tested with a semi-plant size
drying kiln.

a. It was found that if the surface temperature of the drying board
   was held constant during drying, penetration of stain was maximum,
   and a minimum if surface temperature increased over a considerable
   range.

b. High temperature drying the early part of the schedule decreased the
   amount of stain material produced indicating that organic enzyme
   action is important in production of brown stain.

c. Hydrocyanic acid was found to be ineffective under conditions of dry-
   ing in inhibiting the reactions causing brown stain.

2. Further study was made of the reactions of wood and sap to various
chemical reagents.

3. Moisture content of wood as a function of the distance from the
drying surface at different stages of the drying process was studied in a
series of moisture determinations.

ACKNOWLEDGEMENT

APPENDIX I

In this appendix a number of laboratory experiments dealing largely
with the behavior of sap expressed from fresh or partially air-dried sugar
pine will be described and in some cases discussed briefly.

Effect of Iron Salts on Browning of Sap. - To the first of three 20 cc.
portions of filtered sap from partially air-dried sugar pine was added 1
drop of 4% ferric chloride solution and to the second three drops were
added. Nothing was added to the third. These three solutions in 100 cc.
cork stoppered Erlenmeyer flasks were placed in a cabinet heated to 80° C.
After 15 hours the first two were considerably darker than the blank, the
second darker than the first. After 20 hours the same relationship exis-
ted regarding intensity of color.

The above experiment was repeated with a new batch of filtered sap,
adding 1/5, 3/5, 1, 3, 6, and 0 drops of 4% ferric chloride solution to
20 cc. portions of sap in 100 cc. cork stoppered Erlenmeyer flasks. This
time 3 and 6 drops of ferric chloride solution caused a turbidity and bluish-
brown color in the sap. After 8 hours held at 80°C the blank and the first
three were browned, the intensity increasing with increasing amounts of iron.
The coloring in the others was obscured by the turbidity and the color
first produced on adding the iron salt.

This shows definitely that iron is a strong catalyst for the reactions
producing brown stain. In fact it is found to be a strong catalyst for
the production of stain in most vegetable substances that turn brown. For
instance, if one will take two apples of the same variety, cut one in two
with a knife and break the other in two he will find that the one cut
with the knife will turn brown in the air much more rapidly than the one

which was broken. It has often been noticed with the sugar pine that on eht high spots of the rough sawed boards a superficial layer of brown stain develops much more quickly than stain ordinarily develops elsewhere. These spots were probably rubbed against the saw blade during cutting and against iron rolls on the conveyors. Whether this iron picked up during cutting and handling would be carried into the wood before or after the drying period has not been settled. It should also be borne in mind that the wood itself probably contains small quantities of iron.

Experiments with Concentrated Sap. - 425 cc. of sap from partially air-dried boards was evaporated under reduced pressure to about 25 cc. Time taken was 1.5 hours and maximum temperature 40°C. The resulting syrup was dark colored, somewhat bluish, had the appearance of a colloidal suspension, tasted sweet, and gave a warm sensation in the throat as cough remedies often do.

Another batch of sap was dried in the sun in a flat crystallizing dish. A colorless, sweet tasting syrup resulted. After the syrup had become almost completely dry crystals began to separate out and finally spread thru the whole mass.

Five cubic centimeters of the syrup obtained by evaporating under reduced pressure were placed in a large test tube and 0.2 cc. of concentrated hydrochloric acid were added: the solution became straw colored and clear when it was warmed. It was boiled 2 minutes; then, with suction, evaporated down to a pasty mass. A small test tube containing ice water was suspended in the large tube. Then the latter was heated with a free flame; a vapor

was driven off from the mass on the bottom of the large tube which conden-
sed as yellowish-white crystals and water on the small cold tube. This
apparently crystalline material rapidly changed to a dark-brown gummy
substance in the air (in 3-5 minutes). Some of it was quickly scraped
off and dissolved in water made alkaline with NH_4OH and a few drops of
$AgNO_3$ solution were added; a fine black precipitate resulted instantly.

There are several substances among the polyhydroxy phenols which re-
duce silver quickly in ammoniacal solution, and at least one of them,
quinol, $CH_4(OH)_2$ (1,4), gives a crystalline sublimate that turns brown on
exposure of its aqueous solutions to air. Many of these substances also
are produced by acid hydrolysis of glucosides which in turn commonly oc-
cur in plant fruits, leaves, and stems (C).

Further Tests for Tannic Acid. - A gelatin solution containing 10 gm.
of best quality gelatin and 100 gm. of sodium chloride per liter was pre-
pared (D). Equal volumes of this reagent and fresh filtered sap were
mixed; no precipitate or cloudiness resulted. To test the reagent a solu-
tion of tannic acid containing 1 gm. in 15,000 gms. of water was prepared.
One cc. of this gave a distinct white precipitate with the gelatin reagent.
Browning in sugar pine and in sugar pine sap, then, can hardly be attribu-
ted to the presence of tannic acid.

Formation of Staining Agent by Acid Hydrolysis. - To 15 cc. of sap
was added 1 cc. of concentrated hydrochloric acid. This solution was
heated to boiling and kept boiling just 2 minutes. It was then cooled
under the tap and made exactly neutral to litmus with 6 n. ammonium hy-
droxide solution; the solution became slightly browned. This solution

was placed in the cabinet at 80°C in a 100 cc. cork stoppered Erlenmeyer flask. In two hours it had developed considerable brown color and in eight hours it was intensely colored. A blank of the same lot of sap in eight hours under the same heat treatment acquired only a faint brown color. This shows that a treatment commonly used to hydrolyze complex substances can accelerate and increase production of brown stain. It follows that very probably hydrolysis of some complex compound is a part of the process that produces brown stain.

Tests for Glucose. - (E) Three cc. of the concentrated sap described above were diluted with an equal volume of water and 5 drops each of phenylhydrazine and glacial acetic acid were added; the solution became turbid and an orange color was produced. The mixture was immersed in boiling water for 30 minutes; the color had changed to deep red but no other change was evident. A drop examined under the microscope and found to be a suspension of deep-red colored oil drops.

