are obtained by the nitric and glacial acetic acid oxidation of diphenylhalogenofurans, and are assigned configurations on the basis of these syntheses.

The addition of hydrogen chloride to *cis* and *trans*-dibenzoylchloroethylenes under different conditions gives mixtures of *dl* and *meso*-dibenzoyldichloroethanes and diphenyldichlorofuran as independent end-products, the ratios of yields being independent of the configuration of the starting material. These facts are regarded as evidence for the 1,4 mechanism in the addition of halogen acids to α,β-unsaturated ketones.

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[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY,[1] FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Effect of Inorganic Salts upon the Swelling and the Shrinking of Wood[2]

BY ALFRED J. STAMM

Wood, like all other fibrous materials, possesses the property of shrinking and swelling upon the loss or gain of moisture. The swelling, according to the classification of Katz,[3] is of the maximum swelling type. On drying green wood no shrinkage occurs until the moisture content is reduced below the fiber-saturation point (the moisture content below which the activity of the water becomes less than one). The shrinkage as manifested by the percentage change in external dimensions increases with an increase in the density of the wood. It is greatest in the tangential direction (tangent to the annual rings), varying from 6.0 to 12.0%. In the radial direction (from the center of the tree to the periphery) it varies from 3.0 to 7.0% and in the longitudinal direction (parallel to the fibers) it is only a small fraction of one per cent. The practically negligible longitudinal swelling and shrinking is accounted for on the basis of the swelling taking place only between the thread-like micelles which, in general, are oriented parallel to the length of the fibers. The greater shrinkage in the tangential direction than in the radial is accounted for on the basis of ray cells which have their longitudinal component in the radial direction of the wood, restraining the dimension changes in that direction.

x-Ray studies have shown that the swelling of a cellulosic fiber by water does not affect its crystal lattice.[3] The water must go between the constituent units of the structure rather than within these units (intermicellar swelling as contrasted to intramicellar swelling). Concentrated solutions of certain salts such as lithium thiocyanate, as well as of alkalies, however, change the crystal lattice,[4] showing that their action is intramicellar.

Unfortunately, it is extremely difficult to determine the total swelling of fibrous materials from the dimension changes. With wood, where the external dimension changes are easy to follow, it is extremely difficult to even approximate the internal changes that take place in the lumen of the fibers. In a homogeneous material free from stresses and strains the lumen would change in size on swelling and shrinking of the material, the same as the external dimensions of a piece of the material which would just fill the lumen. This, however, is not the case for wood or any other fibrous material. Because of these difficulties, swelling and shrinking measurements have, in general, been made in terms of weight change. This procedure may, however, be very misleading as swelling can only be proportional to the weight change over the sorption range. Absorption by the grosser capillary structure cannot cause swelling. Data for the absorption of salt solutions by wood, such as those of Schwalbe and Fischer,[5] are therefore hardly a measure of the swelling and further give no information as to whether the salts remain in solution in the water which becomes bound, or if they are merely dissolved in the free capillary water. There also seems to be a lack of information on the effect that these salts have upon the subsequent shrinkage of the fibrous materials.

Swelling Measurements

To avoid the foregoing difficulties as far as possible, measurements in the studies reported

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[1] Maintained at Madison, Wis., in coöperation with the University of Wisconsin.

[2] Presented before the Colloid Division, American Chemical Society, Chicago, Ill., September 11–15, 1933.

[3] Katz, *Trans. Faraday Soc.*, **29**, 279 (1933).

[4] Katz and Derksen, *Rec. trav. chim.*, **50**, 149, 737, 746 (1931).

[5] Schwalbe and Fischer, *Kolloid Z.*, **57**, 338 (1931).

here were made on a combined weight change and external dimension change basis on small wood sections of Sitka spruce and white pine, approximately 4 by 4 by 0.2 cm., the short dimension being in the direction of the fiber length. Practically all the fibers were cut across at least once, thus avoiding difficulties in penetration and in removing of air from the sections. For most of the measurements the sections were first oven dried to determine the weight of the oven-dry wood (although this does slightly affect the subsequent swelling, it was shown to have no effect upon the nature of the results). They were then soaked in water with the application of alternate suction and pressure to remove the air. This procedure took practically a day to replace all the air with water. The sections were then rapidly wiped on the surface with a towel, weighed and the dimensions determined. The completeness of the removal of air was tested by a comparison of the weight of the water taken up with the theoretical amount that could be taken up, calculated from the total void volume. The fractional void volume is given by the equation

$$V = 1 - d/d_0 \qquad (1)$$

in which d is the over-all density of the wood and d_0 the density of wood substance determined in water.[6] At the bottom of columns 5 and 6 of Table II such a comparison is given. The agreement is satisfactory, considering the difficulty in removing surface water without removing capillary water when wiping the sections.

The water-soaked sections were then placed in saturated salt solutions with an excess of salt present and allowed to remain for at least two weeks. Swelling beyond the water-swollen dimensions was found to be complete for most of the salts in a few days, but calcium and magnesium chlorides required about a week to come to equilibrium. The swelling of Sitka spruce, which is expressed throughout this section of the paper as the percentage swelling beyond the water-swollen condition in terms of external dimension changes, is given in Table I (columns 10, 11 and 12) for a series of chloride and potassium salts together with some of the physical properties of the salt solutions. In no case was there a measurable longitudinal swelling. The radial swelling was much smaller than the tangential swelling and where the tangential swelling was small the radial swelling was negligible. The order of decreasing tangential and volumetric swelling for the different salts is practically the same as the order of decreasing solubility of the salts in terms of mole equivalents per kilogram of solvent (see Table I, column 3). The only reversal of order occurs with magnesium and manganese chlorides. In this case the solubilities differ but slightly and as magnesium salts stand higher in the lyotropic series for swelling and dispersion of colloids in general, such a reversal might be expected. The relative positions of these two salts with respect to other physical properties given, tends to confirm further this reversal effect. Potassium bichromate is the only salt considerably out of position. This salt seems to be reduced by the wood as shown by the greenish color. The amount taken up by the wood is also abnormal, as shown in Table II, column 7.

