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# A PRIMER ON THE CHEMICAL SEASONING OF DOUGLAS FIR

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UNITED STATES DEPARTMENT OF AGRICULTURE  
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In Cooperation with the University of Wisconsin

A PRIMER ON THE CHEMICAL SEASONING OF DOUGLAS FIR:

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Forest Products Laboratory Research Supplemented by a Field  
Study Made in Cooperation With the West Coast Lumbermen's  
Association, 1938

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The growth of a tree or an idea cannot be taken for granted. Lacking a suitable environment neither will grow enough to be useful to society. If by accident or otherwise a dormant tree is given enough light, its rate of growth is apt to take a spurt; a dormant idea under the stimulus of new concepts and information may take on new life. When the Forest Products Laboratory discovered that wood, after chemical treatment, could be made to dry from the inside out an old dormant idea was released from inhibiting influences. Old drying processes which involved the use of chemicals were immediately dressed in new clothes. Past industrial experience with chemicals as an aid to seasoning could no longer be used to evaluate the new process which offers possibilities of solving the age-old problem of seasoning wood without checking.

To solve this industrial problem, the West Coast Lumbermen's Association cooperated with the Forest Products Laboratory in a preliminary study of the chemical seasoning of Douglas fir.

This article may be considered the first in a series of progress reports to be issued by the West Coast Lumbermen's Association on the chemical seasoning of their products. The primary purpose of this article is to set forth the principles of chemical seasoning in as much detail as consistent with our present understanding of the subject.

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Acknowledgment is made of spontaneous inspiring cooperation of the West Coast Lumbermen's Association, of its officers, members of its Grading and Trade Promotion Committees, and to the Weyerhaeuser Timber Company at Longview, Wash., who were hosts to the field study.

## How It Works

In the following paragraphs the movement of water in wood, as it dries, will be explained so that it will be easier to understand the essential differences between ordinary methods of drying and chemical seasoning.

Moisture moves from the center toward the surface of a piece of wood when the water in the central portion has a higher vapor pressure (analogous to steam pressure) than the water in the outer portions of the piece. In short, moisture moves from a zone of high vapor pressure to a zone of low vapor pressure just as steam would rush from a boiler having a high steam pressure into a boiler having a low steam pressure.

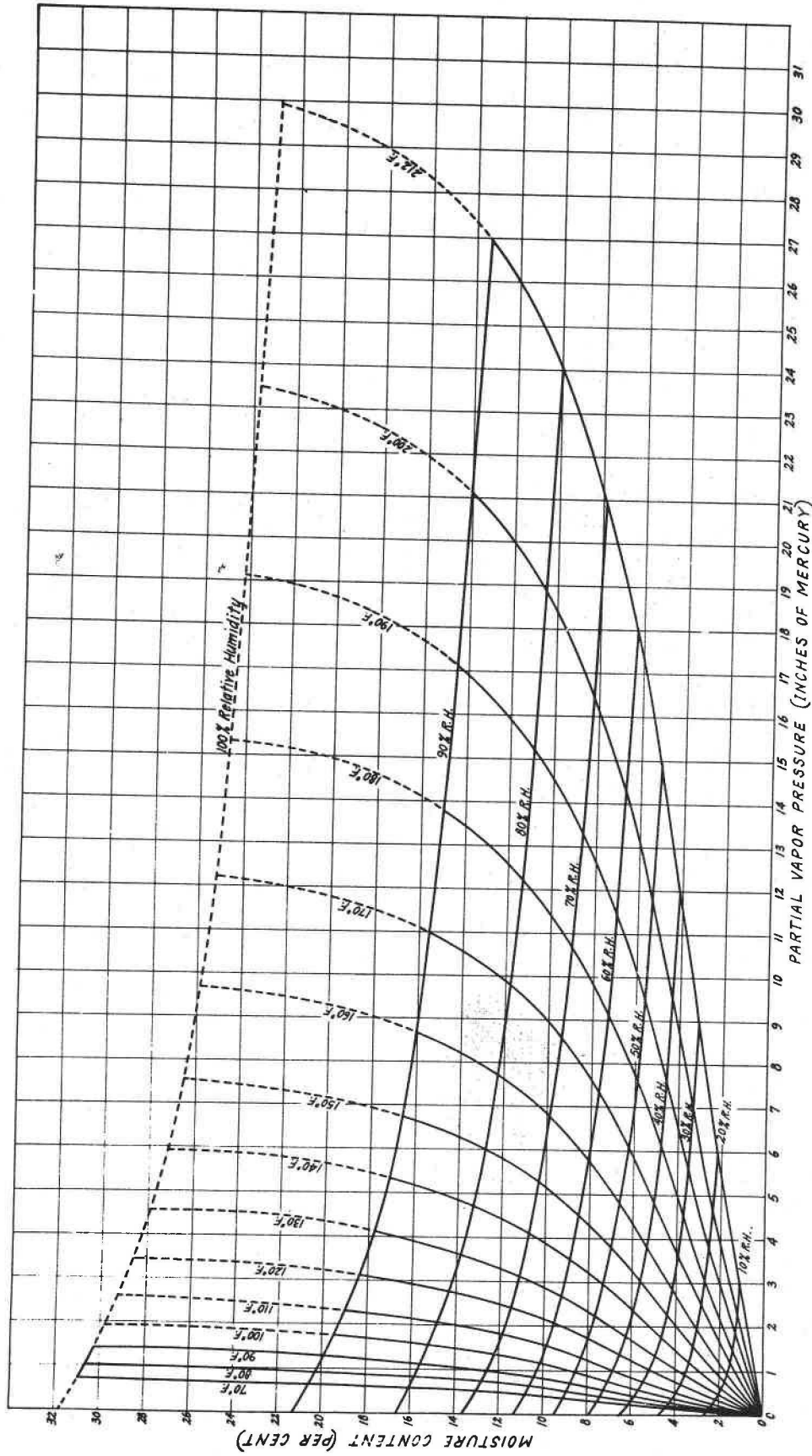
In drying wood by the common methods of air drying or kiln drying the required difference in vapor pressure is obtained by drying the surface fibers first thus setting up a moisture gradient.

In the process of attaining a comparatively low moisture content the vapor pressure of the surface fibers is diminished to a value which almost corresponds to the temperature and humidity of the surrounding air. In drying by conventional means the surface fibers must always be drier than any other part of the stick. Because of the upset in moisture, refractory items of wood are apt to surface check in drying. The steeper the moisture gradient and the greater the tendency of the wood to shrink with a loss in moisture the greater the checking hazard becomes.

Figure 1 shows the moisture content of natural wood in equilibrium with various temperatures and relative humidities and corresponding vapor pressures. With the aid of this family of curves and suitable moisture distribution data one can construct a curve that shows the progressive diminution of vapor pressure from the center to the surface of a piece of wood while drying. Repeating for sake of emphasis, when wood is air dried or kiln dried the difference in vapor pressure, the driving force of moisture movement, is produced by a moisture content gradient. This is not true of chemically treated wood.

### In Chemical Seasoning Vapor Pressure in Wood Depends on Absorbed Chemical

The relationships shown in figure 1 do not hold when the moisture in the cell walls (hygroscopic moisture) acts as a solvent for a chemical. It is a well known fact that at a given temperature the normal vapor pressure of water is lowered when chemicals are dissolved in it. The degree to which the vapor pressure is reduced depends on the characteristics and the amount of the dissolved chemical. If then the hygroscopic moisture is saturated with a given chemical the wood will not tend to lose moisture unless the vapor pressure of the air is lower than the vapor pressure in equilibrium with the saturated solution.



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 THE MOISTURE CONTENT OF SITKA SPRUCE  
 AT EQUILIBRIUM WITH THE INDICATED TEMPERATURE, PARTIAL VAPOR PRESSURE,  
 AND RELATIVE HUMIDITY

Figure 1

## Moisture Retention

Moisture will condense on treated wood when at a given temperature the vapor pressure of the air exceeds the vapor pressure over the contained chemical solution. By way of illustration, table 1 shows the relative vapor pressure of the air at 68° F. at which wood, containing enough chemical to saturate its hygroscopic moisture, starts to gain or lose moisture. For example, after soaking a thin piece of greenwood in a saturated solution of sodium chloride for a day or so at room temperature it cannot dry in a temperature of 68° F. and a relative humidity of 78 percent because the vapor pressure of the solution contained by the wood is in equilibrium with the vapor pressure of the air.