Two cc. of the above mentioned concentrated sap were diluted to 6 cc. with water, boiled 2 minutes with 1 gm. of freshly ignited magnesium oxide and filtered; this treatment removed some of the color. The filtrate was boiled 2 minutes with three drops of concentrated hydrochloric acid, cooled and made neutral to litmus with 6 n. ammonium hodráxide solution. The test for glucose was then made just as in the previous experient and the same result was observed.

About 3 cc. of the concentrated sap were diluted to 6 cc. with water. Horne's Basic Lead Acetate (F) was added in small portions until no more precipitate resulted. The mixture was filtered and sodium sulfide solution was added to the filtrate as long as a precipitate formed, which was also

filtered out. The filtrate was made neutral to litmus with hydrochloric acid, then boiled with acid, neutralized, and tested for glucose just as in the previous experiment; again no evidence of glucose.

It was realized that this would not be a very satisfactory method of testing for small amounts of glucose because other things present would undoubtedly interfere seriously. It was tried, then, on the slim hope that it might work anyway. It would be of considerable interest if it should be possible to detect the presence of glucose, or some of the other simple sugars, in the sap or in hydrolyzed sap, for this would substantiate the theory that there exists in the wood a glucoside which for various causes is decomposed to glucose or other simple sugars and some phenol-like substance which turns brown in the presence of oxygen and moisture. Before any decision is made on this point, a more reliable test for glucose and other simple sugars should be adapted and used.

Test for Phenols by Ehrligh's Reaction. - (G) To 1 cc. of 0.5% sulf-fanilic acid in 2% hydrochloric acid was added 1 cc. of 0.5% potassium nitrite, then 1 cc. of sap to be tested was added and the solution was made alkaline with solid sodium carbonate. A dozen or more samples of sap so tested all gave positive reactions for phenols, i.e., an intensely colored red-brown dye was formed as soon as the solution was made alkaline. There was some difference in the amount of phenolic reactant in the various samples tested. This is considered a very sensitive and reliable test for phenols.

Behavior of Sap with Fehling's Solution. - The standard Fehling's solution test for reducing substances was made on a large number of

samples of sap. Usually a positive, though often faint, reaction was obtained. In one instance a batch of sap was pressed out (during the winter) that gave no test for reducing substances with Fehling's solution. Neither would it turn brown under conditions that had always caused browning before. In general, the intensity of the Fehling's test obtained was proportional to the tendency of the particular sample to brown.

Behavior of Sap with Lead Salts. - A quantity of sap obtained from partially air-dried wood was treated with Horne's basic lead acetate until no more of the light brown precipitate resulted, and then filtered. The filtrate was saturated with hydrogen sulfide and lead sulfide thus formed filtered out. The filtrate was almost colorless. The hydrogen sulfide remaining in it was practically completely removed by shaking it in a large flask pumped out with a suction pump. Two 20 cc. portions of this sap were measured into 100 cc. Erlenmeyer flasks. To one of them 0.5 cc. of concentrated hydrochloric acid was added and the solution boiled two minutes. Then these two portions of treated sap were made neutral to litmus with 6 n. ammonium hydroxide solution as was also a 20 cc. portion of the untreated sap. The three flasks were stoppered and placed in a hot closet heated to 80°C.

Preliminary treatment	Color after preliminary	Color after 1 hour at 80°	Color after 2 hours at 80°
1. None, made nuetral to litmus	Light brown	Intensely brown	Very dark brown
2. PbOHAc, H₂S, made neutral to litmus	Practically colorless	Slightly brown	Brown: about half as intense as 1 and 3
3. PbOHAc, H₂S, boiled with HCl, made neutral	Light brown, less than 1	Intensely brown; almost as brown as 1	Very dark brown, same as 1

Since it was necessary to have the same acidity prevailing in all three
of these solutions they were all made neutral to litmus, which is some-
what more basic than sap usually is. This accounts for the rapid brown-
ing. It will be remembered that although high acidity will produce more
browning after a relatively long treatment, it acts apparently by acceler-
ating the first step in the process rather than the second, which it ap-
parently retards. The more acid of two sap solutions subjected to the
long heat treatment will be the less colored until the two are adjusted
to the same acidity, when the one that was the more acid will be the more
browned, due to the acid-base color change of brown stain, and after a
short time in addition the one which was the more acid will have browned
a great deal more than the other.

This experiment shows that the staining agent is more easily preci-
pitated by Pb⁺⁺ than the substance from which it arises as well as that
brown stain is fairly completely precipitated by Pb⁺⁺. It gives further
evidence also that the staining agent can be produced very rapidly by
acid hydrolysis.

To the browned solution No. 3 obtained in the preceding experiment
2 n. lead acetate solution was added; so much brown and black precipitate

resulted that the whole thing jellied. Nothing further could be done.

Several samples of sap were tested in this way and practically the same results were obtained. It was noted that samples of sap showing less tendency to turn brown also gave less Pb^{++} precipitate.

Regenerating Lead Precipitate. - Some lead acetate precipitate from fresh but slightly browned sap was suspended in warm water which was then saturated with hydrogen sulfide. After a few minutes this mixture was filtered; the filtrate was light brown colored (after it was made certain that all the PbS was filtered out). The solution was subjected to a vacuum and warmed to expell excess hydrogen sulfide, then, in a stoppered 100 cc. Erlenmeyer flask, heated to 80°C. After 14 hours, much more brown had developed.

Effect of Iron and Cyanide Salts. - Eighty cc. of sap were made 0.6 n. in hydrochloric acid and boiled 2 minutes (this sap showed only a weak tendency to turn brown and no other sap was available at the time so it was given an acid hydrolysis treatment before using). It was cooled, made neutral to litmus and filtered. The filtrate was divided into four 20 cc. portions in 100 cc. Erlenmeyer flasks to which were added sodium cyanide and ferrous sulfate as shown in the table below. They were heated at 80°C for 21 hours with the result shown also in the table.

Reagents added	Appearance after 21 hours at 80°C
1. None (blank)	Rather intense brown
2. 10 drops of 0.1 n. NaCN	Browned, but considerably less than 1
3. 1 drop of 0.006 m. FeSO$_4$	Very intense brown
4. 1 drop of 0.006 m. FeSO$_4$ + 10 drops 0.1 n. NaCN	About the same as 2

Otto Warburg (H) has found that certain oxidation reactions can take place only when iron is present (though often only minute traces suffice) to act as a catalyst. He has found also that in the presence of both iron and cyanide these reactions do not take place.