The order of decreasing swelling is also the same as the order of increasing relative vapor pressure over the salt solutions (see Table I, column 5) in all cases but the abnormal potassium bichromate. If the salts entered only the gross capillary structure of the wood and not that within which swelling takes place, the sections should all shrink rather than swell and those which gave the greatest swelling should have shrunk the most for this would be equivalent to having small desiccators throughout the wood for controlling the moisture content of the cell walls, according to the relative vapor pressure. The fact that wood is swollen the most in salt solutions which show the lowest relative vapor pressure is strong evidence that the salt solutions must enter the swelling structure.

It is interesting to note that the order of decreasing swelling is also the order of decreasing surface tension of the saturated salt solutions (see Table 1, column 6) with the one reversal of position of potassium iodide and chromate. The fractional volume of the salt solution occupied by salt in solution (see Table I, column 4)

$$V_{\text{sol}} = \left(\frac{100 + g}{d_s} - 100.1\right)\bigg/\left(\frac{100 + g}{d_s}\right) \qquad (2)$$

where g is the solubility of the salt in grams per 100 g. of water and d_s is the density of the salt solution, follows the swelling order with but two changes of position.

The effect of the hydrogen-ion concentration upon the swelling was determined. The measurements were made with a glass electrode. Hydrochloric acid and potassium hydroxide were used for varying the P_{H} in a salt-free unbuffered sys-

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[6] Stamm, *J. Phys. Chem.*, **33**, 398 (1929).

TABLE I

SWELLING OF SITKA SPRUCE IN SATURATED SALT SOLUTIONS

		Physical properties of satd. salt solns. at 20°					Order of soly. of cellulose in boiling satd. solns.		Swelling of wood beyond water-swollen condition		
Salt 1	Water of crystn 2	Soly., mol. equiv. per kg. solvent 3	Fractiona vol. occupied by salt in soln. 4	Rel. vapor press. P/P_0, % 5	Surface tension, dynes per cm. 6	P_H 7	Mono-valent 8	Di-valent 9	Tangential, % 10	Radial, % 11	Volumetric, % 12
$ZnCl_2$	$1^1/_2H_2O$	54.0	0.538	10.0	152.2	−0.16			1.93	0.90	2.89
LiCl	$1H_2O$	18.8	.282	11.7	100.0	+8.33	1		1.67	.26	1.95
$CaCl_2$	$6H_2O$	13.4	.183	32.3	97.4	4.24		1	1.41	.26	1.75
$MgCl_2$	$6H_2O$	11.5	.147	33.1	93.4	3.60			0.90	.13	1.11
$MnCl_2$	$4H_2O$	11.8	.154	54.3	90.1	3.57			.36	.00	0.36
NaCl		6.1	.117	75.8	82.8	4.94	2		.12	.00	.12
NH_4Cl		6.9	.214	79.2	80.9	3.67	4		.12	.00	.12
KCl		4.6	.124	89.2	79.0	4.98	3		.12	.00	.12
$BaCl_2$	$2H_2O$	3.4	.050	91.6	77.8	4.86		2	.13	.00	.13
KCNS		22.2	.552	47.0	86.2	7.37	1		2.06	.26	2.37
KI		8.7	.297	69.2	80.1	9.33	2		1.54	.26	1.81
K_2CrO_4		6.4	.178	88.5	80.9	8.67			0.38	.00	0.38
KBr		5.5	.169	84.0	79.8	5.98	3		.38	.00	.38
KCl		4.6	.124	89.2	79.0	4.98	4		.12	.00	.12
KNO_3		3.1	.113	95.0	75.6	6.52	5		.12	.00	.12
K_2SO_4		1.3	.024	98.0	74.3	5.63		6	.00	.00	.00
$K_2Cr_2O_7$		0.78	.031	98.8	73.8	4.05			.74	.00	.74
$KClO_3$		.58	.026	99.3	73.0	6.22			.00	.00	.00
H_2O				100.0	72.8	5.27					

Column 3 from "International Critical Tables." Column 4 calculated from columns 2 and 3, Table II, using equation 2. Column 5 calculated from solubility and vapor pressure data, "International Critical Tables." Column 6 calculated from solubility and surface tension data, "International Critical Tables." Columns 8 and 9, Herzog and Beck.[7]

