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# THE HYGROSCOPIC AND ANTISHRINK VALUES OF CHEMICALS IN RELATION TO CHEMICAL SEASONING OF WOOD*

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Considerable work has been done at the Forest Products Laboratory during recent years on the seasoning of wood with chemicals. The process consists in soaking green wood in an aqueous solution, usually saturated, of a chemical or mixture of chemicals and subsequently air drying, kiln drying, or allowing the wood to season in service. Sometimes a "dry salting" method is used, in which the green lumber is bulk-piled with alternate layers of the chemical. In the course of these studies a number of chemicals and mixtures of chemicals have been tried in an attempt to find the most satisfactory chemical or mixture.

A chemical must possess certain characteristics in order to be suitable for use in chemical seasoning. The aqueous solution must cause a considerable reduction in relative vapor pressure or a pronounced antishrink effect when absorbed by wood, or both. It must be cheap and available and readily soluble in water. It must not be dangerous to handle nor corrosive to metals. It may possess additional desirable characteristics, such as decay, insect, or fire resistance. The possession of some of these properties to an unlimited extent is not always wholly beneficial. The solution of a chemical which causes a large reduction in relative humidity is advantageous from the final seasoning point of view but disadvantageous from the standpoint of checking in the chemical bath. When green wood is placed in an aqueous solution of a chemical which possesses a low vapor pressure, moisture is lost from the surface of the wood because of the vapor pressure difference. When the surface layers have become impregnated with the chemical the moisture loss from the surface layers ceases but continues from the interior portions which have not become impregnated. Unless the surfaces are dressed off before the wood is put in service a chemical of this nature will also cause trouble through condensation of moisture from the surrounding atmosphere.

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When green wood is immersed in a chemical solution, it undergoes certain physical changes. Some of the moisture in the wood will pass into the chemical solution because of the difference in vapor pressure between the green wood and the chemical solution. Some of the chemical will diffuse into the wood through the water contained in the wood, the extent of this diffusion depending on the nature of the chemical, the duration of the soaking, the available moisture in the wood, and the morphological characteristics of the wood. Within the penetrated zone, chemical is present in the cell cavities and also in the finer wood structure. If the chemical is positively adsorbed within the finer wood structure, swelling beyond the green dimension takes place; if negatively adsorbed, no swelling takes place, the adsorbed chemical merely replacing an equivalent volume of water. That which is in the cell cavities affects the vapor pressure within the cells and acts as a reservoir of chemical for a further adsorption within the finer wood structure or for further penetration deeper into the wood. A piece of wood, after soaking in a chemical solution, possesses an outer zone which contains a gradient of chemical concentration, and therefore, a vapor pressure gradient. There is also a difference in vapor pressure between the moisture in the untreated part of the wood and in the impregnated zone. (It is assumed, and has been generally demonstrated by experience, that wood impregnated with a chemical reacts like the chemical solution.) These differences in vapor pressure establish a potential for moisture transfusion which is independent of the normal moisture content gradient potential. If this piece of wood is placed in a drying atmosphere, the vapor pressure of which is identical with that of the chemically impregnated outer skin of the wood, no drying will take place. Soon, however, the moisture moving from the interior of the wood to the surface, dilutes the chemical solution raising the vapor pressure, permitting drying to commence. The moisture which is evaporated from the outer surface is continually being replaced by moisture moving from the interior parts, making it possible, by manipulation of the drying conditions during the early stages of drying, to maintain the initial moisture content of the impregnated surface zones. This, in conjunction with the antishrink effect of the chemical, greatly lessens the formation of tension on the surfaces, making the formation of surface checks less likely.

There is a vast amount of information on the properties of simple chemical solutions, but there is little information on the properties of solutions of chemical mixtures that might be used in the chemical seasoning of wood. Where two or more chemicals are mixed in solution, the effect on vapor pressure, or relative humidity at a given temperature, is apparently unknown at the relatively high concentrations that have to be used for chemical seasoning. The purpose of the experiments here described was to determine the relative humidity, at a temperature of 68° F., of chemical solutions of various concentrations and mixtures of chemicals in solution, and to measure the antishrink properties imparted to the impregnated wood. The relative humidities over the various solutions were measured by determining the equilibrium-moisture-content values of wood specimens suspended over the solutions in closed containers. Provision was made for a positive and continuous circulation of air within the containers and for a gentle stirring of the solution. The antishrink effect was measured by completely impregnating strips of wood with the chemicals and comparing their shrinkage with that of normal wood, throughout a controlled drying process.