Behavior of Sap with Hydrocyanic Acid. - Three 20 cc. portions of sap were placed in large test tubes with constricted necks. One was sealed as it was, to the second was added 2 drops (small drops) of 49% hydrocyanic acid, and to the other 6 drops of 49% hydrocyanic acid were added. These last two were then sealed also. They were all placed in the cabinet heated to 80°C.

No.	Amt. HCN added	Appearance after Heating			
		3/4 hours	3 hours	7 hours	20 hours
1	None	Slight brown color	Considerable brown color	Very brown	Very intense brown
2	1 drop, 49%	No change	Slight tinge of brown	Slight brown	Very intense brown
3	6 " 49%	No change	No change	Tinged with brown	Slight brown

Effect of Cyanide on Browning of Wood. - Two blocks (adjacent) were cut from a piece of partially air dried 2 x 12 sugar pine. One was soaked in 2% sodium cyanide solution for 2½ hours and the other at the same time was soaked in distilled water. They were sealed in separate fruit jars and held at 80°C and 100% relative humidity for 17 hours; the block soaked in distilled water was beginning to show brown streaks, the other was bright. After two days more of this treatment the block soaked in distilled water was badly stained, the other only slightly. The blocks were removed from the jars, allowed to dry a little, and then planed down to observe penetration; the block soaked in sodium cyanide, though browned somewhat, was much less browned than the other.

The above experiment was repeated, but instead of soaking one of the blocks in sodium cyanide solution, a small beaker containing 10 cc. of 49% hydrocyanic acid solution was placed in the fruit jar with it. After 14 hours' heat-treatment the block in the jar containing the acid was bright while the other had some intense streaks of brown.

The above experiment was repeated, this time after the jars had remained at 80° for half an hour the jar containing the hydrocyanic acid was opened, and the beaker containing the hydrocyanic acid was removed, emptied, washed, refilled with distilled water and replaced. After 15 hours heating the block treated with hydrocyanic acid was bright, the other stained. After 42 hours the block treated with acid showed a streak of very light stain, the other was intensely stained.

Three adjacent blocks were cut. One was soaked in distilled water half an hour. This block and one of the others were put in fruit jars along with beakers containing 10 cc. of 49% hydrocyanic acid solution. After $2\frac{1}{2}$ hours the hydrocyanic acid solution was removed and replaced by distilled water. The third block was also sealed in a jar with some water in a beaker. These were held at 80° for 21 hours; the blocks treated with hydrocyanic acid were without stain, the blank was badly stained.

It was on the basis of these experiments that the kiln drying experiments with hydrocyanic acid were undertaken (see page 18).

In this appendix, the schedule used for runs 12 and 17 will be discussed in more detail than was done in the main part of the report.

When this schedule was worked out it was assumed that during the drying of a board, water in the liquid state moves out as near to the surface of the board as possible, i.e., as far as the fibers of wood are free of mechanical injury produced in sawing the board from the log, where it is then changed to the vapor state. It was also assumed that both the first substances taking part in the staining process and the brown material itself are soluble in sap. Concerning this second assumption there can be little question, for we know that the colorless substance which later turns brown occurs in the sap expressed from wet wood, and we know that it is possible to extract the brown substance from stained wood with water.

Since none of the schedules had given much encouragement in the way of finding a process that would prevent the formation of the colored material, the schedule for runs 12 and 17 was planned to be one that would cause stain to be deposited very near the surface, and no particular provision would be made to get conditions that were supposed to minimize the production of the brown material. To do this, three factors were taken into consideration, (1) minimizing case-hardening, because moisture does not pass readily thru wood fiber altered by case-hardening (I), (2) to hold the temperature as high as practicable in order that fluidity of the sap may be high, (3) and to avoid changes in conditions during drying which would cause the temperature of the surface of the board to become higher than that of the center of the board, then moisture would be drawn

to the center because of the well known phenomenon that moisture always moves toward the cold region in a permeable material like wood. This would be very undesirable because it would mean that either or both of two things might happen: moisture (sap) at the surface might evaporate and diffuse back thru the board as steam until the wood was heated up, or hot water (sap) near the surface would diffuse back in the liquid state until the board was heated. In the first case the moisture content of the surface might easily become depleted so that the brown substance would become concentrated enough to be deposited on the wood fibers at a greater depth from the surface than would otherwise happen.[a] If the second case were true, the situation would be even worse, because much more water in the liquid state is required to transfer a given amount of heat than is required when the water vaporizes and then condenses (by a factor of about 550 fold) and also, the liquid which has accumulated a large amount of brown material at the surface would be drawn back into the board by such a method of transfer.

It is possible to devise a schedule which will meet these requirements. Such a schedule will start out with high temperature and high humidity which will satisfy conditions 1 and 2, and in order to avoid rises in the temperature of the surface the wet bulb temperature should be continually decreased, by short steps at first and then by larger steps as the wood becomes dry. At first when the wood is wet the temperature of the surface

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a) If the surface of a 2-inch thick board having an average moisture content of 100%, with an average moisture content of 40% in the first 3 mm. from its drying surface were heated so that the temperature of the whole board was increased 1°C, the moisture content of this layer would drop to 36.5% if heat transfer were all due to the effect mentioned.

would be only slightly above wet bulb temperature, but as the wood becomes dryer the temperature of the surface would approach dry bulb temperature. This is why the rate of decrease of wet bulb temperature should become greater as the board becomes dry.

Reference to chart 20 (p. 27) will show the schedule, as well as the temperatures of the center and surface of the board. It will be seen that the schedule chosen turned out to hold the surface temperature as nearly constant as one could wish. As the moisture content went below thirty percent there was a jog upward, but at this point a rise of temperature would probably not bring about a movement of stain, for it would undoubtedly all be deposited on the wood fiber by the time this stage was reached.

The result with respect to distribution of stain, as has been noted before, turned out to be the reverse of what was expected. This means that something was wrong in the original assumptions, because it happened that the experimental part worked out very successfully. The first assumption is probably the one that is wrong, for we have experimental evidence of the correctness of the others involved. That water changes to the vapor state some distance from the surface of the board and subsequently diffuses as a gas to the surface is an unexpected situation, but such an assumption would be in agreement with several other pieces of evidence that are otherwise unintelligible. The data on variation of moisture content of wood with distance from the surface during drying to be discussed in Appendix III would be more easily understood if such an assumption were tenable. Tieman (J) in his patent description of an adiabatic drying process inferred that in such processes evaporation takes place all thru the board, which explains why such a process is so successful in producing lumber

free of defects due to internal strains. A review of the ideas underlying the schedule just described will show that the conditions it maintains are not greatly different from those of an adiabatic drying schedule.