TABLE II

ABSORPTION OF SALT SOLUTIONS BY SITKA SPRUCE AND THE EFFECT OF SALTS UPON SUBSEQUENT SHRINKING WHEN OVEN DRIED

								Shrinkage from salt soln. swollen, to oven-dry condition	
Salt 1	Soly. of salt at 20°, g. per 100 cc. of soln. 2	Density of satd. salt soln., at 20°, g. per cc. 3	Fractional vol. of salt soln. occupied by dry salt at 20° 4	Actual weight of absorbed salt soln., g. 5	Calcd. wt. of absorbed salt soln., g. 6	Actual wt. of abs. salt, g. 7	Calcd. wt. of abs. salt, g. 8	Actual, % 9	Calcd., % 10
$ZnCl_2$	170.0	2.165	0.587	6.87	6.92	5.43	5.44	5.48	5.68
LiCl	56.3	1.283	.273	4.02	3.98	1.81	1.75	9.21	9.48
$CaCl_2$	60.9	1.427	.283	4.43	4.37	1.92	1.87	8.98	9.20
$MgCl_2$	46.7	1.325	.215	4.07	4.03	1.50	1.43	9.44	9.55
$MnCl_2$	62.4	1.470	.210	4.65	4.60	2.00	1.96	9.10	9.18
NaCl	31.8	1.200	.147	3.70	3.66	0.97	0.97	9.88	9.75
NH_4Cl	29.2	1.076	.191	3.27	3.25	.84	.88	9.27	9.24
KCl	29.8	1.174	.150	3.68	3.68	.94	.93	9.67	9.70
$BaCl_2$	33.1	1.279	.086	3.79	3.74	1.01	.97	10.40	10.45
KCNS	97.0	1.417	.508	4.41	4.35	3.02	2.97	6.33	6.50
KI	101.0	1.710	.323	5.45	5.40	3.22	3.19	8.28	8.60
K_2CrO_4	55.2	1.376	.201	4.19	4.12	1.64	1.65	9.45	9.40
KBr	54.0	1.369	.196	4.14	4.10	1.67	1.62	9.45	9.45
KCl	29.7	1.174	.150	3.68	3.68	0.94	0.93	9.67	9.70
KNO_3	28.0	1.165	.133	3.60	3.56	.90	.86	9.93	9.90
K_2SO_4	10.8	1.081	.041	3.20	3.26	.29	.32	10.84	10.73
$K_2Cr_2O_7$	11.5	1.075	.043	3.64	3.29	.68	.35	10.50	11.40
$KClO_3$	7.2	1.045	.031	3.16	3.16	.20	.22	11.05	10.85
H_2O				2.95	2.91			11.32	
				2.87	2.83			11.32	

Column 2 calculated from column 3 and column 3 of Table I. Column 3 from "International Critical Tables." Column 4 calculated from column 2 and the density of the dry salt from "International Critical Tables," using equation 3.

tem. The swelling–*P*H relationship is shown in Fig. 1. There is no swelling on the acid side but an appreciable swelling on the alkaline side at higher *P*H values. The *P*H values of the saturated salt solutions (see Table I, column 7) were also determined. These show no apparent relationships with swelling. Only in the really alkaline salts could any of the swelling effect be attributed to the *P*H.

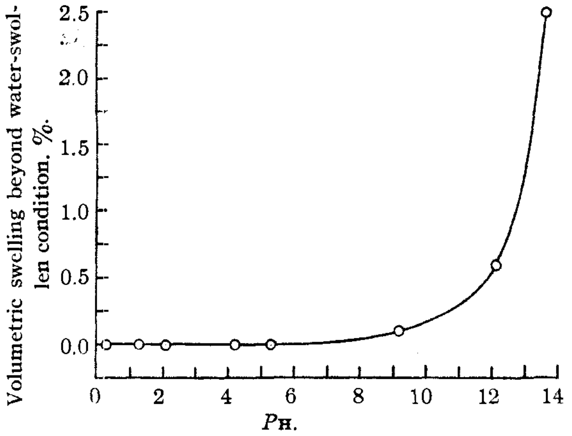

Fig. 1.—Swelling–*P*H relationship for white pine.

The order of the solvent power for cellulose of saturated salt solutions at their boiling point (see Table I, columns 8 and 9) as given by Herzog and Beck,[7] is the same, as far as the data go, as the order of swelling of wood in the salt solutions at room temperature.

Measurements of the swelling of the wood sections were also made by placing the oven-dry sections directly in the saturated salt solutions. The same equilibrium swelling is, in general, established as when the sections were first water swollen, but the process is much slower. The salts tested required at least nine days to give swelling equilibrium. Magnesium chloride, however, required fifty-eight days to swell to the water-swollen volume. After one hundred days the swelling had not yet reached the equilibrium value attained in seven days by previously swelling in water. This effect might be expected on the following basis: water alone enters the fine structure readily, causing swelling. After the fine structure is opened the salts can diffuse therein without any great difficulty. If the dry wood is placed directly in the saturated salt solution, the salt solution, which in the case of calcium and magnesium chlorides shows no tendency to wet wood as indicated by the spherical shape assumed by small drops placed on the surface of dry wood, evidently cannot enter as such. Presumably the wood tries to take the water from the salt, but such a displacement of the salt–water equilibrium requires that additional energy be expended in the adsorbing process. Only a small amount of swelling could thus take place before salt would have to diffuse into the adsorbed water in order to make possible further swelling. This diffusion into an only partially swollen structure would be very slow.

The swelling of wood in the saturated salt solutions is practically reversible for salts which do not hydrolyze. When the salt is removed by repeatedly immersing in fresh water for a couple of weeks, the original water-swollen dimensions are nearly resumed.

Measurements were made of the swelling of Sitka spruce in solutions of lithium chloride and potassium thiocyanate of different concentrations. The sections were oven dried, weighed, soaked in water and the air removed, reweighed, dimensions determined and then placed in a small measured volume of salt solution of known concentration. The containers were sealed and allowed to stand for two weeks to ensure swelling equilibrium. The dimensions of the sections were then determined.