The first step in the analysis of the data was a comparison of the results obtained with this method and apparatus, with those obtained by other experimenters. These results and comparisons are given in table 1.

Table 1.--Relative humidities over saturated chemical solutions at 68° F.

| Chemical | Relative humidity | | | |
|---|---|---|---|---|
| | Stamm[1] | Adams and Merz | Perry and Duus | Present experiments |
| | Percent | Percent | Percent | Percent |
| $NH_4NO_3$ | 63 | 67 | ........... | 68 |
| $(NH_4)_2SO_4$ | ........... | 81 | 80 | 83 |
| $CaCl_2$ | 35 | ........... | 32 | 32 |
| $Ca(NO_3)_2$ | ........... | 55 | ........... | 59 |
| $MgCl_2$ | 33 | ........... | ........... | 32 |
| NaCl | 76 | 78 | ........... | 78 |
| $NaNO_3$ | 76 | 77 | ........... | 76 |
| $CO(NH_2)_2$ | ........... | 80 | ........... | 79 |

[1]Calculated from International Critical Tables.

Note: J. F. T. Berliner has found a relative humidity of 78 percent for a saturated solution of urea.

After having demonstrated that this method and apparatus produced reasonably consistent results, many experiments were conducted with solutions of various concentrations and mixtures of chemicals. A mixture usually consisted of two chemicals, a saturated solution of one which was used as a base with various concentrations of the other. The concentration is expressed by the weight of the anhydrous chemical per 100 grams of water in the solution, regardless of whether, as in the case of a mixture, the water already contains a dissolved chemical.

The relative humidities at a temperature of 68° F., which were found over the solutions of single chemicals, are given in tables 2 and 3.

According to Adams and Merz, when two chemicals chemically inert to each other are mixed in a saturated solution, the vapor pressure of the mixture is less than that of either constituent. In certain instances, however, the two chemicals may form a compound which gives a greater vapor pressure than that of the constituent with the lesser vapor pressure. The vapor pressure in the latter case will also depend on whether the compound alone is present or whether it is accompanied by an excess of either chemical. In this series of experiments, mixtures of chemicals in solution were employed, in most instances using one solution, usually a saturated one, as a base and adding to it various amounts of the other chemical, up to a point in some instances where the available water was saturated by both chemicals, and in other instances where an excess of the second chemical was present.

Although these experiments were conducted at a temperature of 68° F. (20° C.), two special tests were made at 86° F. (30° C.) in order to check the results obtained by other experimenters. A given quantity of water was saturated with urea and also with ammonium nitrate and ammonium sulfate, respectively, and the relative humidities determined. The results are given in table 4.

The values obtained in these experiments do not agree with those obtained by other experimenters, but no reason can be given for the discrepancy.

The relative humidities measured over the mixtures of chemicals in solution are summarized in table 5.

The relative humidities over the solutions of the mixtures were as low as or lower than that over the solution of either constituent except where calcium chloride or magnesium chloride was involved. With these two chlorides, the relative humidities of the mixtures fell between those of the two constituents. The greatest reduction in the relative humidity of the binary mixtures occurred with urea and

Table 2.--Relative humidity in equilibrium with different concentrations of various aqueous solutions at 68° F.

