An Evaluation of Several Vapor Phase Chemical Treatments For Dimensional Stabilization Of Wood

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Abstract

A bench-scale system for the impregnation of wood with volatile compounds was constructed for the purpose of testing the system concept and evaluating various polymeric bulking materials as dimensional stabilizing agents. Provisions were incorporated for recycling the treating material, introduction of two separate materials alternately or simultaneously, timed-cycle treatment, control of wood temperature, and for removal of the treatment cylinder for further off-system processing of the treated wood without violating the treatment atmosphere. Treatment with vinyl chloride was not successful, but treatment with ethylene oxide gave good results. Much better treatment and stabilization were obtained with the oscillating pressure method than with the constant pressure method. Rather high anti-swell efficiency values were obtained with low polymer loading, which suggests that stabilization with ethylene oxide occurred by ethoxylation in conjunction with bulking.

THE TREATMENT OF WOOD with substances in the vapor phase has not as yet been fully exploited. Although a considerable number of studies have dealt with the permeation and movement of permanent gases and vapors of volatile substances in wood, very few studies have been published dealing with the alteration of wood properties by vapor phase treatment.

Vapor phase impregnation appears, from purely qualitative considerations, to offer several advantages over liquid phase treatments. Because of greater mobility of low molecular weight substances in the gaseous state within the structure of wood, diffusion can contribute to the transport process. Vapor phase treatment, therefore, may be more rapid on a volume basis than liquid treatment. Impairment of movement by gas-liquid interfaces and/or blocking of pores by debris can be avoided so that more uniform treatment can be attained. Due to the low viscosity of gas, a much lower pressure differential for permeation is needed. Another potential advantage of vapor phase treatment would be the possibility for recycling the treatment substance without extensive decontamination, as most of the contaminants would be expected to have low volatility.

In order to examine the possibility of vapor phase treatment of wood in some detail, a treating system was designed to study the effect of several vapor phase reactants on the dimensional stabilization of wood. McMillin (4) had previously developed certain parameters for the dimensional stabilization of wood using polymerizable vapors of ethylene oxide, hence this gas was used for this study. Vinyl chloride, which has been implied by Kent *et al.* (2) as having some potential, was also selected for the initial work.

Experimental Procedure

Apparatus

The criteria selected for the apparatus were: inert materials for construction; provisions for achieving an oxygen-free atmosphere; movement of treating vapors by cryogenic pumping; introduction of two treatment gases alternately or simultaneously; and capability of removing treated samples from the apparatus for subsequent off-system processing without changing the atmosphere in the treating vessel.

A simplified schematic diagram of the apparatus is shown in Figure 1. Active portions of the system, from which there might be accidental release of toxic or hazardous gases, were located in a fume hood, with inactive and control sections located on either side and below the hood. All active parts of the apparatus were of type 316 stainless steel, glass, or Teflon. With the exception of a single semi-ball joint greased with silicone lubricant, all couplings were either unions or NPT joints made with Teflon tape sealer and lubricant. Lines carrying only nitrogen were made of copper. Catalyst

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was introduced from the cylinder at position (A). The treatment vessel, located in a polyethylene glycol constant temperature bath (B) was connected with a semi-ball joint. The line (C) is the recovery system by which the entire apparatus was purged. Pressure gages were located on the reservoirs for the two vapor suppliers, and a vacuum manometer was located on the exit side of the treating vessel. Bleed-down or evacuation of the apparatus was accomplished through line (D). Two solenoid valves, located on either side of the entrance line to the treating vessel, were controlled independently by an automatic timer. Preheating of reactant gases, when necessary, was accomplished by wrapping heating tape around the entrance line behind the flow gage. Reactant-gas flow rate was controlled by a micrometer needle valve and flow gage located on the entrance side.