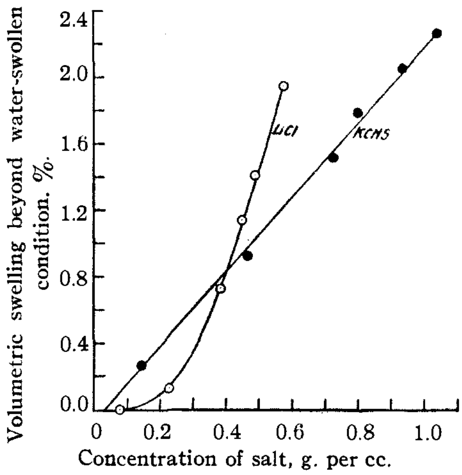

Fig. 2.—Effect of concentration of salts upon the swelling of Sitka spruce.

The equilibrium concentration of the solutions was also determined by evaporating and weighing the residue. The percentage volumetric swelling beyond the water-swollen dimensions is plotted in Fig. 2 against the concentration of the salt solution in equilibrium with the wood. No consistent

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[7] Herzog and Beck, *Z. physiol. Chem.*, **111**, 287 (1920).

variations between the calculated and equilibrium concentrations were obtained, indicating that any selective adsorption is probably small. This is in agreement with earlier measurements of the author which showed that the selective adsorption of ions from dilute solution is very small.[6]

Shrinkage upon Oven Drying

The data given in Table II show the absorption of salts by wood and their effect upon the shrinkage when oven dried. The actual weight of absorbed salt solution (column 5) was obtained from the difference between the weight of a salt-solution swollen section and the original weight of the oven-dry section. The theoretical weight (column 6) was obtained from the void volume (calculated with the aid of equation 1) and the density of the saturated salt solution (column 3). The agreement is as good as could be expected, considering the difficulty in removing only surface solution and not capillary solution when wiping the sections for weighing. The actual weight of absorbed salt (column 7) was obtained from the difference in the weight of the oven-dry wood with and without the salt present. This again is in fair agreement with the theoretical weight of salt (column 8) obtained from the void volume and solubility of the salt in grams per 100 cc. of solution (column 2). Both of these comparisons again indicate that the salts virtually attain the same concentration in the sorbed water as in the free water. It is true that these data, as well as the analytical measurements just cited, do not constitute so conclusive a proof of this generalization as might be desired due to the fact that the sorbed water occupies only a small fraction of the total void volume (in this case 0.155). Any change in the concentration of the salt in the sorbed water would thus be 6.5 times the measured difference for these data and considerably more in the analytical case cited earlier where a still greater excess of liquid had to be present for analysis. Although the differences between the actual and theoretical values given in Table II are practically within experimental error, there seems to be a slight tendency for the former to be greater than the latter, thus indicating the possibility of a slight positive adsorption of salt. According to the following data this adsorption must be very small, however.

The shrinkages of these sections from the salt-swollen condition to the oven-dry condition (the sections having been dried at room temperature over phosphorus pentoxide prior to oven drying at 115°) are given in Table II, column 9. The measurements show a retardation of the shrinkage even after the moisture is virtually all removed. The more soluble salts in general retard the shrinkage to the greatest extent, as would be expected if these salts were deposited in the swelling structure. Assuming that the retardation of shrinkage is entirely due to this effect and that the sorbed-water-salt concentration is virtually the same as the free-water concentration, it is possible to calculate the expected shrinkage from the fractional solution volume occupied by dry salt (column 4) by means of the equation

$$V_{\mathrm{dry}} = g_s/d_d \qquad (3)$$

where g_s is the solubility of the salt in grams per 100 cc. of solution and d_d is the density of the dry salt. The expected shrinkage is

$$S = (1 - V_{\mathrm{dry}})S_0 \qquad (4)$$

where S_0 is the shrinkage from the completely swollen condition to the dimensions that would be obtained on drying if no salt were present. These theoretical values are given in column 10. In general, they agree quite well with the actual measured values, especially where the swelling correction is very small. This agreement furnishes the best evidence obtained that the sorbed water attains a salt concentration virtually the same as that in the free water. The quantity measured here is a function of the sorbed water and not of the total water as in the other comparisons so that the differences obtained cannot be due to a larger change in a small part of the system.[8] This virtually uniform concentration of the salts in the swollen wood structure and in the bulk water is not in contradiction to Donnan membrane equilibrium. Neale[9] has estimated the ionization constant of cellulose to be of the order of 2×10^{-14}. This extremely low ionization constant, together with high salt concentrations, would give an unmeasurable concentration difference.

Shrinkage measurements were at first made on salt-treated sections that were dried in the oven at

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[8] In connection with some earlier electrical conductivity measurements by the author [*J. Phys. Chem.*, **36**, 312 (1932)] it was concluded that dilute salt solutions do not enter the cell wall because of the reduced conductivity at the fiber-saturation point. This explanation of the experimental facts is undoubtedly wrong. The results can still be explained, however, on the basis of the salt solution dispersion not being sufficiently continuous to give the full conductivity effect. No change in the calculations or other conclusions drawn in the paper need be made because of this correction.

[9] Neale, *J. Textile Inst.*, **20**, T373 (1929).

115° without first drying at room temperature over phosphorus pentoxide. These sections gave smaller shrinkages than those given in Table II for the same salts. This was especially noticeable for sections treated with salts, the solubility of which increased greatly with an increase in temperature. Apparently the concentration of the solution in the gross capillary structure increased as water was evaporated and the salt diffused to a greater extent into the swelling structure because of the increased solubility.

Shrinkage and Moisture Content at Different Relative Vapor Pressures

Salt-treated sections were dried in humidity chambers to obtain the shrinkage and moisture content at different relative vapor pressures.