The fact that the temperature of the center of the board is lower than that of the surface may be explained in one of two ways: if it is assumed that vaporization takes place only at the surface and moisture moves in the wood as liquid, then one would feel that since there is a moisture gradient, a temperature gradient should also be set up to maintain equilibrium, or if it is assumed that vaporization takes place all thru the wood, a temperature gradient would be necessary to get the heat necessary for vaporization into the wood. A computation (see Appendix III, p. 11) of the amount of heat that could get to the middle of the board as a result of this temperature difference indicates that enough heat could diffuse in to evaporate all the water that dries out of the wood in the inner regions of the board. This combined with the first explanation just suggested would make a vapor-phase mechanism for the diffusion of moisture seem very reasonable.

In this appendix data will be presented and discussed which were obtained in a series of moisture content determinations. The purpose of this series of determinations was to find how the moisture content of a board varied with the distance from the surface and with time of drying, and thus test the conclusions of Mr. Steinour's calculations given in Appendix B of his Thesis (A), and of the treatment of the problem by Tuttle(K).

The moisture content determinations were made on chips one sixteenth of an inch thick, two and a quarter inches wide, and three inches long cut parallel to the drying surface from a piece of two inch sugar pine. The first chip so cut was bounded on one of its surfaces by the drying surface of the board. These chips were cut from blocks taken from selected pieces of 2 x 8 inch stock which was being dried under moderate drying conditions (145°F dry bulb and 60% relative humidity).

Four inches of the end of the board (it had previously been end painted to prevent excessive drying) were cut off and discarded. Then a piece three inches long was cut and from the center of this a block two and one quarter inches wide was cut. This gave a block two inches thick, two and one quarter inches wide, and three inches long bounded on its upper and lower surfaces by drying surfaces of the board from which it was cut. Five surfaces of the block were then coated with paraffin (excepting the surface from which cutting was to start) by dipping it in melted paraffin. This afforded a protection against loss of moisture, and added little to the weight of each chip as was found by preliminary tests. The block was clamped in a machine which shaved off the above mentioned six-

teenth-inch chips which were immediately weighed to within 0.005 gm. on a pulp balance. Then they were placed in racks and dried at close to 100°C in an electrically heated laboratory oven for ten to fifteen hours, cooled in a desiccator and weighed. From these weights the moisture content of each chip was calculated. The values thus obtained were plotted against the distance from the surface of the board which was obtained as follows:- rather than to actually measure the distance the weight of oven-dry wood between the surface and the plane for which the moisture content for the fifth chip from the surface was plotted against the sum of the oven-dry weights of the first four chips plus half of the oven-dry weight of the fifth chip.