Preparation of Samples

Matched samples of southern yellow pine (*Pinus* sp.) measuring 1- by 1-inch in cross-section and 1/2-inch along the grain were prepared for the preliminary study to determine the feasibility of several treating methods. For treatment by the oscillating pressure method with ethylene oxide, three variables consisting of four species (loblolly pine, *Pinus taeda* L.; shortleaf pine, *P. echinata* Mill.; longleaf pine, *P. palustris* Mill.; and slash pine, *P. elliottii* Engelm.); two specific gravity classes (< 0.62 and > 0.62, ovendry volume basis); and two wood-type classes (corewood or 0-15 years, and maturewood or 25-40 years) were studied. For each combination of variables, four replicated samples were used, giving a total of 160 treated and untreated samples. All samples were conditioned to an equilibrium moisture content of about 20 percent before treatment. The presence of some moisture in the wood appears to improve the stabilizing effect by serving as a plasticizer and swelling agent. Apparently some water is necessary to obtain good stability with the glycols (4, 5).

Treatment Process

In a typical experiment, specimens were placed on wire-mesh screen supports in the treating vessel, which was sealed and attached to the apparatus. The entire system was purged, a section at a time, with nitrogen, and pumped down to a minimum reading on the vacuum manometer to less than 1 Torr. The catalyst and treating vapor was each drawn into its reservoir by condensation at liquid-nitrogen temperature. Following charging of the two reservoirs, the liquid nitrogen was removed and replaced with heating baths which were adjusted to give the desired treating temperature.

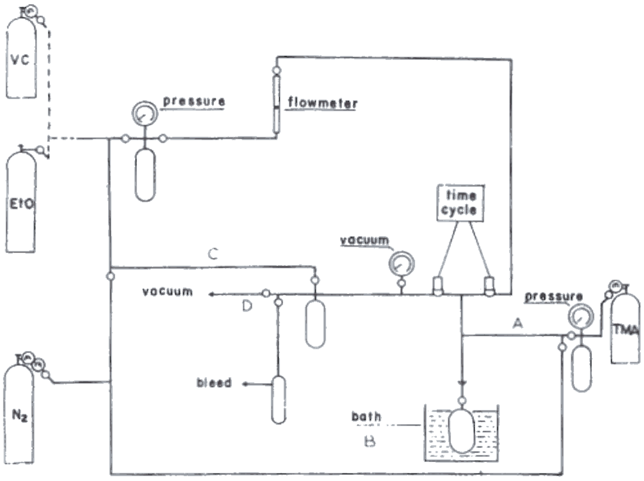

Figure 1. — Schematic drawing of the vapor phase impregnation apparatus.

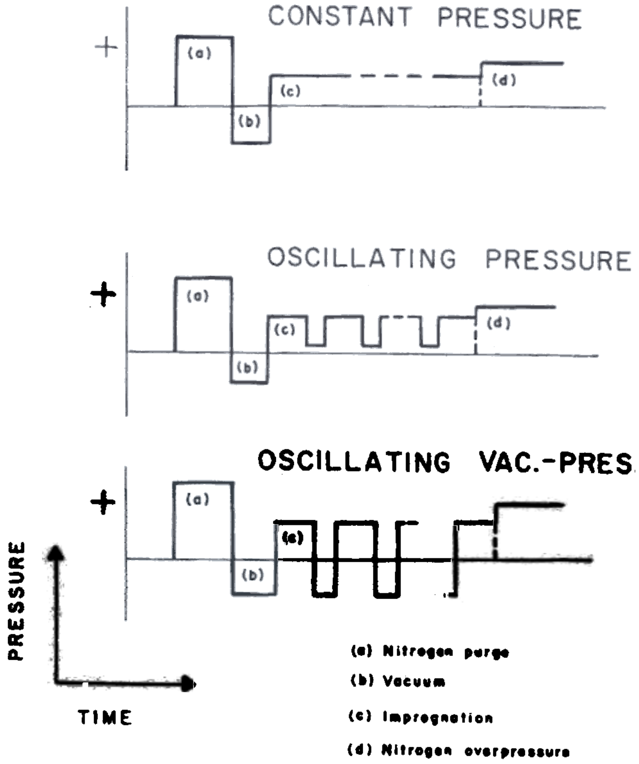

Figure 2. — Diagrammatic representation of the treatment methods used in the vapor phase impregnation of chemical into wood.