Table 1<sup>1</sup>

Saturated aqueous solution of --	:Relative vapor pressure of the air over the solution at 68° F.
Calcium chloride.....	0.32
Magnesium chloride..	.32
Calcium nitrate.....	.59
Ammonium nitrite....	.68
Sodium nitrate.....	.76
Sodium chloride.....	.78
Urea.....	.80
Ammonium sulfate.....	.81

<sup>1</sup>Data from an unpublished report "The Effect of Solutions of Various Chemicals and Mixtures of Chemicals on Relative Humidity, Equilibrium Moisture Content of Wood and on Shrinkage" by E. C. Peck.

When thin wood that has been soaked in a chemical solution is successively brought to an equilibrium weight with various relative humidities it will attain equilibrium moisture values that are higher than corresponding values for normal wood. Figure 2 shows the equilibrium moisture content of natural wood and thin specimens of wood treated in a saturated solution of sodium chloride.

These curves contain the first basic principles of chemical seasoning, which may be described as the water retention influence. They show that when chemically-treated wood is subsequently dried in a given relative humidity the zones which actually contain the chemical have a higher moisture content than the adjacent untreated zone. The

moisture retention property of the chemical tends to maintain the surface fibers at a higher than normal moisture content and accordingly tends to decrease the drying stresses. Where the relative humidity during a subsequent drying process is in equilibrium with the relative vapor pressure of the treating solution the surface fibers of the wood will not dry or tend to shrink but the untreated portions of the wood dry at a normal rate. Thus by ordinary methods wood dries from the outside in, while chemically-treated wood dries from the inside out.

#### Moisture Gradient in Chemically-Treated Wood

From a moisture gradient standpoint the movement of water in chemically-treated wood seems to be an "uphill" process. This is not the case, however, as the controlling vapor pressure gradient is quite normal due to a chemical gradient extending from the surface into the wood.

The moisture distribution from the center of the specimen to the zone in which the concentration of chemical is becoming appreciable is quite normal. Projection of a moisture distribution curve to the surface gives a moisture content value at the surface that would have been obtained by drying untreated wood in the same temperature and relative humidity. See figure 3, which illustrates the moisture and salt distribution in a treated 6 by 12 Douglas fir timber after a 5-day drying period in 160° F. and 72 percent relative humidity. In this drying condition normal wood will attain an equilibrium moisture content of about 10 percent. The fact that the inner part of the chemically-treated wood has a moisture gradient identical to that which develops in untreated wood in the same interval of time indicates that the driving forces in the two cases must be equal. Hence, provided the drying conditions are the same, treated and untreated timbers of the same size dry at the same rate. Keeping the moisture content of the treated zones above normal values near the surface does not interfere with normal drying as the controlling vapor pressure gradient is normal. But by reason of the higher moisture content of its surface fiber the treated wood can be rapidly and safely dried in relative humidities that cause untreated wood to check. For example, a large untreated Douglas fir timber will surface check when dried by relative humidities as high as 90 percent; whereas if the same timber were treated with sodium chloride the surface fibers would remain damp and unshrunk in a relative humidity of 75 percent.

By way of emphasis it may be well to repeat that the moisture-retention principle of chemical seasoning operates most effectively when the vapor pressure of the drying atmosphere is in equilibrium with the vapor pressure of the treating solution. By following this technic the untreated wood can be dried to a moisture content that is in equilibrium with the drying condition while the surface fibers remain in their green dimension. This reaction of chemically-treated wood profoundly modifies the normal drying stresses.

In normal drying the surface fibers of a timber are stretched the most and as a consequence checks are initiated on the surface. In drying chemically-treated wood in properly controlled

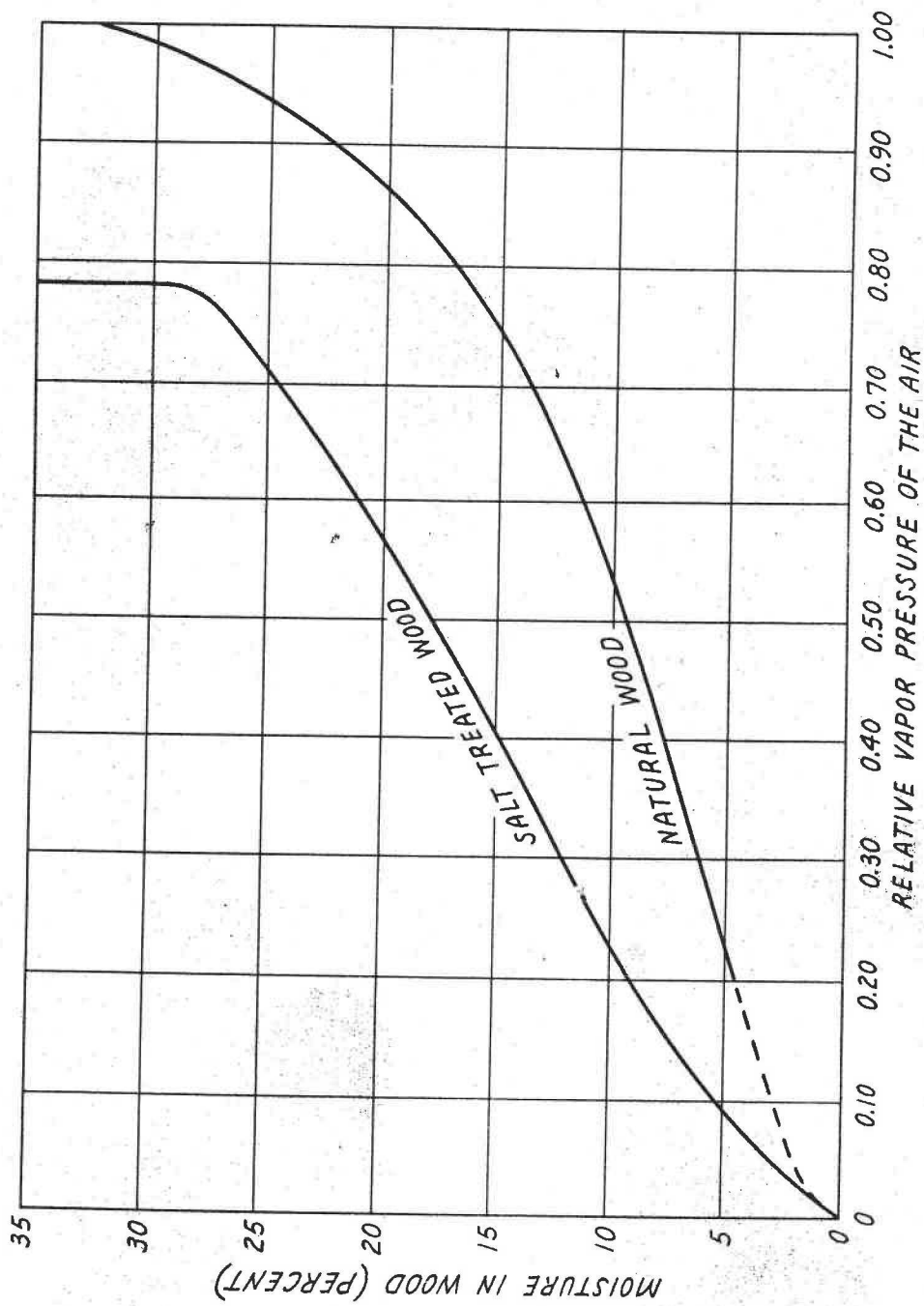


FIG. 2  
 EQUILIBRIUM MOISTURE CONTENT OF NATURAL WOOD  
 AND WOOD TREATED WITH A SATURATED SOLUTION OF SODIUM CHLORIDE.  
 BOTH CURVES FOR A TEMPERATURE OF 70°F.

relative humidities the fibers which are stretched the most are located in the untreated wood just beneath the treated zones. Being stretched, these fibers receive a tension set proportionate to the drying stresses; that is, the innate shrinkage of the untreated fibers has been reduced by their being stretched beyond their elastic limit. It will be noted from figure 3 that the point of departure from the normal moisture distribution corresponds to the depth to which the salt has penetrated and also the zone having the maximum tension set. The zone of maximum tension set is very significant. When the relative humidities are reduced enough to permit the chemically-treated zone to dry, surface checking becomes possible. However, if the chemically-treated timber has been sufficiently dried in properly regulated relative humidities the checks will not penetrate into side-cut timbers beyond the zone of maximum tension set, that is, to a depth of about one-half inch.

