Heat Effects on Fire Retardant-Treated Wood

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INTRODUCTION

FIRE RETARDANT WOOD has had many decades of commercial application. Over this time a variety of fire retardant formulations have been used; however, most are primarily inorganic phosphates. A newer patented formulation is based on the synergistic combination of an organic phosphate and boric acid [1].

Until the mid-1970's, the primary criteria for fire retardant treated wood (FRTW) in the United States were fire properties: i.e., flame spread, after glow, etc. In the following decade, new criteria for hygroscopicity were added and design parameters regarding strength loss were changed. At the same time, new second generation fire retardants were introduced and building code changes were made that allow the use of FRT plywood in roofs. Reports of heat degradation and subsequent strength loss with some formulations prompted a reexamination of the parameters associated with the degradation of wood by chemical reaction of fire retardant chemicals at high temperatures and humidities.

In order to address this latter issue, laboratory thermal analysis and strength data were generated with the final goal of producing a correlation capable of predicting lifetime(s) of fire retarded wood products.

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RESULTS AND DISCUSSION

Normal combustion of wood produces highly flammable gases which further support the combustion process [2–8]. Thus the wood is eventually converted to the major gaseous products of carbon monoxide, carbon dioxide, and water. In order to prevent this complete combustion, fire retardant chemicals are introduced into the wood structure such that when wood is exposed to flames or very high temperatures, the decomposition products are carbonaceous materials, i.e., char, and water, which do not support further combustion [2,7,9].

This latter dehydration reaction of cellulose is either acid or base catalyzed. Presently, most commercial formulations are acidic or yield acids when heated. However, if the fire retardant chemicals are too acidic, this dehydration reaction takes place at normal roof temperatures which are far below flame temperatures. Obviously, premature dehydration causes degradation and weight loss followed by subsequent strength loss.

To further explore the nature of the dehydration, a laboratory investigation was initiated to determine the impact of heat and phosphate-containing, acidic fire retardants on the strength of wood. The samples investigated in this study were: untreated southern yellow pine (SYP), SYP treated with monoammonium phosphate (MAP), SYP impregnated with guanylurea phosphate (GUP, 1:1 salt), and SYP treated with Dricon®, a patented formulation containing GUP and boric acid (70:30 weight ratio).

Ultimately, the intent of this work was to develop a relationship from thermal weight loss that would be capable of predicting strength loss.

Thermal Analysis

Thermal analysis techniques were used to examine these samples. The first of these consisted of conventional thermogravimetric analysis (TGA), which measures the weight loss of the sample versus temperature. Coupled with this method was an analysis of the gases produced during this thermal process. This method employed standard TGA in conjunction with Fourier Transform Infrared Spectroscopy (TGA-FTIR). The second technique was differential scanning calorimetry (DSC), which gives information concerning whether the sample gained or released heat. The third technique was isothermal thermogravimetric analysis (IsoTGA), whereby the sawdust sample was maintained at a constant temperature and its weight monitored versus time. All the thermal analysis samples were prepared by impregnating sawdust with aqueous fire retardant chemical and air drying several days at ambient temperature. The samples were also analyzed for retention.

TGA

The TGA data gave an indication of the fire retardancy of the formulation. These data were obtained using a DuPont Model 951 for both "dry" air and air saturated with water vapor at 25 °C to determine if humidity impacted fire retardancy. The samples analyzed were: SYP, MAP-SYP and Dricon-SYP. Figures 1 and 2 show TGA and DSC analyses, respectively, for MAP in SYP.

The results indicated that the moisture content of air, at least at that low level, had little relationship to the weight loss. The TGA, Figure 1, showed that three "events" typically occurred: one small weight loss at 50–60 °C, another about 200 to 250 °C and the major loss at 260 to 325 °C.

However, the DSC for MAP-SYP showed a major decrease in the exotherm when run at the wetter condition (Figure 2) while the other samples did not. This shows that humidity can play a role in the thermal events for MAP-SYP.

TGA-FTIR

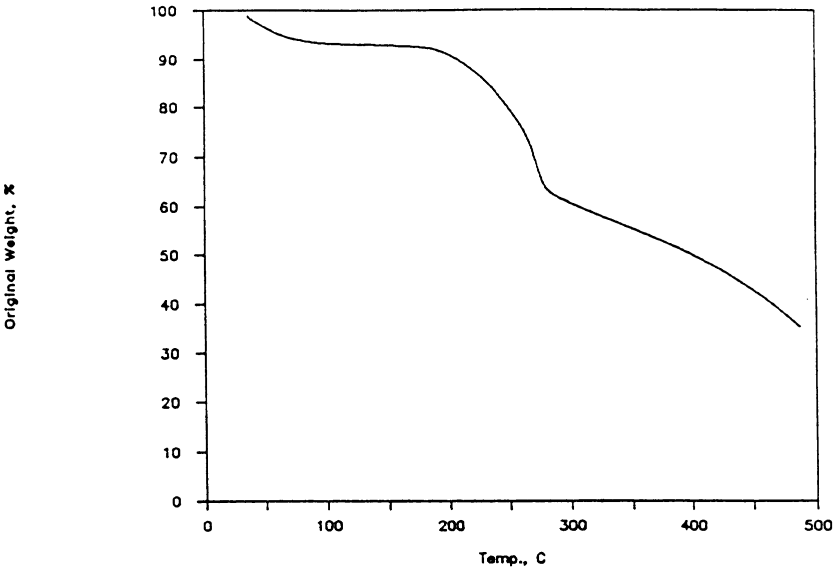
TGA-FTIR analysis was done using a Bomem TG/plus instrument which can provide information concerning the nature and quantity of the gases evolved during a particular thermal event. The samples were run in atmospheres of both helium and helium + 10% oxygen to simulate air. The gases evolved from the samples consisted of water, carbon monoxide, carbon dioxide, methane, methanol, and acetic acid.