| Chemical | Relative humidity | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Grams of chemical per 100 grams of water | | | | | | | | | | | | |
| | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 | 110 | 120 | 120+ |
| | Percent | Percent | Percent | Percent | Percent | Percent | Percent | Percent | Percent | Percent | Percent | Percent | Percent |
| Invert sugar | 99 | 98 | 98 | 97 | 96 | 96 | 95 [1](67) | ... | ... | ... | ... | ... | ... |
| Diethylene glycol | 99 | 98 | 97 | 96 | 94 | 93 | 92 | 90 | 89 | [2]87 | ... | ... | ... |
| Calcium nitrate | 99 | 98 | 97 | 95 | 93 | 90 | 84 | 77 | 71 | 66 | 63 | 61 | 59 (129) |
| Urea | 98 | 96 | 94 | 92 | 90 | 88 | 86 | 84 | 82 | 80 | 79 (105) | ... | ... |
| Ammonium sulfate | 98 | 95 | 93 | 91 | 89 | 86 | 84 | 83 (75) | ... | ... | ... | ... | ... |
| Sodium nitrate | 97 | 96 | 94 | 93 | 90 | 86 | 82 | 78 | 76 (88) | ... | ... | ... | ... |
| Ammonium nitrate | 97 | 94 | 91 | 88 | 86 | 83 | 81 | 79 | 77 | 76 | 74 | 73 | 68 (192) |
| Sodium chloride | 95 | 89 | 82 | 78 (36) | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| Calcium chloride | 90 | 80 | 70 | 61 | 52 | 44 | 36 | 32 (75) | ... | ... | ... | ... | ... |
| Magnesium chloride | 86 | 72 | 60 | 48 | 37 | 32 (55) | ... | ... | ... | ... | ... | ... | ... |

[1]The figures in parentheses are concentration values which do not fall on the even intervals used in the table.

[2]The last relative humidity value given is that over the saturated solution, except in the cases of invert sugar and diethylene glycol.

Table 3.--Relative humidity in equilibrium with different percentages of saturation of various aqueous solutions at 68° F.

| Chemical | Relative humidity — Percent of saturation: 20 | 40 | 60 | 80 | 100 |
|---|---|---|---|---|---|
| | Percent | Percent | Percent | Percent | Percent |
| Ammonium sulfate | 96 | 93 | 90 | 86 | 83 |
| Urea | 96 | 92 | 86 | 83 | 79 |
| Sodium chloride | 96 | 92 | 87 | 83 | 78 |
| Sodium nitrate | 96 | 94 | 89 | 82 | 76 |
| Ammonium nitrate | 89 | 80 | 74 | 70 | 68 |
| Calcium nitrate | 97 | 92 | 79 | 65 | 59 |
| Calcium chloride | 85 | 70 | 57 | 44 | 32 |
| Magnesium chloride | 85 | 69 | 56 | 44 | 32 |
| Invert sugar | ... | ... | ... | ... | [1]23 |
| Diethylene glycol | ... | ... | ... | ... | [1]0 |

[1]Approximate value for anhydrous chemical.

Table 4.--Relative humidities in equilibrium with saturated solutions of mixtures of chemicals at 86° F.

| Chemicals | Relative humidity — Adams and Merz | Relative humidity — Present experiments |
|---|---|---|
| | Percent | Percent |
| Urea and ammonium nitrate | 18.1 | 49.0 |
| Urea and ammonium sulfate | 56.4 | 62.0 |

Table 5.--Relative humidity in equilibrium with saturated chemical solutions and saturated solutions of mixtures at 68° F.[1]

| Chemical | Relative humidity | Chemical | Relative humidity | Chemical | Relative humidity | Mixture Relative humidity |
|---|---|---|---|---|---|---|
| | Percent | | Percent | | Percent | Percent |
| Invert sugar 40 percent[2] | 95 | Sodium chloride | 78 | .......... | .......... | 73 |
| Do.......... | 95 | Urea | 79 | .......... | .......... | 79 |
| Do.......... | 95 | Magnesium chloride | 32 | .......... | .......... | 80 |
| Do.......... | 95 | Sodium chloride | 78 | Urea | 79 | 57 |
| Sodium chloride | 78 | Magnesium chloride | 32 | .......... | .......... | 70 |
| Do.......... | 78 | Calcium chloride | 32 | .......... | .......... | 44 |
| Urea | 79 | Ammonium nitrate | 68 | .......... | .......... | 58 |
| Do.......... | 79 | Ammonium sulfate | 83 | .......... | .......... | 65 |
| Do.......... | 79 | Glycerin[3] | [4]73 | .......... | .......... | 73 |
| Do.......... | 79 | Monoammonium phosphate | 80 | .......... | .......... | 75 |

[1]In the mixtures the water was assumed to satisfy all chemicals.