#### The Chemical Diffuses Into the Wood

Because a piece of cloth or a sponge readily absorbs water or an aqueous solution, naturally one suspects that a piece of dry wood would readily soak up or absorb a solution when submerged in it. Experience has shown, however, that water and chemical solutions soak into wood very slowly. For example, 4-inch Douglas fir planks weighed less than 50 pounds per cubic foot after soaking in water for 12 years whereas if completely saturated with water they would have weighed about 71 pounds per cubic foot.

Fortunately for chemical seasoning, the rate at which the treating chemical moves into wood does not depend primarily upon the forces of capillarity. In fact the quantity of solution which is drawn into wood by them is negligible. The force which causes a chemical to penetrate into the wood is mainly diffusion pressure, a force that is akin to osmotic pressure. For aqueous solutions that are in equilibrium with 75 percent relative humidity the osmotic pressure is about 400 atmospheres (6,000 pounds per square inch). With forces of this magnitude at work during the process of chemically treating wood it is evident that the rate of penetration obtained by diffusion would not be stimulated materially by ordinary pressure treatments.

The chemical diffuses from the surrounding solution into the water in the wood. If the moisture content of the wood is not high enough to provide a continuous film of water into which the chemical can diffuse, the action is greatly impeded. Consequently, the amount, rate, and depth of penetration of chemical diffusion are directly associated with the moisture content of the wood. The sapwood of a green Douglas fir timber has a high enough moisture content to permit a chemical to diffuse into it rapidly. The rate at which a chemical can diffuse into the heartwood of thoroughly air-dried Douglas fir is no more rapid than the wood can soak up the solution which as previously shown is a very slow process. Even when green, Douglas fir heartwood has but little more moisture than is necessary to saturate the cell walls. Consequently fibers do not have



to dry very much before they lose their free water, leaving all the remaining moisture in the cell walls.

Thus while Douglas fir is soaking in a chemical solution, the chemical diffuses into the water in the wood and the water just beneath the treated zone moves outward in response to the vapor-pressure gradient and is eventually lost to the solution. Owing to its original low moisture content, the heartwood of Douglas fir, when steeped in a hot chemical solution having a comparatively low vapor pressure, soon dries enough to reduce materially the rate at which the chemical will diffuse into it. For this reason it is impossible, in a reasonable length of time, to get a deep penetration of a chemical into the heartwood of a Douglas fir timber. The green sapwood of all species on the other hand is easily penetrated and deep penetration can be effected even in green 7 by 9 white oak ties by means of diffusion.

Douglas fir timbers dry in a chemical solution at about the same rate as matched untreated timbers do when exposed to the attained bath temperature and a relative humidity that is in equilibrium with the vapor pressure of the treating solution. The bath temperature and the relative vapor pressure of the treating solution need to be considered carefully in working out appropriate treating technic. If the items being treated can be dried rapidly without end or surface checking, the temperature and the concentration of the bath may be high. Timbers like boxed-heart 12 by 12's, however, cannot be treated so drastically.

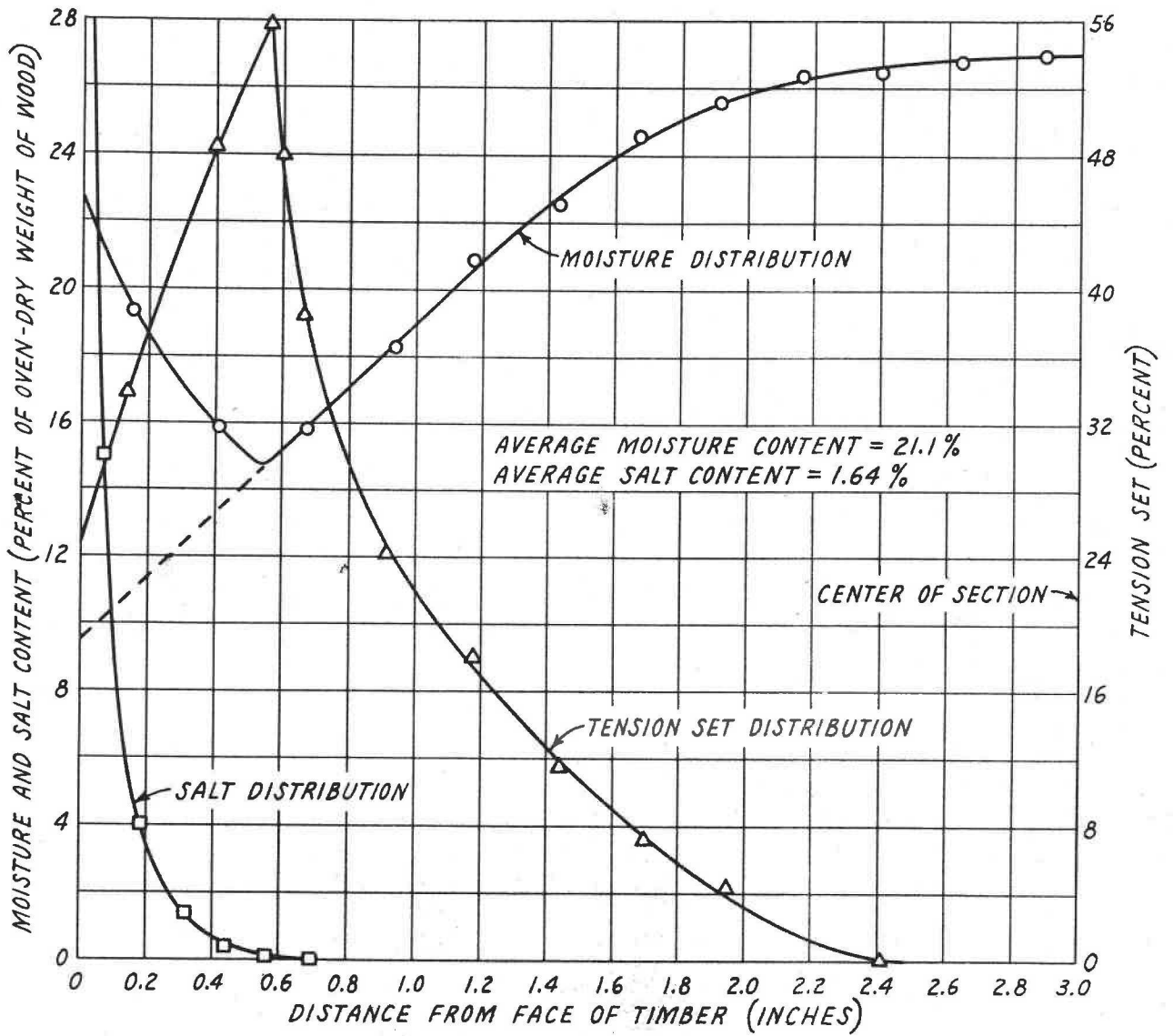
Theoretically the rate at which a chemical will diffuse into wood containing a given amount of free water is proportional to the absolute temperature of the bath. Because the inherent properties of Douglas fir prohibit bath temperatures much in excess of 160° F. the range of temperature encountered in chemical seasoning is comparatively small. Within the temperature range of 80° to 160° F. the osmotic pressure does not vary much more than 14 percent. Hence, for practical purposes the rate at which a chemical will diffuse into Douglas fir may be considered a constant throughout the temperature range. With the exception of increasing the drying rate during the soaking process, elevated bath temperatures are not particularly useful and their use should be avoided in treating items that check easily.