To summarize the results of these experiments: treated SYP produced considerably more water and carbon dioxide than untreated; whereas, untreated SYP produced more carbon monoxide, acetic acid, and methanol. Figures 3 to 5 illustrate the water, carbon dioxide and carbon monoxide evolution for untreated and Dricon MAP treated wood samples, respectively.

The quantities of the other gases evolved were small and the untreated samples showed the presence of nitrogen containing chemicals in exceeding small amounts.

IsoTGA

Isothermal TGA was done using a DuPont Model 951. The sample was maintained in a constant temperature environment while its



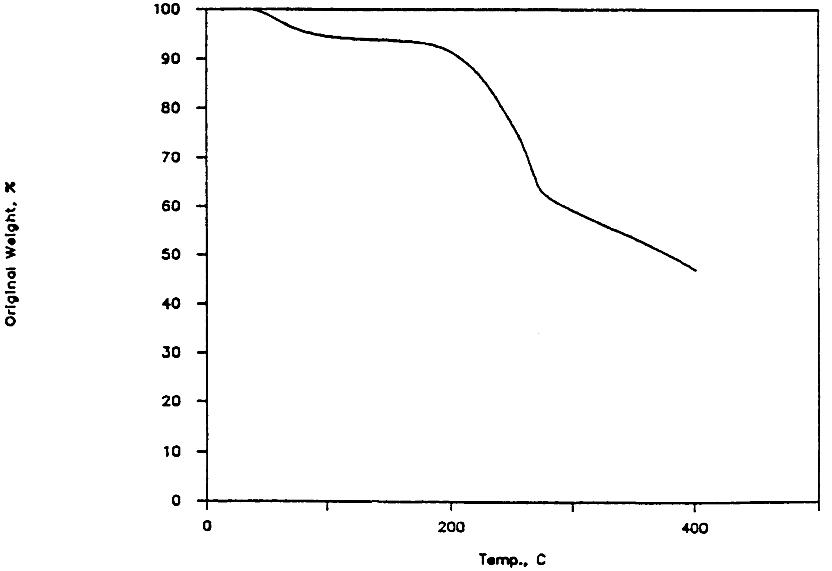


Figure 1. Comparison of TGA for MAP-SYP in dry air (top) and air with water vapor (bottom).