The catalyst was admitted to the treating vessel for a controlled time period, at the end of which the unreacted vapor in the treating vessel was either condensed back into the reservoir or exhausted through the vacuum line. Liquid nitrogen was then placed around the collection reservoir or exhausted through the vacuum line, and treatment was begun. By opening the entrance side solenoid, the treating chemical was allowed to enter the treating vessel; after a pre-set time, this solenoid was closed and the exit side solenoid opened, permitting the vapor to be exhausted and condensed into the collection reservoir for a pre-set time. The ultimate pressures of the exhaust cycle were read on the manometer. This procedure was repeated until the desired total treating time was reached, after which the residual vapor was condensed into the collecting reservoir, and nitrogen was bled into the treating cylinder until atmospheric pressure was attained.

A two-component vapor-phase treatment was studied in which ethylene oxide was used as the treating gas, and trimethylamine as the catalyst. Three different treatment methods were used: constant pressure treatment, oscillating pressure treatment, and oscillating vacuum-pressure treatment (Fig. 2). The reaction temperature,

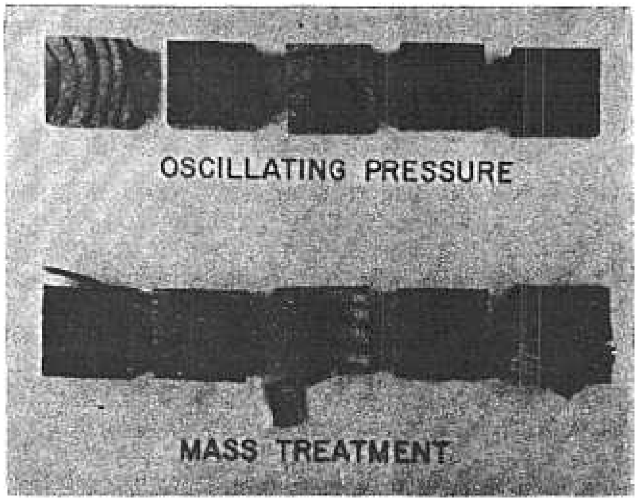

Figure 3. — A comparison of ethylene oxide samples treated by the constant pressure and oscillating pressure techniques.

gas pressure, and total treating time were 200°F., 10 psig, and 60 minutes, respectively. The cyclic time was 6 minutes pressure and 3 minutes atmospheric pressure or vacuum. Trimethylamine catalyst was introduced at 10 psig and was allowed to diffuse into the wood structure for 15 minutes prior to treatment with the ethylene oxide reactant gas.

A single-component vapor-phase treatment with vinyl chloride was also studied. In this case, the reaction temperature, gas pressure, and total treating time were 25°C., 40 psig, and 60 minutes, respectively. The cyclic time for oscillating treatment was the same as for the two component treatment. The vinyl chloride was subsequently polymerized by radiation at a dose rate of 1.31 x 10^{6} rads/hr in a Cobalt-60 source until a total adsorbed dose of 1.5 Mrads was attained.

A dual vapor phase - condensed phase treatment was also evaluated. The wood samples were soaked for 48 hours in liquid ethyl acrylate, then treated with vinyl chloride gas under the same conditions as stated for the single-component vapor phase treatment. The ethyl acrylate was to act as a plasticizer and probably also undergo co-polymerization. The chlorine content of vinyl chloride-treated samples was obtained by fast-neutron activation analysis.

The efficiency of treatment was evaluated in terms of polymer loading, anti-swell efficiency (ASE), and bulking coefficient. Polymer loading was calculated from the net weight change of ovendry samples and expressed as a percent of weight gain relative to the original ovendry weight. Dimensional changes of the specimens were measured with a dial gage accurate to 0.001 inch for samples subjected to a modified ASTM D1037-49T sorption test technique from ovendry condition to water-soaked condition. ASE values were obtained by dividing the difference between the swelling of untreated and treated samples by the swelling of the untreated samples. The volumetric swelling value was determined as the summation of radial and tangential swelling values, and the bulking coefficient was obtained by dividing the difference in the ovendry volume of treated and untreated samples by the ovendry volume of untreated samples.

Results

Significant polymer loadings were obtained for the samples which were subjected to both constant pressure treatment and oscillating pressure treatment with ethylene oxide, but not with the oscillating vacuum-pressure treatment. With the latter, the reactant gas did not react rapidly enough with the catalyst in the wood.