A series of experiments such as just described was run on a block from each of four boards every day for six consecutive days and on two other boards two successive days. The determinations were discontinued on these last two, because there was not enough time in even a long day to do all the work involved for six pieces. This gave four families of curves six curves each and two families of two curves each. Two of the six-curve families were for tangentially sawed (slash-cut) boards (A and B) and from parts of those boards containing only sap-wood. One of the two-curve families was from a board (C) of the same description, although it was not as exactly tangentially sawed as were the other two. The remaining two six-curve families were from boards (D and F) which were almost exactly radially cut (quarter-sawed) and of heart-wood. The other two-curve families are from a board (E) which was also radially cut and of heart-wood, but not as exactly radially cut as the other two. The curves are shown in charts 21 to 26.
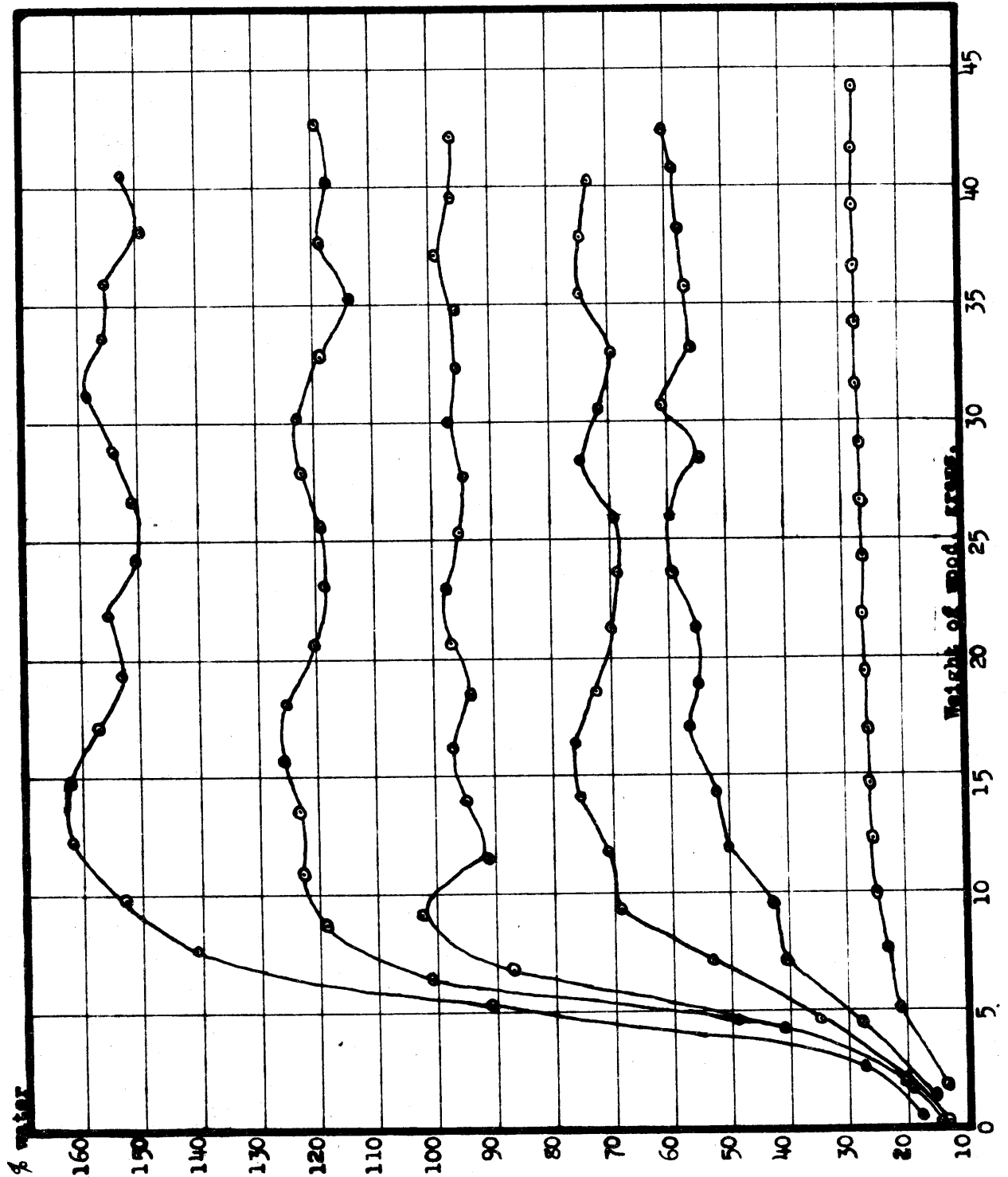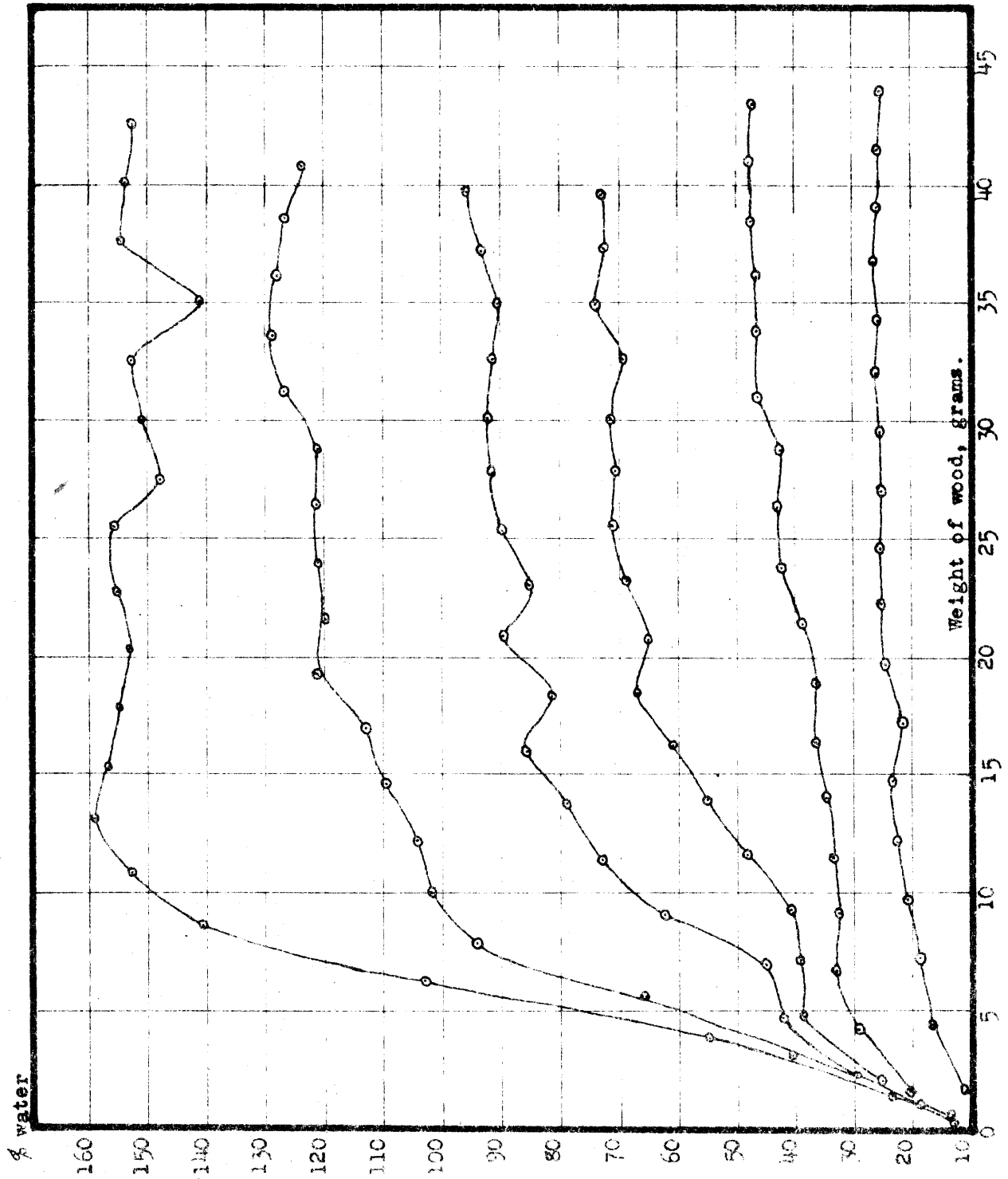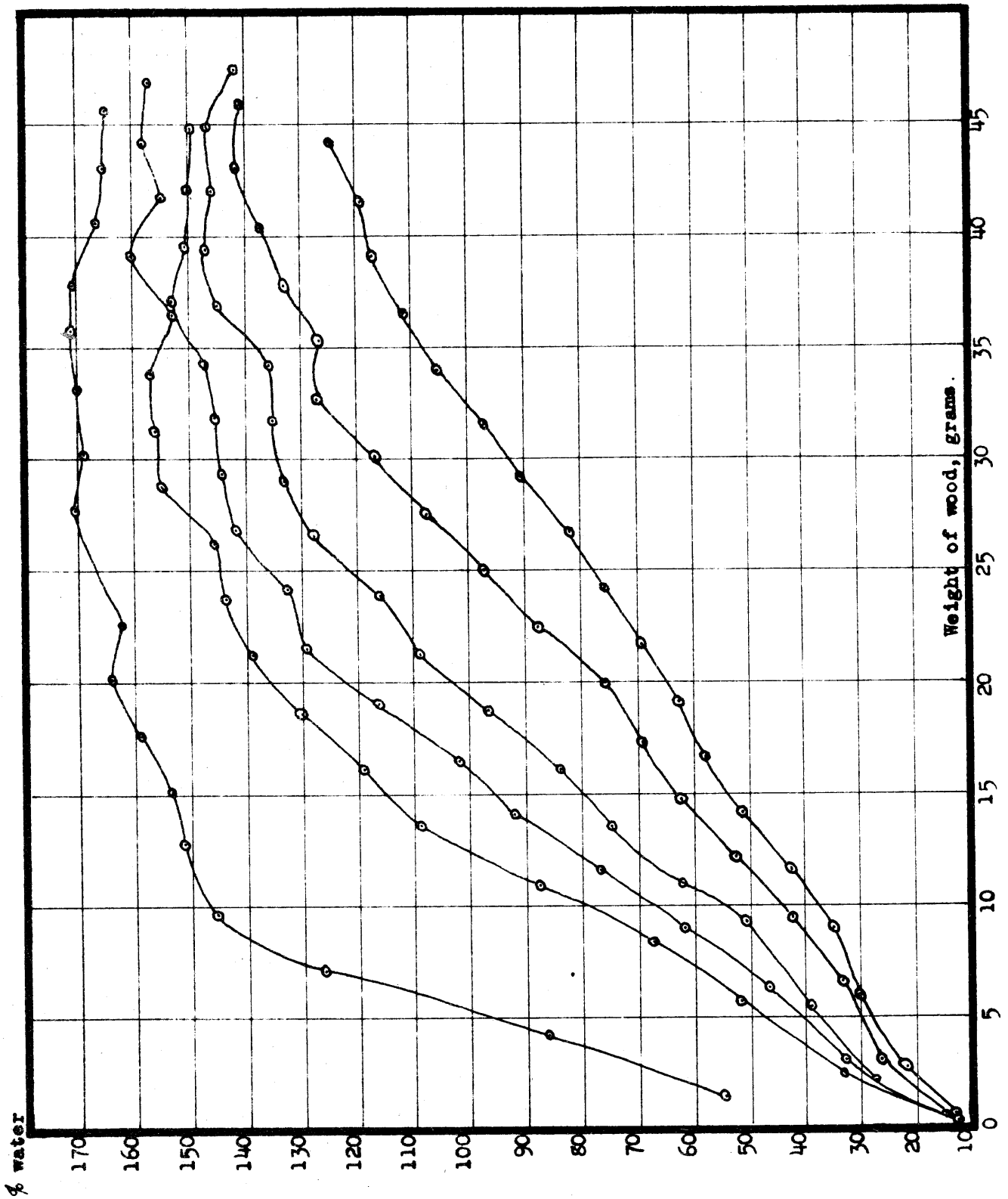
Chart 21, Board A