#### Absorbed Chemicals Affect the Dimension of Wood

The foregoing presents a rough concept of the mechanism of impregnating wood by the methods used in chemical seasoning. But the story would not be complete without a discussion of the antishrink effects of the chemical which, during the process of treating and subsequent drying, diffuses into the hygroscopic moisture (moisture in the cell wall; the loss of which causes shrinkage). In choosing a chemical seasoning agent its antishrink as well as its water-retention properties should be

Figure 3.--Moisture, salt, and tension set.  
Distribution in a 6 by 12  
Douglas fir timber after 5 days  
of drying at 160° F. and 72 per-  
cent relative humidity.

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$$\text{TENSION SET (IN PERCENT)} = \frac{\text{TOTAL NORMAL SHRINKAGE} - \text{TOTAL OBSERVED SHRINKAGE} \times 100}{\text{TOTAL NORMAL SHRINKAGE}}$$

FIG. 3

considered. Various chemical solutions will subsequently be compared with respect to these properties. At this point the discussion will be limited to an explanation of how the dimension of wood is affected at various stages of the chemical seasoning process.

In the process of absorbing a chemical, wood undergoes certain physical changes. Within the penetrated zone, the chemical is present in the cell cavities and also in the fine wood structure in the cell walls. In the outer fibers the hygroscopic moisture in the cell walls and the free water in the cell cavities attain a chemical concentration that is practically equal to that of the treating solution. In diffusing into the hygroscopic moisture the chemical causes the cell walls to expand more or less beyond their green dimension. The chemical concentration decreases from the surface of the timber to the other side of the treated zone which contains practically no chemical. See figure 3. As previously explained, in this region the chemical concentration gradient creates a vapor pressure gradient and also causes different degrees of swelling.

From the standpoint of antishrink the absorbed chemical plays its most significant role when the treated timbers are subsequently dried. When the vapor pressure of the surrounding air (relative humidity) is lower than the vapor pressure of the chemical solution in the wood, the treated fibers gradually lose their moisture and the dry chemical is precipitated in both the cell walls and cell cavities. The chemical that is deposited in the cell cavity of course has no effect on the ultimate shrinkage of the wood. The chemical that is deposited in the cell walls, however, acts as chinks between the fibrils, thus reducing the shrinkage of treated wood in proportion to the volume of the chemical in the fine wood structure.

The antishrink effect is modified by the concentration of the treating solution.<sup>2</sup> In one experiment thin sections of wood were treated in different concentrations of sodium chloride. The shrinkage of the specimens treated with 36, 25, and 15 grams of sodium chloride per 100 grams of water was almost identical for each. Figure 4 shows that the shrinkage of the specimen treated with 5 grams of salt per 100 grams of water was slightly greater, and the shrinkage of the specimen treated with 2 grams of salt per 100 grams of water was considerably greater. The shrinkage of the latter specimen almost equalled the shrinkage of the untreated control. The experiment shows that when the wood specimens are slowly dried the salt concentration of the unsaturated solution in the wood structure increases and that the salt eventually diffuses into the cell wall.

Very often it is advantageous to chemically treat wood so that the chemical will continue to diffuse into the cell wall during the drying process. This action cannot be obtained, however, if the moisture in the cell walls becomes saturated during the original treatment. There is then no mechanism by which the supply of chemical in the cell cavity can find its

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<sup>2</sup>"Effects of Inorganic Salts Upon the Swelling and the Shrinking of Wood" by Alfred J. Stamm.

way into the cell wall. By drying wood that has been treated in a saturated solution of a single chemical, the reserve supply of chemical solution in the cell cavity will dry first and the dry chemical will be precipitated in consequence. When deposited in the cell cavities the chemical has no antishrink effects.

In order that the over-all absorbed chemical may have its maximum effect on the antishrink of the wood, partially saturated solutions must be employed. As the concentration in the cell cavities gradually increases, diffusion will continue; little if any free chemical remaining in the cell cavity at the end of the drying process.

An excellent chemical seasoning agent would be one that (1) contains a high percentage of solid without being too viscous; (2) has a relative vapor pressure of 0.75 or 0.80 at time of treatment; (3) remains in a liquid state in the cell cavities at relative humidities as low as the wood will encounter in service. The over-all shrinkage of a timber treated with such a solution would not be materially affected but it would tend to reduce the shrinkage and consequently the tension stresses in the treated portion.

With antishrink effects in mind a mixture of chemicals in solution best suits our purpose; a solution in which the same water acts as a solvent for both chemicals.

The first chemical chosen would be highly soluble, would have a relatively small molecule, and when dissolved in water would not be too viscous and its saturated solution would have a relative vapor pressure of 0.75 to 0.80. This chemical would be added to a partially saturated solution of a chemical which would not crystallize out when the treated wood was subsequently dried in usual relative humidities. The latter chemical should preferably be highly soluble in water and its concentration should be so adjusted that its relative vapor pressure will not materially affect the vapor pressure of the saturated solution of the first chemical.

Glycerine, diethelene glycol, invert sugar, and hydrol are examples of the second chemical and quite a number of chemicals would serve reasonably well for the first. A typical treating solution and perhaps one of the best for water retention and antishrink alike is a 40 percent solution of invert sugar to which is added a pound of urea for every pound of water in the sugar solution. Both chemicals diffuse into the wood during treatment and because they remain in solution in relative humidities as low as 25 percent they continue to diffuse into the cell walls as the concentration in the cell cavities increases during drying.

#### The 5-C's of Chemical Seasoning Plus Antishrink Effect

In estimating the value of a chemical for chemical seasoning purposes the 5-C yard stick may be used which appraises the quality of the

- ⊗ No salt
- 2 grams sodium chloride per 100 grams of water
- 5 grams sodium chloride per 100 grams of water
- 25 grams sodium chloride per 100 grams of water
- 36 grams sodium chloride per 100 grams of water