The samples from the constant pressure treatment were of poor quality after soaking, hence no quantitative data could be obtained. They exhibited separation of the growth rings, considerable dimensional distortion, and a spongy, waxy feel. McMillin (4) reported that no significant degradative effect was observed on hard maple with a similar treatment method. This disparity in treatment results due to species can be attributed, at least in part, to anatomical distinctions and differences in mechanical properties of these woods. Hard maple, being a diffuse porous wood, exhibits very little anatomical variation within growth rings, whereas the southern pines have abrupt zones of summerwood and springwood. The springwood, being less dense than the summerwood, is weaker and therefore is more susceptible to degradative action. The degradative effect noted in southern pine points out the need for a proper set of reaction parameters for different species before an optimum treatment result can be obtained.

The samples treated by the oscillating pressure method showed no discernible distortion. The only visual effect of treatment was a slight darkening. A comparison of

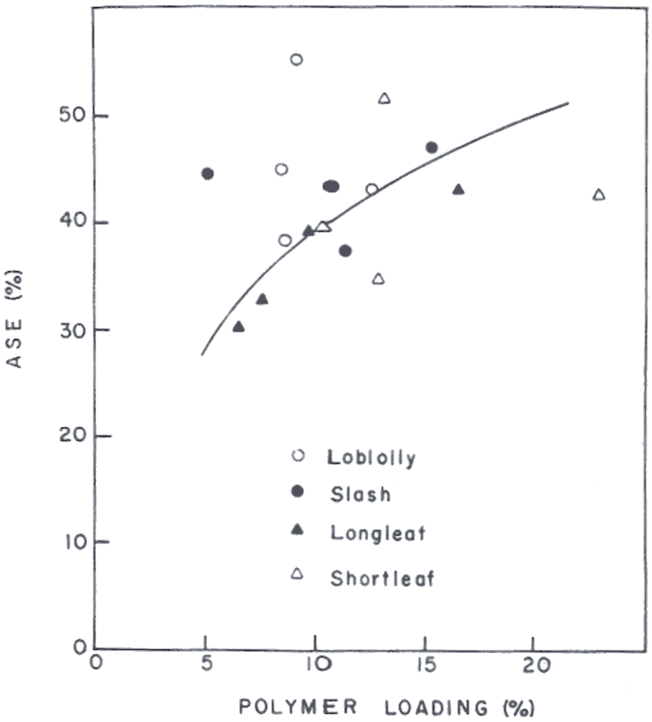

Figure 4. — Relationship of ASE and polymer loading. Each data point represents the mean value for a particular age class - density combination within each species.

samples treated by the constant pressure and oscillating pressure methods is shown in Figure 3. A somewhat similar result was reported by Lantican *et al.* (3) who found that the oscillating pressure treatment with ozone gas proved more satisfactory than the constant pressure treatment, but in both methods there was an increase in permeability due to enlargement of the pit membrane opening as a result of chemical degradation by the volatile ozone. Hudson and Henriksson (1) also obtained better treatment with the oscillating method with liquid. They stated that this was due to the pit acting as a valve controlling the even flow of liquid. From these results, the use of fluctuating pressure seems to have several advantages. In the vapor phase it is possible to introduce the chemical in several stages, removing volatile products and unused catalysts at each pressure fluctuation. This should not only give a more effective and deeper penetration into wood, but should also make the treatment more efficient.

A graphical representation of the regression of ASE value on polymer loading is presented in Figure 4. An increase in polymer loading shows a corresponding increase in ASE value because more chemical entered the wood, and if polymer loading is inversely proportional to specific gravity, the less dense wood should be more stable.

Table 1 shows that the average values of ASE, polymer loading, and bulking coefficient were 41.8, 11.4 and 5.6 percent, respectively. These values compared well with McMillin's (4), whose optimum values for hard maple were 48.0, 11.4 and 7.5 percent, respectively. The relatively high ASE value is an indication that good dimensional stability was achieved because the polymerizable vapors could easily react with the hydroxyl groups of the cellulose-bound water matrix in the amorphous areas of the cell wall structure of wood. The low polymer loading suggests that excellent cell wall treatment may have been obtained because of increased accessibility of the gas to the ultrastructure of wood. The increase in volume of the treated wood (bulking coefficient) is not only due to the monomer acting as a swelling agent, but also to the polymerized products bulking the cell wall and keeping the treated wood in a swollen condition.