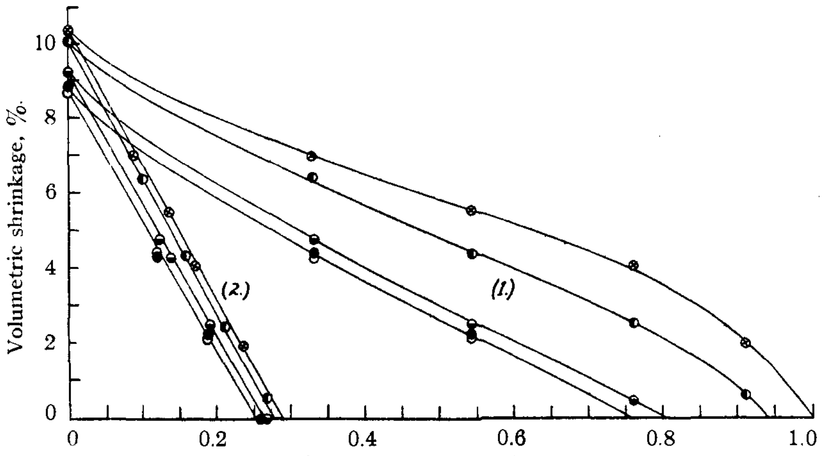

Fig. 3.—(1) Relative vapor pressure–shrinkage and (2) moisture content–shrinkage relationships for white pine treated with different concentrations of sodium chloride solution: ⊗, no salt; ◐, 2 g. NaCl per 100 g. H_2O; ◒, 5 g. NaCl per 100 g. H_2O; ◓, 15 g. NaCl per 100 g. H_2O; ●, 25 g. NaCl per 100 g. H_2O; O, 36 g. NaCl per 100 g. H_2O.

Air was drawn through towers containing saturated salt solutions with an excess of salt present. The towers contained about 2.5 cm. of mercury on the bottom. The air supply tubes dipped below the mercury surface to prevent the tubes from becoming clogged with salt crystals. The air from the towers was then bubbled through open dishes of the saturated-salt solutions placed in the bottom of vacuum desiccators which served as the humidity chambers. Air was drawn through the system under a vacuum of about half an atmosphere at the approximate rate of 10 liters per hour. Under these conditions the theoretical relative vapor pressures in equilibrium with the saturated salt solutions were virtually attained. The temperature of the desiccators was not automatically controlled as the change in relative vapor pressure with moderate changes in temperature was small for the salts used. Measurements were made with barium chloride, sodium chloride, manganese chloride, magnesium chloride and lithium chloride in the humidifiers. The equilibrium relative vapor pressures for each of these salts are given in Table I, column 5.

The dimensions and weights of the conditioning sections were determined at varying intervals to ascertain the shrinkage and moisture content. The salt-treated sections in general required longer to attain equilibrium than the controls. Several weeks' time was required to ensure complete equilibrium. Difficulty was encountered in making the moisture determinations on sections that had been treated with saturated salt solutions because of the flaking off of surface-deposited salt while determining the dimensions. It was necessary when the salt concentration was high to use two matched sections, one for shrinkage data and the other, which did not require handling, for moisture content data.

The percentage volumetric shrinkage is plotted for a number of different salts and two woods in Figs. 3, 4, 6 and 8 against the relative vapor pressures and in Figs. 3, 5 and 7 against the moisture content. In all cases the shrinkage begins when the relative vapor pressure under which the section is being dried is slightly less than the equilibrium relative vapor pressure of water over the salt solution at the concentration attained when evaporation has proceeded to the fiber-saturation point.

Figure 3 gives the data obtained by drying sections treated with different concentrations of sodium chloride. The points for sections treated with 36, 25 and 15 g. per 100 g. of water all fall on the same curve. The shrinkage is slightly greater for 5 g. per 100 g. of water and considerably greater for 2 g. per 100 g. of water. When the sections are dried slowly the concentration of the unsaturated solutions increases in the void structure and evidently diffuses into the swelling structure. In the white pine the sorbed water occupies 0.137 of the total void volume so that when the moisture content is reduced to the fiber-saturation point, the concentration is increased 7.3 times. This would cause saturation in all but the most dilute solution, and in the section treated with a solution containing 5 g. per 100 g. of water the concentration would just slightly exceed that required to give saturation. Under these conditions any slight deposition of salt in the grosser structure would prevent complete saturation of the swelling structure and account for the slightly greater shrinkage. According to the relative vapor pressure at which shrinkage begins for this specimen the effective concentration is 30 g. per 100 g. of water instead of 36.5 as calculated for complete diffusion into the swelling structure. The former concentration gives a calculated oven-dry shrinkage of 9.2%, which is practically identical with the measured value. For the most dilute solution the effective concentration, according to the relative vapor pressure at which shrinkage begins, is 10 g. per 100 g. of water instead of 14.6 as calculated for complete diffusion into the fine structure. The former gives a calculated oven-dry shrinkage of 10.05%. This again agrees nicely with the actual measured value. The maximum anti-shrink effect can thus be obtained at a concentration slightly in excess of that which will give saturation upon evaporation to the fiber-saturation point.