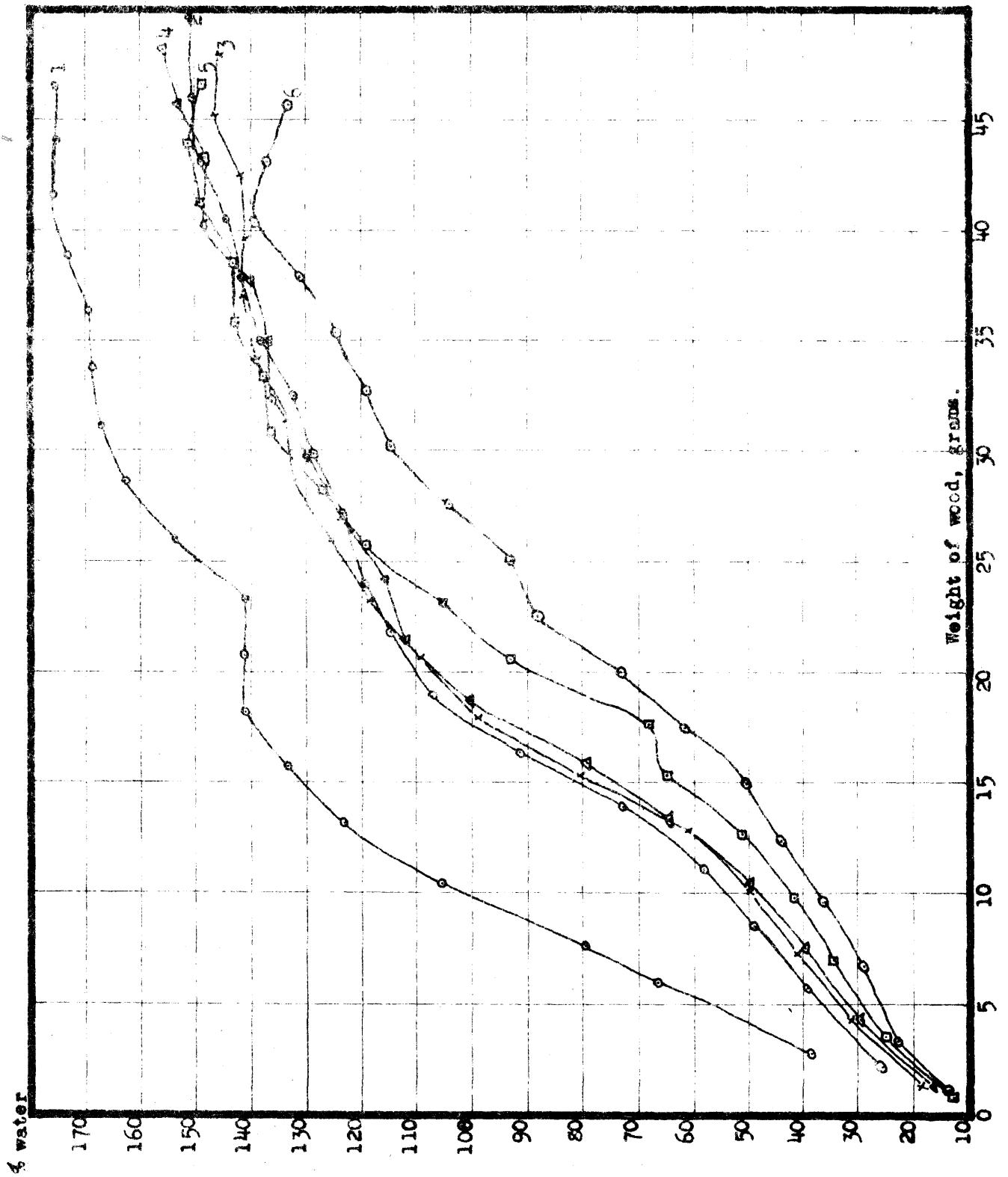Chart 22, Board B

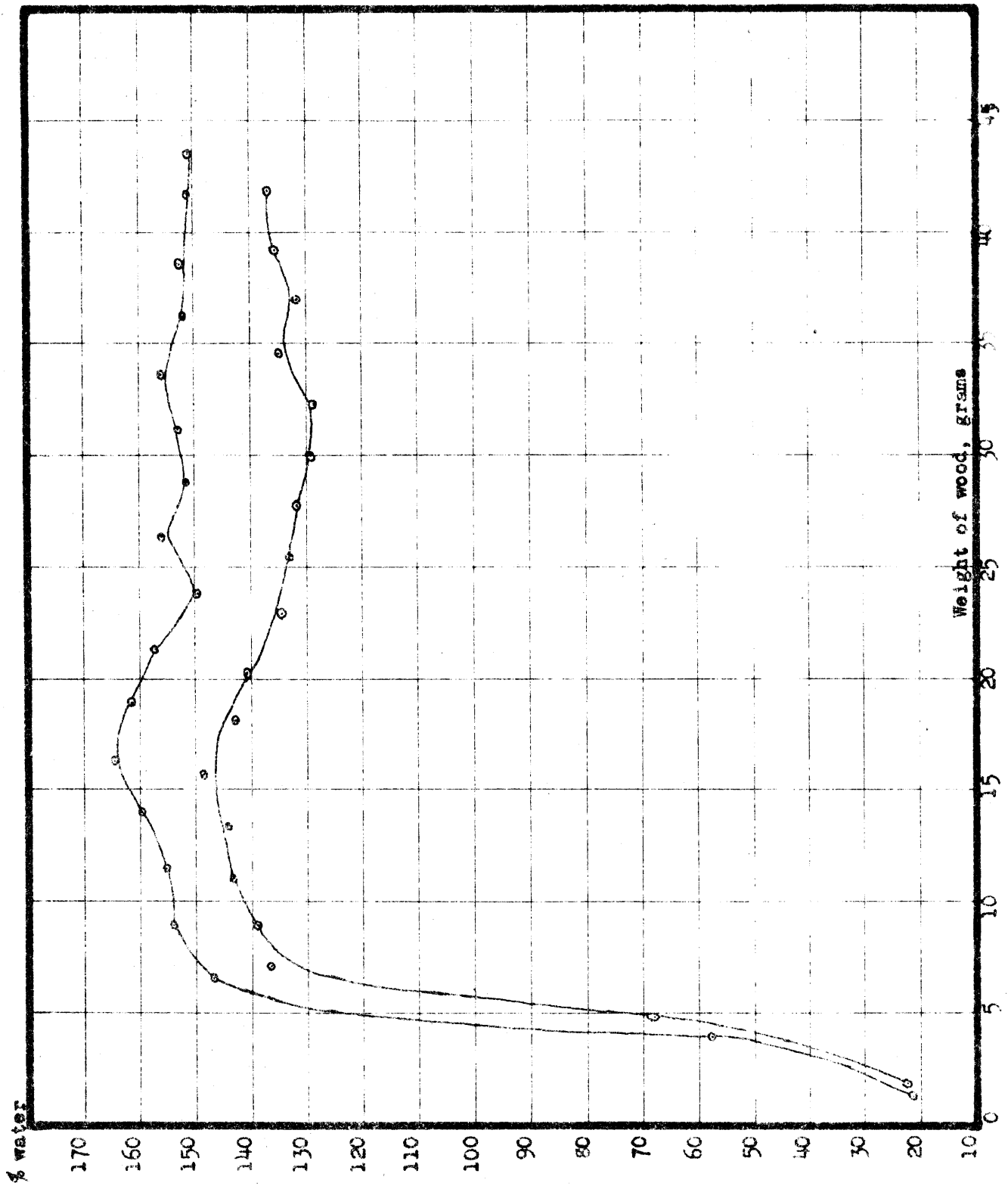Chart 23, Board D

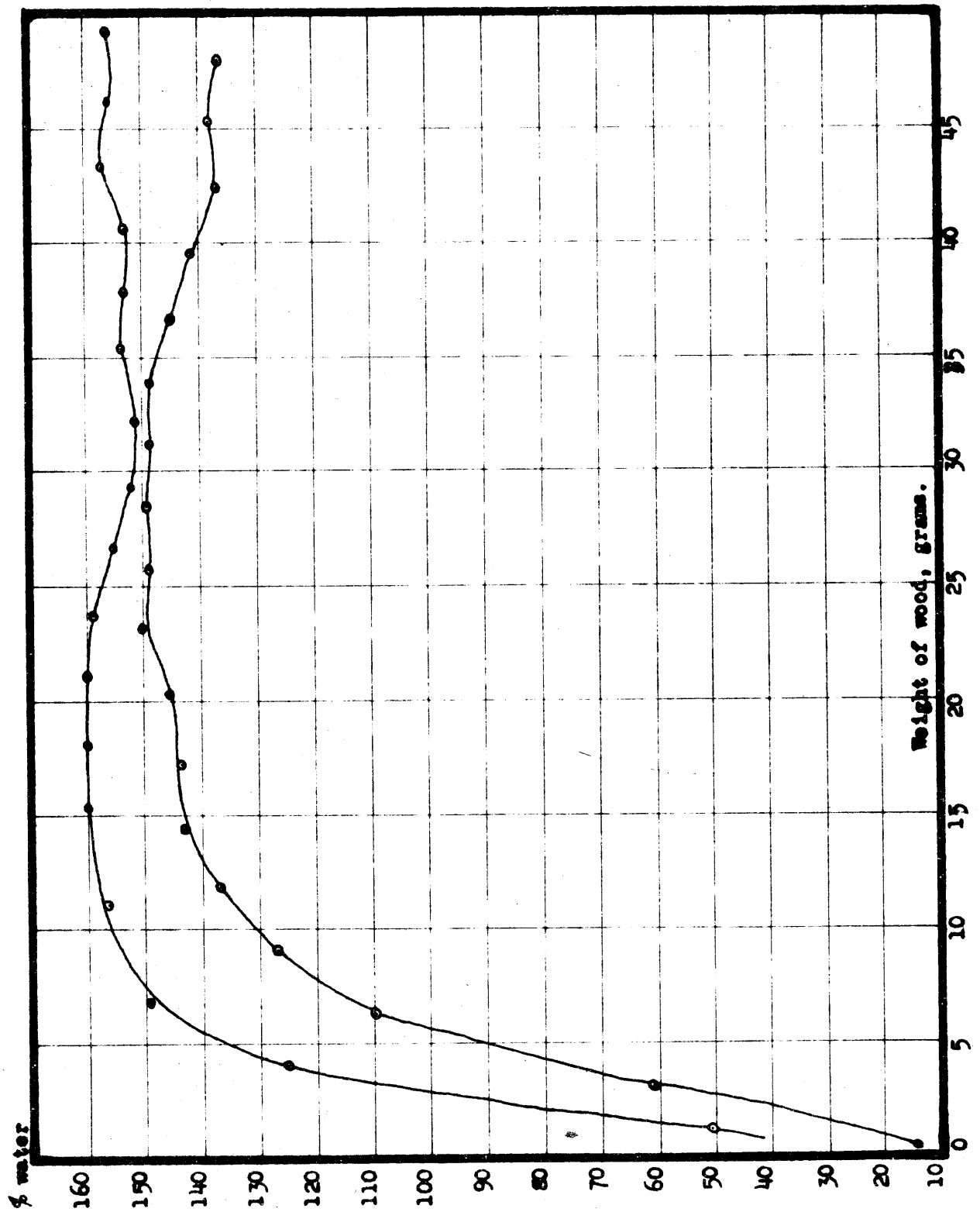Chart 24, Board F

Chart 25, Boar d C

Chart 26, Board E

There should not have been appreciable errors in the actual mois-
ture determinations, because the errors of weighing should have been
insignificant compared with the magnitude of the weights involved. There
are some other sources of slight uncertainty; the size of the block cut
each day varied a little in its dimensions, and also the density of the
wood may have varied somewhat so that distance from the surface as obtain-
ed from the weight of wood did not correspond exactly for the several
curves in each family, the cooling effect on the surfaces of the block
produced when the block was clamped into the metal chip-cutting machine
may have caused a migration of moisture thru the block which caused a
change in the moisture-gradient, and there may have been spurious effects
due to end drying of the board or non-uniformity of the wood. The second
source of error, if it existed, would, of course, have been serious; and
from what we know so far it is hard to tell how great the magnitude of the
effect might have been, but during the time that it could have taken place
(it took 45 to 60 minutes to complete all the operations described for one
board each day exclusive of the second weighing of the chips) it probably
produced no great change. The other difficulties mentioned would be of
negligible importance.

Inspection of these several sets of curves shows some unexpected re-
sults. Curves for the tangentially-cut sap-wood pieces are entirely dif-
ferent from the others, and due probably to the ability of the medullary
rays, which were almost perpendicular to the drying surface, to conduct
moisture with ease. The fact that wood an inch from the surface seems to
have dried at the same rate as wood only slightly over a quarter inch from
the surface and that the moisture leaving the wood that was an inch from

the surface migrated most of the way toward the surface along an almost zero moisture gradient is, indeed, difficult to explain. The writer feels that more study should be made of this case before conclusions are drawn.