Table 1. — MEAN VALUES OF SELECTED PHYSICAL DATA FOR THE VAPOR PHASE TREATMENTS WITH ETHYLENE OXIDE BY OSCILLATING PRESSURE.

Combinations[1]	Volumetric Anti-Swell Efficiency	Polymer Loading	Bulking Coefficient
Loblolly Pine			
C-Low	42.95	13.40	6.96
C-High	55.01	9.40	7.57
M-Low	45.09	8.61	4.44
M-High	38.15	8.78	6.42
Slash Pine			
C-Low	47.66	15.23	4.45
C-High	46.20	5.12	2.25
M-Low	37.58	11.22	6.94
M-High	43.68	10.27	7.46
Longleaf Pine			
C-Low	43.16	16.63	4.04
C-High	30.17	6.62	3.55
M-Low	39.61	9.96	5.58
M-High	32.74	7.68	5.68
Shortleaf Pine			
C-Low	41.35	23.32	5.54
C-High	39.76	10.41	4.89
M-Low	51.73	13.15	5.21
M-High	34.63	12.93	8.23
Average	41.84	11.42	5.58

[1] C = corewood; M = maturewood; Low = low specific gravity (<0.62, ovendry basis); High = high specific gravity (>0.62).

An effective treatment requires a very high ASE value. An ASE value of 100 percent is achieved when shrinkage or swelling in treated wood is prevented by complete bulking of the cell wall. This is theoretically possible when the polymer loading is 30 percent of the ovendry weight of wood and the polymer is in the cell wall. In this condition, the weight fraction of the polymer is $(0.29)(1.2/1.11) = 0.313$ gm/gm o.d. wood, assuming that the maximum swelling takes place at a fiber saturation of 29.0[1] percent, the average bound water density is 1.11[2] gm/cc, and the density of the polymer is 1.2 gm/cc. The maximum bulking coefficient would then correspond to the total volumetric swelling of wood, or about 16.3[1] percent for southern pine. Table 1 shows that the average ASE value for ethylene oxide obtained from this study is 42 percent, which is a little high for a bulking coefficient of 5.6 percent. The theoretical weight fraction of the polymer at this ASE value is $(0.131)(0.42) = 0.131$ gm/gm o.d. wood or 13 percent polymer loading; but the average polymer loading obtained experimentally is 11.4 percent, which is about 12 percent less than the theoretical value if the process is by bulking. Therefore, stabilization was probably accomplished by ethoxylation (reduction in hygroscopicity) alone, or by ethoxylation in conjunction with bulking.

An analysis of variance on ASE data indicates no significant difference in either the species or age class (wood-type) - density variables but slightly higher ASE values were obtained with loblolly pine than with the other species. An analysis of variance of polymer loading, however, shows a highly significant ($P = 0.01$) difference in the two variables. Shortleaf pine has the highest polymer loading. The low density wood is more treatable than the high density wood. Despite higher resin content, the corewood gives somewhat better treating results than the maturewood.

Results of all vinyl chloride treatments were inconclusive. Only one out of more than 60 samples had a chlorine content of more than 2 percent after removing the polymer from the wood surface. This particular sample was pre-treated with ethyl acrylate. To get ap-

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[1] Taken from "Effect of several wood factors on the dimensional stabilization of the southern pines" by E. T. Choong and H. M. Barnes (in press).

[2] Taken from "Textbook of Wood Technology" Vol. II, by H. P. Brown, A. J. Panshin, and C. C. Forsaith, McGraw-Hill Book Co., N.Y. (p. 8)

preciable polymer loading, the vinyl chloride should be polymerized during the vapor phase treatment.

Conclusions

1) Polymerizable vapor of ethylene oxide is very effective in reducing the hygroscopicity of southern pine wood. High ASE values were obtained with low polymer loading. However, a poor quality product was obtained when constant pressure treatment was used.

2) An oscillating pressure treatment technique appears to be superior in stabilizing wood with ethylene oxide vapor, since it tends to increase the accessibility of the ultrastructure of the wood and at the same time eliminates the degradative effect of the catalyst.

3) Treatment of wood with vinyl chloride was not successful because of insufficient polymer loading.

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