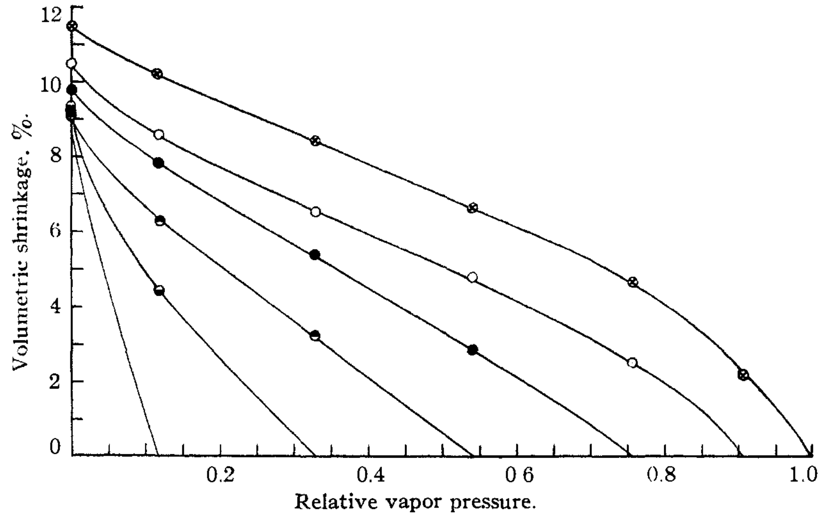

Fig. 4.—Relative vapor pressure–shrinkage relationship for Sitka spruce treated with different quarter-saturated salt solutions: ⊗, no salt: ○, BaCl₂; ●, NaCl; ◓, MnCl₂; ◒, MgCl₂: ◐, LiCl.

Figures 4, 6 and 8 give the volumetric shrinkage–relative vapor pressure curves for other salts. Figures 4 and 6 give data for sections of Sitka spruce and white pine treated with quarter-saturated salt solutions and Fig. 8 gives data for sections of white pine treated with saturated salts which also act as fire retardants. In the quarter-saturated solutions the swelling is negligible but upon drying to the fiber-saturation point swelling takes place as if the sections had been soaked in saturated solutions, thus giving further evidence that the salts diffuse into the fine swelling structure while drying. The shrinkages are calculated from the saturated salt-swollen volume rather than the initial volume to make the results comparable with those given in Table II. The shrinkages to the oven-dry condition shown in Fig. 4 are nearly identical with those given in Table II for sections treated with saturated solutions.

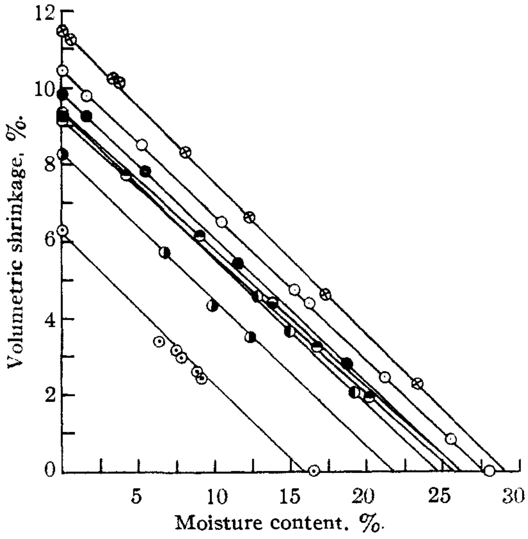

Fig. 5.—Moisture content–shrinkage relationship for Sitka spruce treated with different quarter-saturated salt solutions: ⊗, no salt; ○, BaCl₂; ●, NaCl; ◓, MnCl₂; ◒, MgCl₂: ◐, LiCl; ◑, KI; ◉, KCNS.

The volumetric shrinkage-moisture content data are plotted in Figs. 3, 5 and 7. In all cases a linear relationship exists between the shrinkage and the moisture lost from the fiber-saturation point to oven dry. A similar linear relationship exists between the tangential shrinkage and moisture content and the radial shrinkage and moisture content, thus showing that the ratio of tangential to radial shrinkage is constant over any moisture content range. Further, the ratio of the tangential to the radial shrinkage is the same for salt-treated specimens, for which the swelling beyond the water-soaked dimensions was small, as it is for the controls. In sections treated with swelling salts the ratio is somewhat affected as would be expected, due to the abnormal tangential swelling.

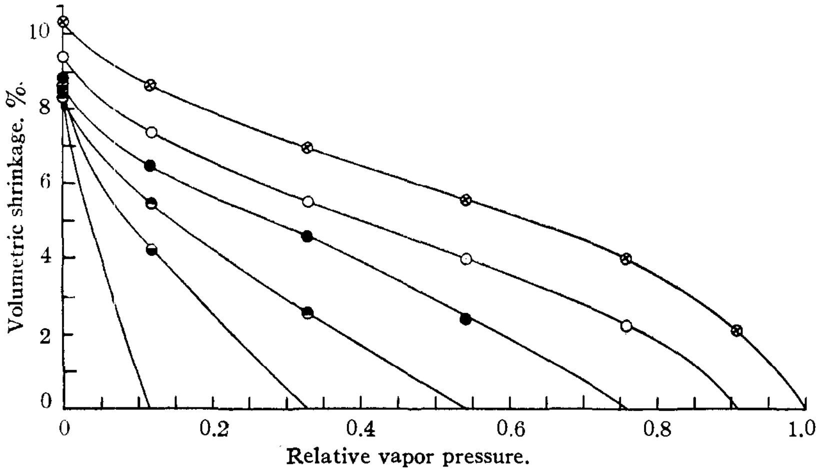

Fig. 6.—Relative vapor pressure–shrinkage relationship for white pine treated with different quarter-saturated salt solutions: ⊗, no salt; ○, $BaCl_2$; ●, NaCl; ◓, $MnCl_2$; ◒, $MgCl_2$; ◐, LiCl.