The radially-cut heart-wood is apparently a different case. The set of curves for board F are not of much use, because this was apparently one of the boards that one occasionally finds among heart-wood sinker stock that simply will not dry out in a reasonable length of time, no matter what the conditions. The curves for board D (the best of the two for this type) do not fit the expectations of Mr. Steinour's assumptions, and an attempt to fit them to the work of Tuttle (K) is hardly any more satisfactory. At the present time the problem seems to be very complex so that any simple set of assumptions such as Tuttle or Steinour made will not describe the pehnomenon completely. This opinion is also held at present by the investigators at the Forest Products Laboratory at Madison, Wisconsin, where extensive study of the whole problem is being made. For instance, the fact that there is a temperature difference between the surface and the center of the board (see Appendix II) introduces two sources of complexity, first, a calculation of the variation of inhibition pressure wit h temperature shows that a difference of temperature of $2°C$ in wood containing 14% moisture and at $142°F$ (the vapor-pressure vs. moisture-content curves in Koehler and Thelen (L) were used) gives a difference of inhibition pressure of the same order of magnitude as a difference in moisture-content of 10%. Secondly, if with the aid of the specific thermal conductivity constant for _dry_ wood the amount of heat that could get in to the center of the board is calculated, the amount thus found would be enough to

evaporate all the water that leaves that part of the wood during drying. These two difficulties alone make a simple treatment of the phenomenon almost out of the question. We must therefore look to very extensive studies such as the Forest Products Laboratory of Wisconsin is making for a solution of this particular phase of the problem of preventing brown stain.

BIBLIOGRAPHY

A. Master's Thesis, California Institute of Technology,
      H.H.Steinour, 1926.

B. Monographs on Biochemistry, "The Simple Carbohydrates and
      the Glucosides", E.F.Armstrong, pp. 149-154.

C. Reference B, p. 155.

D. The True Tanning Value of Vegetable Tanning Materials",
      J.H.Wilson, C.J.Kern, J.Ind. and Eng.Chem., $\underline{12}$, 465 (1920).

E. "The Chemistry of Plant Products", Haas and Hill, p. 60. Longmans Green

F. "Handbook of Sugar Analysis", C.A.Browne, p. 212, Wiley and Sons, 1912.

G. "Physiological Chemistry",
      Mathews, p. 983, 4th ed., Wm. Wood and Son.

H. "Iron, the oxygen Carrier of Resperation Ferment",
      Otto Warburg, Science, $\underline{61}$, 576 (1925).

I. "Kiln Drying of Lumber",
      Koehler and Thelen, p. 39, McGraw-Hill, 1926.

J. U.S.Patent 942150, H.D.Tiemans (1909)

K. "A Mathematical Theory of the Drying of Wood",
      Fordyce Tuttle, Jour. Franklin Inst., $\underline{200}$, 609 (1925).

L. Reference I, p. 43.