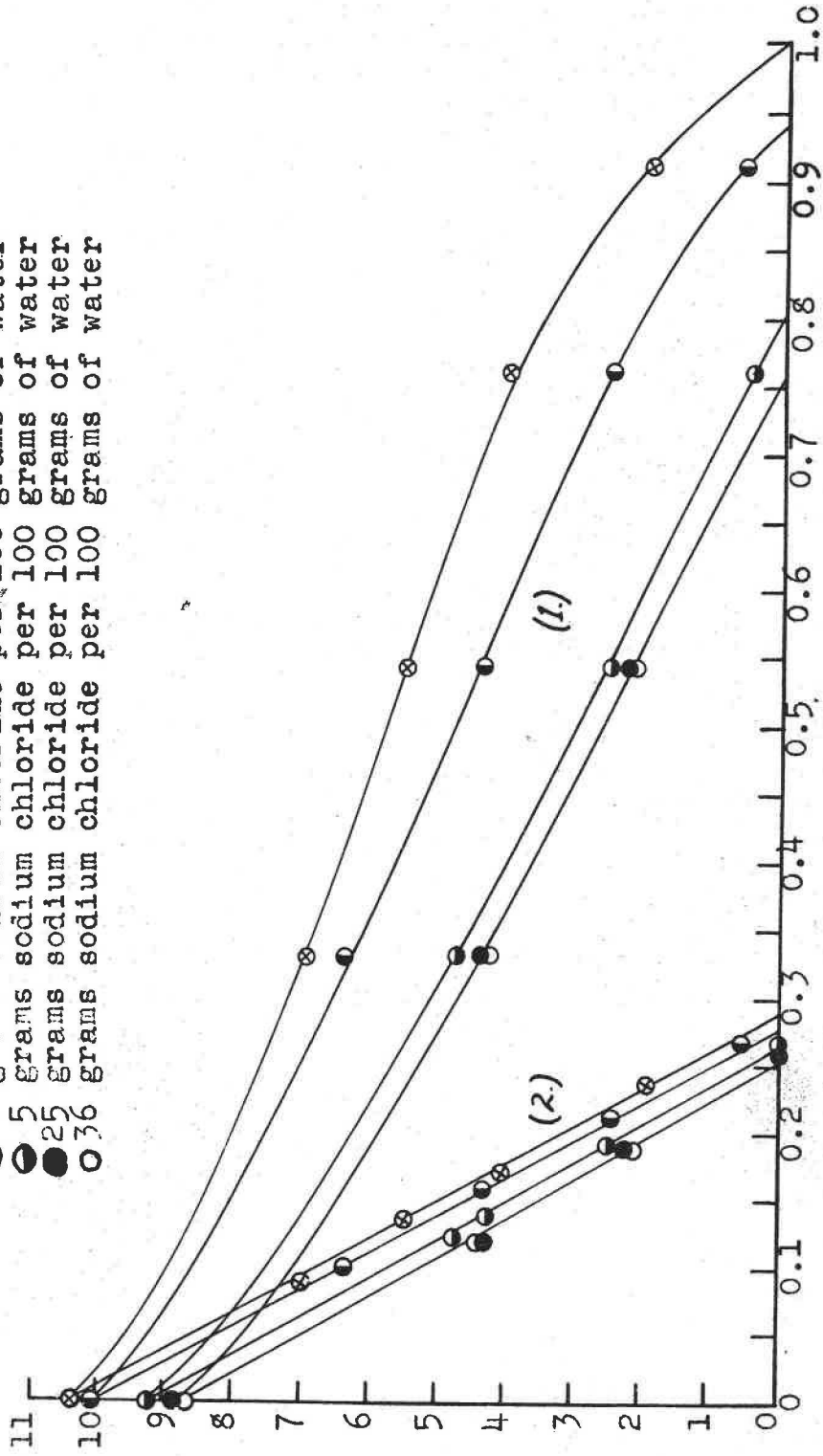


Figure 4.--(1) Relative vapor pressure-shrinkage and (2) moisture content-shrinkage relationships for white pine treated with different concentrations of sodium chloride solution.

Figure 4

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chemical with respect to (1) cost, (2) condensation problems, (3) corrosion effects, (4) conductivity (electrical), (5) color. In addition to these items the antishrink property of a chemical should also be evaluated.

Table 2 was prepared with no thought of finality but just by way of first, focusing attention on the fact that the list of chemicals having promise of being suitable for the chemical seasoning of Douglas fir is surprisingly short; second, indicating a technic which may be employed in assaying the value of any chemical as an aid to seasoning.

Cost.--While the quantity of chemical needed for chemical seasoning has not been definably established a value of 40 pounds per thousand board feet may be assumed for estimating the cost of the chemical used in treating the wood. Hence everything else being the same, the unit cost of a chemical is an important factor in selecting a chemical seasoning agent. Common chemicals, in the order of increasing cost up to 10 cents per pound, are listed in table 2.

But in addition to the cost of a chemical, consideration must be given the following properties, some of which have been discussed previously.

Condensation problems.--The relative humidity with which a chemical solution is in balance establishes the minimum relative humidity to which the treated wood may be exposed without causing shrinkage.<sup>2</sup> Moreover, if the treated wood is exposed to a relative humidity in excess of the equilibrium relative humidity, it will tend to become wet by the moisture which it condenses from the air. In the interest of a rapid drying rate and minimum seasoning degrade the treating solution should have a low relative vapor pressure. When treated with such a chemical, the relative humidities used in subsequent drying may be correspondingly low. In this respect, as will be seen from column 4, sodium dichromate with its relative vapor pressure of 52 percent is superior to sodium chloride, for example. When the former salt is used even the most refractory item can be dried in a relative humidity of 52 percent, whereas when the latter salt is used relative humidities less than 75 percent are apt to cause checking.

However, as atmospheric relative humidities usually exceed 52 percent, wood treated with sodium dichromate will sweat in use much of the time. Treating solutions that are in equilibrium with relative humidities ranging from 75 to 80 percent are preferable for purposes of chemical seasoning. When treated with these chemicals wood will dry at a reasonably rapid rate in atmospheric humidities that are not often exceeded. Hence the treated wood will become damp infrequently in use.

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<sup>2</sup>For some reason yet understood, some chemicals do not cause the treated wood to sweat in relative humidities that exceed the relative vapor pressure of the solution. For example: while the relative vapor pressures of saturated solutions of sodium chloride and urea respectively are about the same, salt-treated wood will become damp in a relative humidity of 75 percent whereas urea-treated wood remains dry to the touch in relative humidities as high as 90 percent.

When Douglas fir is treated with any of the listed chemicals, it can be kiln dried without surface checking more readily than untreated wood provided the relative humidities are maintained in accordance with the water-retention properties of the solution employed. But the treating chemicals that have the lower vapor pressures permit the safe use of correspondingly lower drying humidities. Consequently from the standpoint of drying rate such chemicals are preferred to chemical seasoning agents having a higher relative vapor pressure.

Starting from lead nitrate which is almost useless as a chemical seasoning agent, the values of the chemicals with respect to drying rate increase in proportion to their water-retention properties. Opposed to this trend is a series of values which, due to condensation problems, begins with the chemical having the lowest relative vapor pressure and steadily rises as the water-retention properties of the chemical decrease. When, for chemical seasoning work, it is necessary to choose a chemical which is the best compromise between the desire for a rapid safe-drying rate and a minimum of condensation problems, the list of cheap chemicals becomes surprisingly short. Of course, the water retention of an aqueous solution can be modified by adjusting the concentration of a single chemical or by combining two or more chemicals in solution. But flexibility in this respect is not great because of other properties required of a chemical seasoning agent.

Antishrink.--The more soluble chemicals in general reduce the shrinkage of wood to the greater extent. This would be expected from the hypothesis that the antishrink property is proportional to bulk of the dry chemical which diffuses into the moisture contained by the fine swelling structure of the wood. Assuming that the reduced shrinkage is entirely due to this effect it is possible to calculate the antishrink effect by means of the following equations:

$$\begin{aligned} \text{Volume of chemical} \\ \text{which will dissolve} \\ \text{in 100 cc. of water} \\ \text{at a given} \\ \text{temperature} &= \frac{\text{Grams of chemical in 100 cc. of water}}{\text{Density of dry chemical}} \\ \\ \text{Volume}^{\frac{1}{2}} \text{ of resultant} \\ \text{solution} &= \text{Volume of chemical} + 100 \text{ cc. of water} \\ \\ \text{Antishrink} &= \frac{\text{Volume of chemical in 100 cc. of water}}{\text{Volume of the water and chemical} \\ &\quad \text{in solution}} \\ \\ \text{Antishrink expressed} \\ \text{in percent} &= \frac{\text{Reduction in shrinkage of chemically-} \\ &\quad \text{treated wood}}{\text{Shrinkage of untreated controls.}} \times 100 \end{aligned}$$

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<sup>1/2</sup>This is not strictly correct because the water is slightly compressed by the forces associated with the processes of dissolving the chemical.