The linear relationship obtained on the external-shrinkage basis might be expected to hold on a total shrinkage basis over the sorption range if the adsorption compression effect is negligible. The fact that it holds for the shrinkage manifested externally indicates that internal shrinkage in the grosser capillary structure must be either proportional to the external change or practically negligible. For the small specimens thus far tested the following relationship seems to hold

$$S = d \times f \qquad (5)$$

where S is the fractional shrinkage from the fiber-saturation point to the oven-dry condition, d is the density of the wood on a dry weight–green volume basis, and f is the fiber-saturation point expressed as a fraction. The relationship requires that the volume of the grosser capillaries does not change with changes in moisture content. This internal swelling is being studied more critically at the present time by a different means. If it is found to be practically negligible according to the foregoing indications, it will account for the linear relationship on the external dimension shrinkage basis.

With the preceding relationship it is possible to calculate the moisture content of the salt-solution swollen specimens at the fiber-saturation point. For example, if a section of Sitka spruce could be swollen to the volume obtained in saturated lithium chloride solution in water alone, the fiber-saturation point would be raised from 29 to 33.9%. The fractional volume of the solution occupied by dissolved salt is, however, 0.282 (see Table I, column 4) so that (1 − 0.282) × 33.9 = 24.4 gives the percentage of water held at the fiber-saturation point. This is in good agreement with the value obtained in Fig. 5 by extrapolating to a zero shrinkage. The values calculated for the sections treated in the same manner with potassium iodide and potassium thiocyanate are 23.6 and 15.7%, respectively, which are also in good agreement with the values obtained from Fig. 5. According to this the salts can in part displace the sorbed water. The balance between the forces of attraction of wood for water,

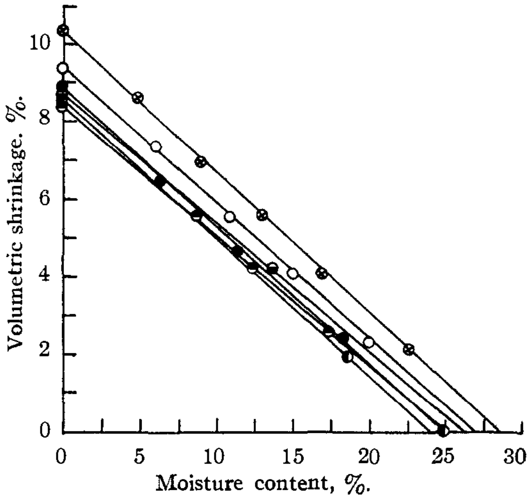

Fig. 7.—Moisture content–shrinkage relationship for white pine treated with different quarter-saturated salt solutions: ⊗, no salt; ○, $BaCl_2$; ●, NaCl; ◓, $MnCl_2$; ◒, $MgCl_2$; ◐, LiCl.

salt for water and the resistance to swelling of the wood beyond the normal green dimensions results in the wood taking up a greater volume of salt than the volume of sorbed water displaced, thus causing swelling. From this it follows naturally that swelling should be greatest with the most soluble salts.

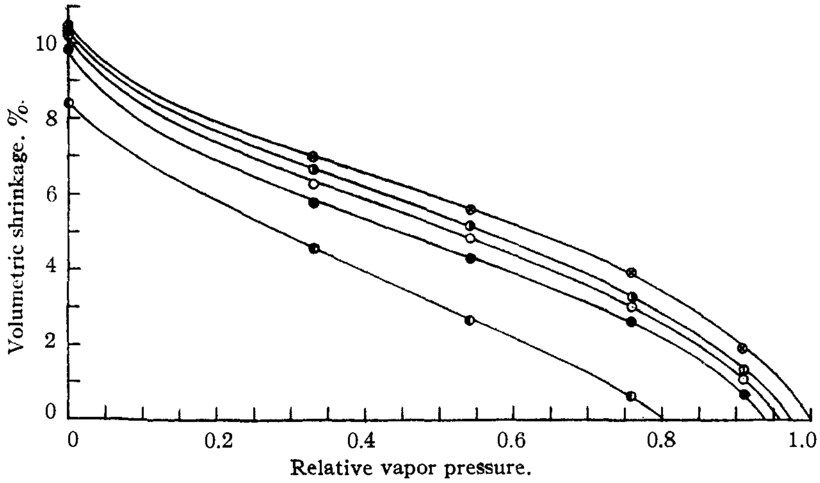

Fig. 8.—Relative vapor pressure–shrinkage relationship for white pine treated with saturated fire-retardant salt solutions: ⊗, no salt; ◑, H_3BO_3; ○, $Na_2B_4O_7$; ●, Na_2HPO_4; ◐, $NH_4H_2PO_4$.

From Figs. 4 and 6 it is obvious that no anti-shrink benefit from the standpoint of constancy of dimensions can be obtained with any of the salts if the prevailing relative humidities are always below the relative vapor pressures in equilibrium with the saturated salt solutions for the rate of change of shrinkage with changes in relative humidity is greater for all of the salt-treated sections than for the control. From the standpoint of seasoning, however, where the extent of degrade in the form of checking and warping of the wood is a direct function of the total shrinkage, the anti-shrink effect of the salt treatment may be of considerable value.

From Figs. 4 and 6 it also appears that treatment with a very soluble salt such as lithium chloride would solve the shrinking problem completely, for relative humidities below 11% are very rarely encountered. Unfortunately, however, sections treated with a saturated solution of lithium chloride are always wet and sticky at humidities just slightly above 11%. They tend to take on more moisture from the air but as the capillary structure is already full of solution, dripping at the surface will occur with the loss of salt. This will continue until a concentration is reached that has a relative vapor pressure the same as the prevailing relative humidity. Treatment with quarter-saturated solutions will give the same anti-shrink effect but the sections will not drip unless the relative humidity is above 78%, which is the relative vapor pressure for this concentration. Similarly, a section treated with quarter-saturated magnesium chloride will not drip unless the relative humidity is above 82%. Although the sections treated with quarter-saturated salts will not lose salt as readily as those treated with saturated salt solutions, they will be wet and sticky above the equilibrium relative humidities.