[2]Not a saturated solution, 67 grams per 100 grams of water.

[3]Not a saturated solution, 100 grams per 100 grams of water.

[4]Stamm's value.

ammonium nitrate while the greatest reduction occurred with the trinary mixture. The relative humidity of the mixture was compared with the average relative humidity of the constituent chemicals to obtain a measure of the reduction in relative humidity. Where magnesium chloride was used in a mixture, the resultant relative humidity was greater than the average for the constituents. Although not shown in the table, in some instances the chemicals which were added to the first solution were added in excess of the amount required to saturate the water present in the solution. In the mixture of sodium chloride with calcium and magnesium chloride, respectively, excess amounts of the latter two chemicals were added. This was also done with the invert sugar and magnesium chloride mixture. The addition of excessive amounts of the second chemical, apparently in some instances, caused the first chemical to crystallize from solution giving a saturated solution of the second chemical with the first chemical present in the solid phase. When 100 grams of calcium chloride and 300 grams of magnesium chloride, respectively, were added to a saturated solution of sodium chloride containing 100 grams of water, the relative humidity over the resultant solution was approximately that of the saturated solution of the second chemical, i.e., calcium or magnesium chloride. One hundred grams of magnesium chloride added to a 40 percent invert sugar solution containing 100 grams of water produced a relative humidity of 66 percent compared with a relative humidity of 80 percent when just enough (54.5 grams per 100) magnesium chloride to saturate the water in the solution was added. In all these mixtures, after the second chemical had been added in sufficient amount to cause saturation, an increase in the amount of the excess of the second chemical produced a progressively decreasing relative humidity in the final solution.

An important criterion in estimating the value of a chemical for the chemical seasoning of wood is the magnitude of its antishrink effect. The reduction in shrinkage of wood impregnated with chemicals is caused by two things: the bulking volume of the chemical within the fine wood structure, or the modification of the hygroscopic properties of the wood. The latter causes the wood to retain more moisture when exposed to a given relative humidity. Whatever the cause, the value of a chemical in the chemical seasoning of wood can be gaged by the shrinkage of the impregnated wood at equilibrium with a definite relative humidity. Table 6 summarizes the antishrink effect obtained on strips of black gum, impregnated with various chemicals and mixtures.

Wood impregnated with a saturated solution of calcium nitrate shrunk only 7.7 percent as much as normal wood at an equilibrium with 100° F. and 30 percent relative humidity.

## Summary

Of the chemicals and mixtures studied, the ones that showed the most promise for use in the chemical seasoning of wood, both from the standpoint of relative humidity and antishrink and at the same time lacking undesirable properties, were urea, invert sugar, and a mixture of invert sugar and urea. Some of the chemicals studied are obviously too expensive, whereas others possess undesirable properties, such as corrosiveness or increased inflammability. Since in commercial practice it is difficult to maintain a solution in any form but a saturated one, some chemicals produce too low a relative humidity with consequent danger of surface checking in the seasoning bath. The safe relative humidity for most lumber items is probably between 70 and 85 percent.

Table 6.--The tangential shrinkage at equilibrium with 100° F. temperature and 30 percent relative humidity, of strips of wood impregnated with solutions[1] of various chemicals and mixtures of chemicals in percentage of that of the controls

| Chemical or chemicals | Shrinkage |
|---|---|
| | Percent |
| Calcium nitrate | 7.7 |
| Ammonium nitrate and urea | 11.6 |
| Invert sugar 50 percent | [2]14.0 |
| Ammonium nitrate | 16.4 |
| Sodium chloride and urea | 16.9 |
| Invert sugar 40 percent and urea | 17.9 |
| Ammonium sulfate and urea | 20.5 |
| Invert sugar 40 percent, sodium chloride and urea | 37.2 |
| Urea | 44.7 |
| Invert sugar 40 percent | 47.4 |
| Sodium nitrate | 56.5 |
| Ammonium sulfate | 65.4 |

[1]The solutions are saturated unless otherwise stated.

[2]Data from Stamm.