Table 2

Rank according to price	Chemical	Prices per pound	Water retention Relative humidity in equilibrium with saturated solution, 68° F. b	Antishrink <sup>c</sup> Observed	Calculated	Corrosiveness <sup>d</sup>	Color	Fire hazard	Condensation	Electrical conductivity	Toxicity	Degree of use permitted by individual properties	
												(13)	(14)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
		Dollar	Percent										
1	Sodium chloride.....	0.0075	75	512.7	14.1	3	1	1	2	2	1	NaCl	59
2	Ferrous sulfate.....	.01	93	7.6	7.6	2	3 or 4			2	1	FeSO <sub>4</sub> ·7H <sub>2</sub> O	61
3	Sodium sulfate.....	.01	81	10.7	10.7	4	1	1	1	2	1	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	20
4	Aluminum sulfate.....	.012	81	527.8	28.5	4	1	1	2	2	1	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	20
5	Ammonium sulfate.....	.014	56, 65° F.	30.2	30.2	*1	1	3	3	2	1	Ca(NO <sub>3</sub> ) <sub>2</sub>	70
6	Calcium nitrate.....	.014	95	0	0	1	1	1	1	2	1	Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	47
7	Calcium acetate.....	.0165	87	3.98	3.98	*1	1	1	1	2	1	Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O	38
8	Sodium phosphate.....	.021	76	22.7	22.7	*2	1	1	1	2	1	Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O	38
9	Sodium carbonate.....	.023	90	524.6	24.5	*1	Bleaches	3	2	2	1	NaNO <sub>3</sub>	.....
10	Sodium nitrate.....	.029	86, 75° F.	5.8	5.8	3	1	1	1	2	1	ZnSO <sub>4</sub> ·7H <sub>2</sub> O	.....
11	Zinc sulfate.....	.029	95	14.5	14.5	4	1	1	1	2	1	BaCl <sub>2</sub> ·2H <sub>2</sub> O	65
12	Barium chloride.....	.04	78	14.5	14.5	4	1	1	1	2	1	CuSO <sub>4</sub> ·5H <sub>2</sub> O	.....
13	Copper sulfate.....	.045	95	55.8	43.9	3	1	1	1	2	1	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	.....
14	Urea.....	.045	95	55.8	43.9	3	1	1	1	2	1	KCl	62
15	Potassium chloride.....	.05	95	55.8	43.9	3	1	1	1	2	1		.....
16	Invert sugar 75 percent solids 0.04; Dry.....	.053	95	61.4	29.7	4	1	1	1	1	2		.....
17	Ammonium chloride.....	.06	77.2	18.2	18.2	4	1	1	2	2	1	NH <sub>4</sub> Cl	19
18	Tribasic calcium phosphate.....	.085	52	0	0	1	3 or 4	1	3	2	1		36
19	Calcium arsenate.....	.0675	85, 86° F.	33.3	33.3	*1	2	1	1	2	1	MnSO <sub>4</sub> ·4H <sub>2</sub> O	39
20	Sodium dichromate.....	.07	93	19.9	19.9	3	1	1	1	2	1	MnCl <sub>2</sub> ·4H <sub>2</sub> O	18
21	Manganese sulfate.....	.075	93	19.9	19.9	3	1	1	1	2	1	KNO <sub>3</sub>	67
22	Manganese chloride.....	.075	93	19.9	19.9	3	1	1	1	2	1	Sr(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	.....
23	Potassium nitrate.....	.079	98	7.9	7.9	2	1	1	1	2	1		.....
24	Strontium nitrate.....	.08	86	31.4	31.4	*2	1	1	1	2	1	MgSO <sub>4</sub> ·7H <sub>2</sub> O	39
25	Ammonium carbonate.....	.08	88	42.1	42.1	*1	1	1	1	2	1	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	18
26	Magnesium sulfate.....	.08	98	22.3	22.3	4	1	1	1	2	1	AlCl <sub>3</sub> ·6H <sub>2</sub> O	16
27	Ammonium phosphate.....	.08	98	7.9	7.9	2	1	1	1	2	1	Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·2OH	.....
28	Aluminum chloride.....	.10	98	7.9	7.9	2	1	1	1	2	1	Pb(NO <sub>3</sub> ) <sub>2</sub>	.....
29	Lead acetate.....	.10	98	7.9	7.9	2	1	1	1	2	1	Normal wood	83
30	Lead nitrate.....	.10	98	7.9	7.9	2	1	1	1	2	1		.....

<sup>a</sup> Prices are quotations given in Oil Paint and Drug Reporter, October 1938. (Most prices are in carload lots f.o.b. production plant.)  
<sup>b</sup> Values indicate minimum relative humidity at which treated fibers will not shrink. Relative humidities higher than those indicated will cause condensation.  
<sup>c</sup> Antishrink properties are expressed as the percentage reduction in total shrinkage (green to oven dried) based on shrinkage of untreated controls. <sup>a</sup> Effect of inorganic salt upon the swelling and shrinking of wood, by Dr. Stamm; <sup>b</sup> unpublished data by Johnson and Loughborough; <sup>c</sup> except when checking experimental values calculations are made on solubility at 32° F. calculated values marked C based on solubility of dehydrated chemical. When antishrink of urea-treated wood is based on dimension of wood after treatment the antishrink is 45.6 checking the calculated value 43.9 very nicely.  
<sup>d</sup> Arbitrary ranking as to corrosiveness. \*Indicate ranking based on accelerated test. \*\*Fire-tube data. Values indicate weight loss in percent under conditions of standard test.

Ranking given in columns 7 to 12 is arbitrary but indicates:  
 1. Very extended use (presence of chemical practically no handicap to use).  
 2. Extended use (wide application but effects deleterious or inadequate for some items of wood and special uses).  
 3. Limited application but may not exclude use of chemical for some purposes.  
 4. Very limited (very deleterious may exclude chemical for seasoning work).

The antishrink effects of saturated solutions of several of the tested chemicals on completely impregnated wood have been determined experimentally. The expected antishrink was calculated under conditions of the experiment by means of the above equations. The other calculated antishrink values are based on the solubility of the chemical at 32° F. In calculating the antishrink of some of the chemicals it was necessary to use the density values given for chemical plus water of crystallization. When calculated in this way, the antishrink values are too large, but even as calculated the values indicate the relative antishrink effects of the various chemicals.

Where the expected antishrink values are calculated from conditions of actual test they agree quite well with the actual measured values. The exceptions to the general rule are those calculated for urea and invert sugar.

In the case of these two chemicals the experimental values exceed the calculated values considerably.

The discrepancy in the case of the invert sugar can be explained on the basis of a previously given hypothesis, viz., when wood, treated with a partially-saturated solution is subsequently dried slowly the concentration of the solution in the cell cavities increases and the chemical eventually diffuses into the cell wall. The hygroscopic moisture in Douglas fir occupies 0.175 of the total void volume so that when the moisture content of wood which has been completely filled with a partially-saturated solution is reduced to 29 percent the concentration of the solution is increased 5.7 times. This would saturate all but the most dilute solutions of invert sugar. On a solution basis concentrations of invert sugar greater than 75 percent are so viscous, however, that little diffusion could be expected. Assuming that, in drying, a 40-percent sugar solution attained a concentration of 75 percent, that is, 300 grams of sugar per 100 grams of water, the calculated antishrink value would be 65 percent. This value agrees reasonably well with the observed value of 61.5 percent. The calculation tends to confirm the hypothesis regarding the mechanism by which absorbed partially-saturated chemical solutions affect the shrinkage of wood.

The discrepancy between calculated and observed antishrink effects of urea is due to a different phenomenon. Urea is selectively adsorbed by wood hence causes wood to swell considerably beyond its green or water swollen dimension. If shrinkage and antishrink values are based on the urea-swollen dimension the observed antishrink value turns out to be 45.6 as against a calculated value of 43.9

The antishrink effects of various chemicals have been discussed in detail (1) to present evidence that the chemical diffuses into the cell walls; (2) to create reasonable confidence that the antishrink effects of any chemical can be calculated quite accurately if the solution concentration and density of the dry chemical are known; and (3) to show that urea and invert sugar both have outstanding antishrink effects.

The significance of antishrink as far as chemical seasoning is concerned is not that a treated timber will shrink less than an untreated control. The significance lies in the ability of a chemical to minimize the tendency of the treated wood to shrink when, as in air seasoning, the relative humidity of the drying atmosphere is less than the relative vapor pressure of the absorbed chemical.

In this connection it should be realized that the full antishrink of invert sugar cannot be realized during air drying. Because of the low water-retention properties of a 40-percent invert sugar solution, the treated portion of the wood loses moisture in air drying more rapidly than the chemical can diffuse from the cell cavity into the cell wall. Hence in order to make use of the antishrink properties of invert sugar solution its water-retention properties must be increased by mixing it with other chemicals.

When Douglas fir timber is treated in a suitable solution of invert sugar and urea mixture, no shrinkage from green dimension occurs in the surface fibers as long as the relative humidities during drying do not fall below 50 percent. The total observed antishrink effect of a 40 part by weight of invert sugar, 60 part of water, and 60 part of urea was 71.5 percent. So far as known, a chemical seasoning agent which imparts a lesser degree of antishrink will not prevent 12 by 12-inch boxed-heart timbers from checking during air drying. Even this high degree of antishrink is not adequate.