Summary

1. The increased swelling of water-swollen wood in saturated salt solutions was measured. (a) The order of increasing volumetric swelling was practically the same as the order of increasing solubility of the salts, increasing fractional volume of the salt in solution, increasing surface tension of the salt solutions, and decreasing relative vapor pressure over the salt solutions. (b) The P_H of the solution had practically a negligible effect upon the swelling, although the wood swelled in alkalies and not in acids. (c) Swelling equilibrium was attained more slowly when dry wood was placed directly in the saturated salt solutions than when previously swollen in water.

2. The shrinkage and moisture content obtained on drying salt-treated sections at different relative humidities were measured. (a) Shrinkage started when the relative humidity under which the sections were dried was less than the relative vapor pressure over the treating solution at the concentration attained when evaporation had proceeded to the fiber-saturation point. (b) The shrinkage occurring on oven drying of the salt-treated sections was less than that of the controls because of the taking up of salt by the structure within which swelling took place. This shrinkage was also calculated from the fractional solution volume occupied by dry salt by assuming that the salt concentration was the same inside

and outside of the swelling structure. Other evidence was also obtained to show that the sorbed water virtually attained the same salt concentration as the free water. (c) The shrinkage of all the sections was directly proportional to the moisture lost. The salt was shown to partly displace the sorbed water from the wood. Those salts which tended to displace the most sorbed water caused the greatest swelling.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY]

Preparation of Primary *n*-Alkyl Sulfates

BY CHAS. BARKENBUS AND JOHN J. OWEN

Many references can be found stating that alkyl sulfates are good alkylating agents; however, with the exception of methyl sulfate, ethyl sulfate, and possibly *s*-butyl sulfate, no easy methods for making them are available.

The action of alcohols on sulfuric acid is of no value, except in the case of methyl sulfate, because of the formation in large amounts of alkyl acid sulfates, ethers, and unsaturated compounds. The action of alcohols on sulfuryl chloride has been investigated by Bushong and others,[1] who have found that the chief products formed are alkyl chlorosulfonates, alkyl acid sulfates, alkyl chlorides and some alkyl sulfates. It is claimed[2] that both of the chlorine atoms in sulfuryl chloride are attached to the sulfur by co-valent bonds but we have observed that chemically they are widely different, which accounts for the poor yields when starting with this compound. Recently McKee[3] has patented the action of alcohols on sulfuryl chloride but in our experience with *n*-butyl alcohol the chief product formed was *n*-butyl chlorosulfonate. By using alkyl chlorosulfonates with sodium alcoholates Bushong[1] has made several alkyl sulfates though the yields were low and the method rather tedious. It was hoped that magnesium alkoxy bromide could be substituted for the sodium alcoholates since this type of reagent has been used successfully by Porter and Yabroff[4] in making *t*-isobutyl phenylacetate. In carrying out this reaction with *n*-butoxymagnesium bromide and *n*-butyl chlorosulfonate it was found that the chief product was *n*-butyl bromide, some *n*-butyl chloride, and that the sulfate group had combined with the magnesium as magnesium *n*-butyl sulfate. It is remarkable that the bromine leaves the magnesium for the butyl group.

The action of alkyl chlorosulfonates on alkyl nitrites, alkyl carbonates and alkyl orthoformates[5] has been used but low yields were obtained in all cases. The action of unsaturated hydrocarbons on either sulfuric acid or alkyl acid sulfate has been patented[6] though the alkyl sulfates beyond the ethyl cannot be primary. The patents also mention making mixed sulfates.

The oxidation of alkyl sulfites has been suggested[7] as a possible method of attack but outside of the use of potassium permanganate and chlorine, both of which gave poor yields, no further mention of this method could be found. The recent excellent synthesis of alkyl sulfites by Voss and Blanke[8] made the oxidation of sulfites a possible method of entering the alkyl sulfate series and led us to investigate this method rather extensively. Although no method of oxidation was found, it may be worth while to record a few of our observations.

It was found that an anhydrous medium is necessary, otherwise hydrolysis with formation of alkyl acid sulfates and sulfuric acid will result. This limits the number of oxidizing agents that can be used, and in addition the reagent must furnish oxygen. Dry nitrogen dioxide gas oxidizes the sulfites but apparently attacks only the carbon since sulfur dioxide was evolved and oxalic acid formed. Ozone has no effect, while hydrogen peroxide dissolved in quinoline was unsuccessful. The most promising reagent was benzoyl hydrogen peroxide dissolved in dry chloroform but yields of only 10% could be obtained with *n*-butyl sulfite since the carbon chains were attacked at the same time. Much time was spent

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(2) Sugden, Reed and Wilkins, *J. Chem. Soc.*, **127**, 1525 (1925).

(3) McKee. U. S. Patent 1,641,005 (Aug. 30. 1927).

(4) Porter and Yabroff. THIS JOURNAL, **54**, 2453 (1932).

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(6) Hunt. U. S. Patents 1,744,164, 1,744,207, 1,744,227 (Jan. 21, 1930). Shell Development Co., U. S. Patent 1,854,581 (Apr. 19, 1932).

(7) Levaillant. *Compt. rend.*, **188**, 261 (1929); **189**, 465 (1929).

(8) Voss and Blanke. *Ann.*, **485** 258 (1931).