Where refractory Douglas fir sizes are to be subsequently air dried, they must first be treated with chemical solutions that impart a high degree of antishrink. The antishrink aspects of a treatment, however, are not particularly significant if the timbers are to be dried under properly controlled conditions of relative humidity as in kiln drying. The water-retention property of the chemical seasoning agent alone is sufficient to protect the timber from checking provided the relative humidities are properly controlled.

Corrosion.--When a chemical is imbibed by wood, it naturally modifies the properties of the wood. Some salts are particularly corrosive to ferrous fastening. Moreover, if during kiln drying it is necessary to use relative humidities which are in excess of the relative vapor pressure of the absorbed chemical solution, the timbers will drip salty water on the metal parts of the kiln, thus corroding rails, track supports, pipe, and so forth. If the items being dried will stand relative humidities which are lower than the relative vapor pressure of the salt solutions corrosive treating solutions may be used without material damage to the kiln. But the presence of such chemical in the wood after drying still creates a corrosion hazard to metal fastening when the wood is put in use.

Under certain circumstances and for certain conditions of use, timbers treated with corrosive chemicals may be satisfactory. Obviously, however, regardless of cost, the use of a corrosive salt in chemical seasoning work is limited. The corrosion hazard further reduces the list of chemicals which can profitably be used.

Conductivity.--Salts on going into solutions ionize and thus the electrical conductivity of salt solutions is greater than that of water alone. Hence, if high electrical insulating values are required as in the case of cross arms and poles, the wood should not be treated with a salt solution. For most purposes high electrical resistance is not required of

wood. But when it is required, a treatment with an organic chemical solution is much preferable to a treatment with a salt solution like sodium chloride, monoammonium phosphate, etc.

Color.--Chemicals differ in their effect on the color of wood. A distinctive color might be an advantage in selling chemically-seasoned Douglas fir dimension and cuttings. However, the chemical seasoning agent should be chosen with the ultimate use of the wood in mind.

Other properties.--Other properties to be considered besides those previously mentioned are fire resistance, inflammability, insect resistance, and decay resistance.

In table 2, the chemicals have been given an arbitrary ranking with respect to most of these properties with the view of showing the extent that the presence of the chemical in the wood may limit its use. According to the system employed, normal wood was given the ranking of one. This scheme does not credit a chemical with the beneficial properties it imparts to wood. For example, with the exception of the nitrates the salts are, to some degree, fire retardants; aluminum sulfate, ammonium sulfate, sodium carbonate, ammonium chloride, manganese chloride, ammonium phosphate, aluminum chloride and possibly calcium arsenate rank high as fire retardants.

In the concentrations used in chemical seasoning most of the salts are somewhat decay resistant for a while and zinc sulfate is perhaps equal to zinc chloride. However, like zinc chloride, high concentrations of zinc sulfate tend to hydrolyze wood.

The ammonium salts, including urea, tend to separate into their component parts at kiln temperature. For this reason urea controls surface checking most effectively when the treated wood is dried at low temperatures, that is, air dried. When wood treated with the other ammonium salts is subsequently kiln dried, the corrosiveness as given in column 4 is apt to be increased. (See item 5 -- ammonium sulfate.) Accelerated corrosion tests indicate that nails are corroded less when driven into Douglas fir that has been treated with sodium dichromate and calcium nitrate than nails driven into matched untreated material.

A study of the table, in the light of what is known about the properties that are required of a chemical seasoning agent, leads to the conclusion that the use of each chemical is more or less restricted; some chemicals cannot be employed if the timbers are to be subsequently air dried; other chemicals impart properties to the wood which make it more or less unfit for certain uses. But of all the chemicals listed, urea has the best chance of wide application.

By combining chemicals, undesirable water-retention properties can be improved, antishrink properties increased and beneficial properties such as decay and fire resistance retained. As a general rule it can be said that when two chemicals are mutually dissolved by the same water, the relative vapor pressure of the solution is lower than the

vapor pressure of a solution of either chemical alone.<sup>5</sup> Sometimes it is not possible to anticipate the effects of a solution of two or more chemicals. For example, experience has indicated that urea plus ammonium sulfate is not as good a chemical seasoning agent as urea alone.

### General Statement About the Chemical Seasoning of Douglas Fir

The previous observations throughout this report have been reduced to a few generalities with the view of showing the status of the chemical seasoning study in bolder relief. Additional research may change the picture somewhat, but in the light of present information this is the way it appears.

Chemicals to be suitable for use as chemical seasoning agents must be water-soluble and must possess one or both of the following properties in suitable degree.

Water retention.--The relative vapor pressure of a satisfactory chemical seasoning agent generally should be in equilibrium with a relative humidity of about 75 percent.

Antishrink.--When large chemically-treated 3 by 12 and larger Douglas fir timbers are air dried, a chemical seasoning agent should considerably reduce the amount of shrinkage which occurs when the wood dries. When large chemically-treated Douglas fir timbers are subsequently kiln dried, the antishrink effect of the treating chemical is unimportant if it has the proper water-retention properties.

Chemicals such as sodium chloride, ammonium sulfate, and mono-ammonium phosphate have good water-retention properties but relatively poor antishrink properties. Urea possesses good water-retention properties and very good antishrink properties. Mixtures of urea and invert sugar possess good water-retention properties and excellent antishrink properties.

Few chemicals cost as little as 10 cents a pound. If each low-priced chemical is considered with respect to its effects on the color, corrosiveness, fire resistance, and inflammability, decay resistance, insect resistance, electrical resistance, and hygroscopicity of the wood, the resultant process of elimination will leave the list very short.

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<sup>5</sup>"Hygroscopicity of Fertilizer Materials and Mixtures," Adams and Wertz, Industrial and Engineering Chemistry, Vol. 21, No. 4, April 1929;  
"Drying Gases by Absorption," Perry and Duus, Chemical and Metallurgical Engineering, February 1934.

In appraising the commercial significance of chemical seasoning a distinction must be made between what the process will do under ideal conditions and what it will profitably do under average commercial conditions. To say that timbers of a given size can be chemically seasoned without surface checking is quite different from saying that treated timbers of the same size can be safely or profitably kiln dried in the average run of commercial kilns in a practical length of time.

With laboratory care and refined drying equipment Douglas fir ranging in size from 1-inch lumber to boxed-heart 12 by 12 timbers can be chemically seasoned to a low moisture content without surface checking. In kiln drying the more refractory items after chemical treatment, a hair-trigger control of drying conditions is required which is not often attainable in commercial kilns. Moreover, because of the drying periods there is little promise of being able to profitably kiln dry timbers larger than 6 by 12's after chemical treatment. We must look forward to the development of chemical treatments which will permit large timbers to dry in place.

The commercial feasibility of kiln drying items of Douglas fir after chemical treatment generally depends on how well the kiln can be regulated and on the period required to dry them to the desired moisture content. Figuring the kiln rental at 30 cents a thousand a day, drying periods in excess of a week or 10 days are apt to be prohibitively expensive. After a chemical treatment 3-inch planks can be kiln dried in less than a week and 4-inch planks can be kiln dried in about 10 days. Side-cut timbers up to 6 by 12's can be kiln dried enough in a week's time to stand storage in the vicinity of Chicago. But by and large, the number of sizes that may be profitably kiln dried after chemical treatment is limited.

The commercial feasibility of kiln drying items of Douglas fir after chemical treatment also depends on the likelihood of the treating chemical setting up a corrosion hazard in the kiln.

In drying items treated with sodium chloride, for example, a corrosion hazard is set up in the kiln when the required humidities are in excess of 73 percent. Unless the normal corrosive action of salt can be materially reduced, salt-treated 12 by 12-inch boxed-heart timbers cannot be expediently dried in a kiln because in drying this item relative humidities in excess of 75 percent are required. It is not necessary to create a corrosion hazard in the kiln when drying salt-treated boards, planks, and side-cut timbers up to 6 by 12's. In drying these items the humidities required to prevent checking are 73 percent or less.

The feasibility of kiln drying items of Douglas fir after a chemical treatment is therefore limited by the cost of the process, the suitability of drying equipment, and by the corrosion hazard set up in the kiln when drying large timbers that have been treated with a corrosive chemical.

Choice of treating chemical influences not only the feasibility of kiln drying but also the air drying of the treated timbers.

The good antishrink and water-retention properties of a saturated urea solution make its use as a chemical seasoning agent more flexible than any other single chemical thus far tried. Urea-treated Douglas fir can be kiln dried just as satisfactorily as Douglas fir treated with any other cheap chemical. Moreover, the danger of checking during subsequent air drying is less when urea is used than any other single chemical thus far tried. Moreover, urea, which is noncorrosive, does not materially alter the natural color of Douglas fir; in the concentration used in chemical seasoning urea increases the decay resistance and reduces the inflammability of the wood somewhat.

A solution consisting of a 40-percent solution of invert sugar to which is added a pound of urea for every pound of water is technically the best chemical seasoning agent so far tried. The invert sugar slightly improves the water-retention properties of urea alone and greatly augments its antishrink property. After being properly treated with the solution, it now seems that 12 by 12-inch boxed-heart Douglas fir timbers will not surface check badly when subsequently air dried or when permitted to dry in place provided they do not become wet while seasoning. Moreover, a treatment with this combination of chemicals prior to kiln drying has a number of advantages over a treatment with a single salt solution.

End coatings seem essential in order to minimize the end checking of chemically-treated timbers larger than 3 by 12-inch planks.

### Conclusions

We are on top of the job as far as the fundamentals of Douglas fir chemical seasoning are concerned. It is no longer necessary to speculate as to the results of this or that process or the feasibility of using this or that chemical. Further research undoubtedly will produce refinements, but it will not alter the basic principles of the process as now understood. Laboratory and field experiments show that the process has a place in the commercial drying field. It permits the operator to dry rapidly various sizes of Douglas fir that heretofore either had to be dried slowly or could not be dried at all without checking. Rough calculations indicate that certain sizes can now be profitably chemically seasoned.

Further advances are in prospect when the project emerges from the swaddling clothes of laboratory technic into a full-grown industrial drying process. The essence of such advancement is simplification with the view of reducing costs. The most forward step to be taken at present would be the development of means of treating wood without the use of tanks or similar equipment. The so-called dry and sprinkling methods deserve a commercial trial, but in adapting chemical seasoning to commercial needs the basic principle of the process must be borne in mind. Chemical seasoning is a sharp tool that may cut the operator's throat if he doesn't know how to handle it. Hence, a study of the primer is not a bad beginning, but commercial processes can best be developed by the cautious experiments of men who are not satisfied with the status quo of the present seasoning methods.

Typical methods for chemically seasoning Douglas fir

Schedule:	Size	Chemical treatment			Drying treatment		
		Days	Concentration	Temperature	Days	Dry bulb	Relative humidity
No.				°F.		°F.	Percent
1-A	3 by 12-inch side cut or boxed heart	<u>Soak in Sodium Chloride Solution</u>			<u>Kiln Schedule</u>		
		1/2	Saturation	41 to 160	2	160	70
		1-1/2	Saturation	160	1	170	60
					1	180	50
Remarks: Dried to 14 percent moisture content. Dripped water on damp days; Only sap corners attracted moisture from air when planks dressed to standard dimensions.							
1-B	3 by 12-inch side cut or boxed heart	<u>Soak in Sodium Chloride Solution</u>			<u>Kiln Schedule</u>		
		2	Saturation	40	2	160	73
					1	170	60
					1	180	50
Remarks: Dried to 16 percent without degrade; No condensation problem after dressing to standard dimensions.							
1-C	3 by 12-inch side cut or boxed heart	<u>Soak in 40 Percent Solution of Invert Sugar to Which Was Added 1 Pound Urea Per Pound of Water in Solution</u>			<u>Store on Sticks in a Hot Dry Room Simulating a Hot Dry Climate</u>		
		4		40 to 60	2-1/2	100 to 120	25
Remarks: Planks in a perfect condition after attaining a moisture content of 13 percent. Their color was natural and they did not condense moisture from the air. Full length planks after having been given the 1-C chemical treatment could probably be put into service any place in the United States without further drying.							
2-A	6 by 6-inch side cut	<u>Soak in Sodium Chloride Solution</u>			<u>Kiln Schedule</u>		
		4	Saturation	40 to 60	2	160	73
					2	170	70
					2	175	70
			1	180	55		
Remarks: The treatment will dry 6 by 6-inch timbers to a moisture content of 18 to 20 percent. The drying time seems too long to be practical. Danger of corroding iron in the kiln if humidities range about 73 percent.							
2-B	6 by 6-inch side cut	<u>Soak in Urea Solution</u>			<u>Kiln Schedule</u>		
		3	Saturation	40 to 60	2	160	71
					2	170	70
					1	175	62
			1-2/3	180	56		
Remarks: Without an end coating timbers dry perfectly to 18 to 20 percent moisture content and will not subsequently check in relative humidities as low as 25 percent.							
2-C	6 by 6-inch boxed heart	<u>Soak in Urea Solution</u>			<u>Kiln Schedule</u>		
		5	Saturation	40 to 60	9-3/8	120	70
Remarks: When so treated and dried 6 by 6-inch boxed-heart timbers will not degrade in a relative humidity of 25 percent.							
2-D	6 by 6-inch boxed heart	<u>Soak in Sodium Chloride Solution</u>			<u>Kiln Schedule</u>		
		5	Saturation	40 to 60	3	140	77
					2	140	75
					2	140	70
			2	160	70		
			2	160	60		
Remarks: Will dry to moisture content of 16 to 18 percent. The 11 day period in the kiln may not be economical. Also danger of corroding kiln trucks, kiln rails, track supports, etc.							
2-E	6 by 6-inch boxed heart	<u>Soak in a 40 Percent Solution of Invert Sugar Saturating the Solution with Urea</u>			<u>Air Dry in Humidities not Less Than 55 Percent in an Unheated Shed for 60 to 90 Days</u>		
		5		40 to 60			



Typical methods for chemically seasoning Douglas fir (Continued)

Schedule	Size	Chemical treatment			Drying treatment		
		Days	Concentration	Temperature	Days	Dry bulb	Relative humidity
No.				°F.		°F.	Percent
		<u>Soak in Sodium Chloride Solution</u>			<u>Kiln Schedule</u>		
3-A	6 by 12-inch side-cut	3	Saturated	120	5	160	73
					18	160	73
Remarks: Five-day drying period will season side cut timbers to stand storage in sheds in the vicinity of Chicago. Eighteen days of drying required to reduce their moisture content to 16 to 18 percent.							
		<u>Soak in Sodium Chloride Solution</u>			<u>Kiln Schedule</u>		
3-B	6 by 12-inch boxed heart	6	Saturation	120	8	160	73
					24	160	73
Remarks: As always kiln control must be exact relative humidities in excess of 75 percent will cause timbers to sweat and drip salt water on tracks, pipes, etc. Eight-day drying will season boxed-heart timber enough to stand storage in unheated shed in vicinity of Chicago; 24 days will dry timbers to a moisture content of 14 to 16 percent when they can be used in dry climate.							
		<u>Soak in Urea Solution</u>			<u>Air Dry Preferably in a Shed</u>		
3-C	6 by 12-inch side cut	6	Saturated	40 to 80			
		<u>Soak in 40 Percent Solution of Invert Sugar: Saturate With Urea</u>			<u>Air Dry Preferably in a Shed</u>		
3-D	6 by 12-inch boxed heart	8		40 to 80			
Remarks: Either 3-C or 3-D may permit the use of respective timbers directly from the bath.							
		<u>Soak in 40 Percent Solution of Invert Sugar: Saturate Solution With Urea</u>			<u>Air Dry in a Shed</u>		
4-A	12 by 12-inch boxed heart and side-cut	15		40 to 80			
Remarks: It seems that planks up to 4 inches in thickness can be chemically treated and subsequently kiln dried. Timbers 6 inches and thicker, for economy's sake should be chemically treated and either air dried or allowed to dry in place. Timbers or planks thicker than 3 inches should be end coated.							