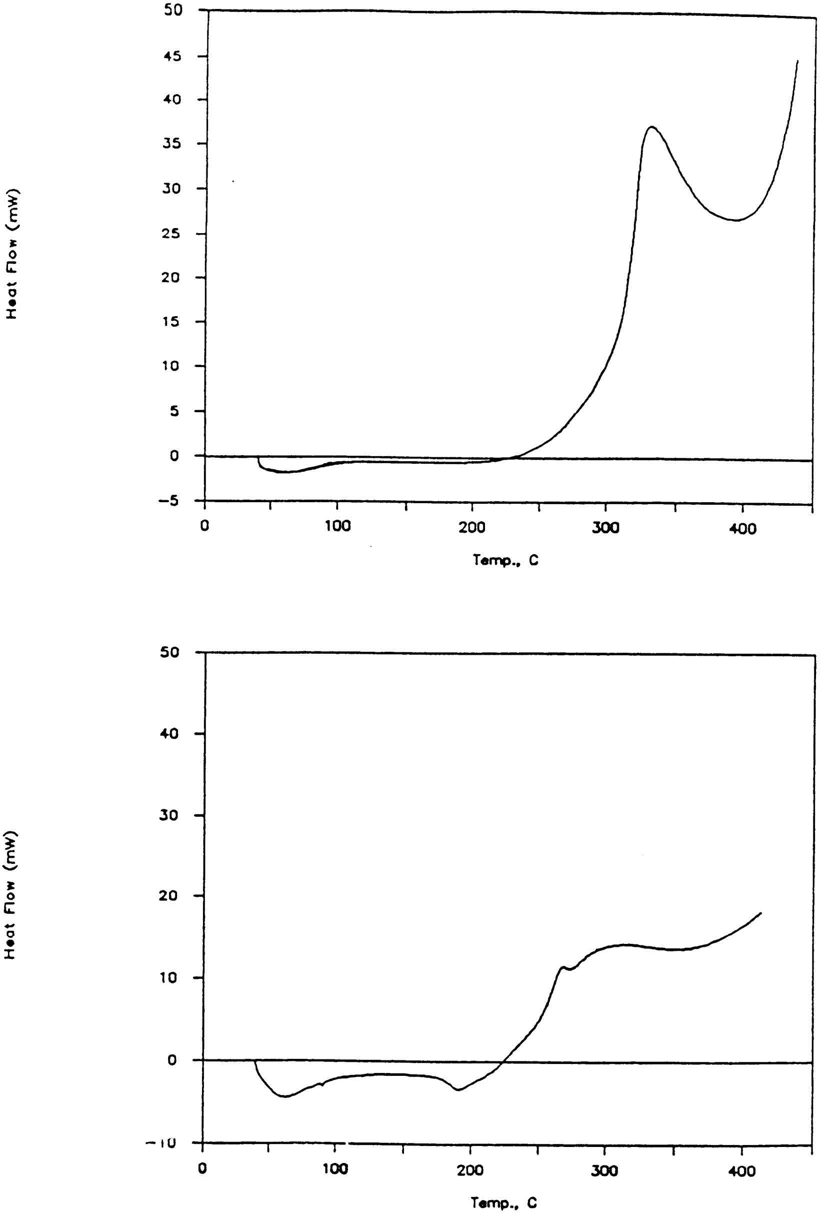


Figure 2. Comparison of DSC for MAP-SYP in dry air (top) and air with water vapor (bottom).

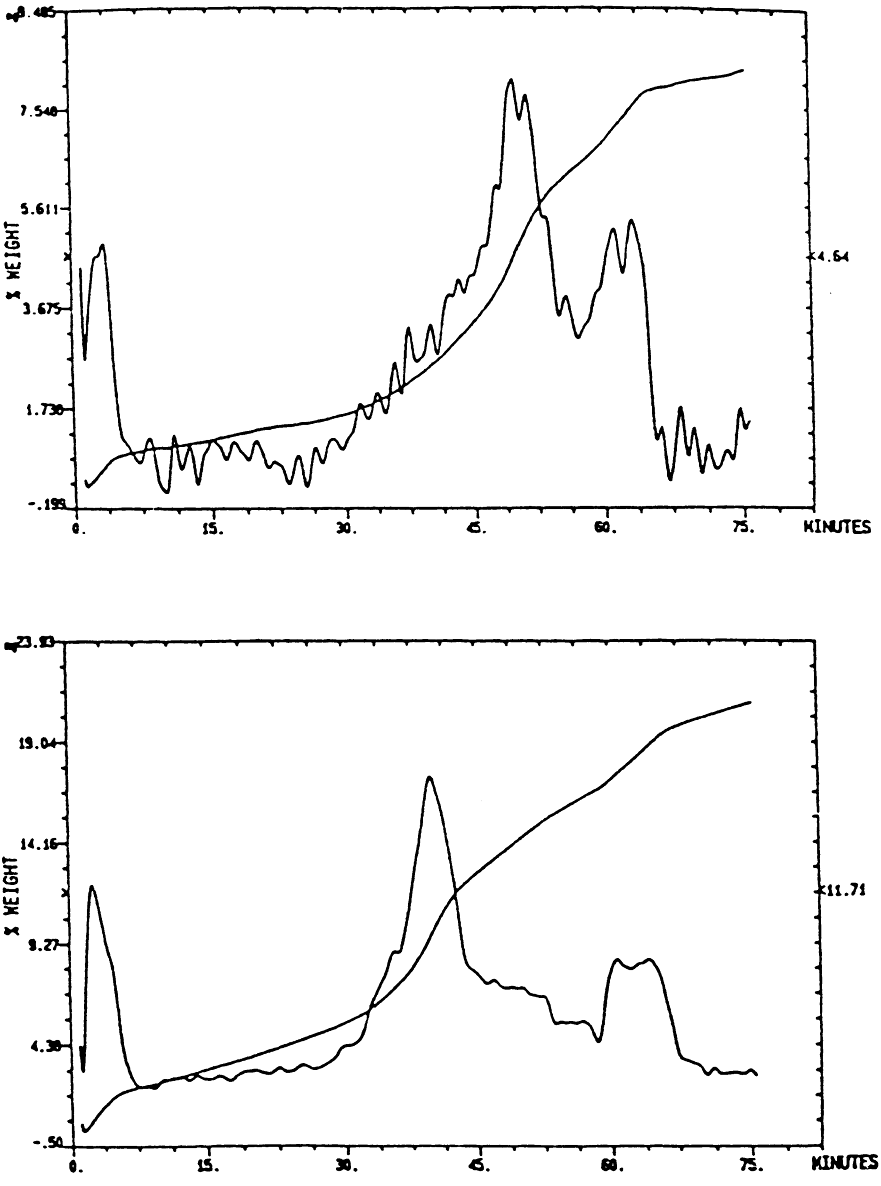


Figure 3. Comparison of water evolved in air from untreated (top) and Dricon fire retardant treated wood (bottom) by the TGA-FTIR techniques. (Ordinates not to same scale.)

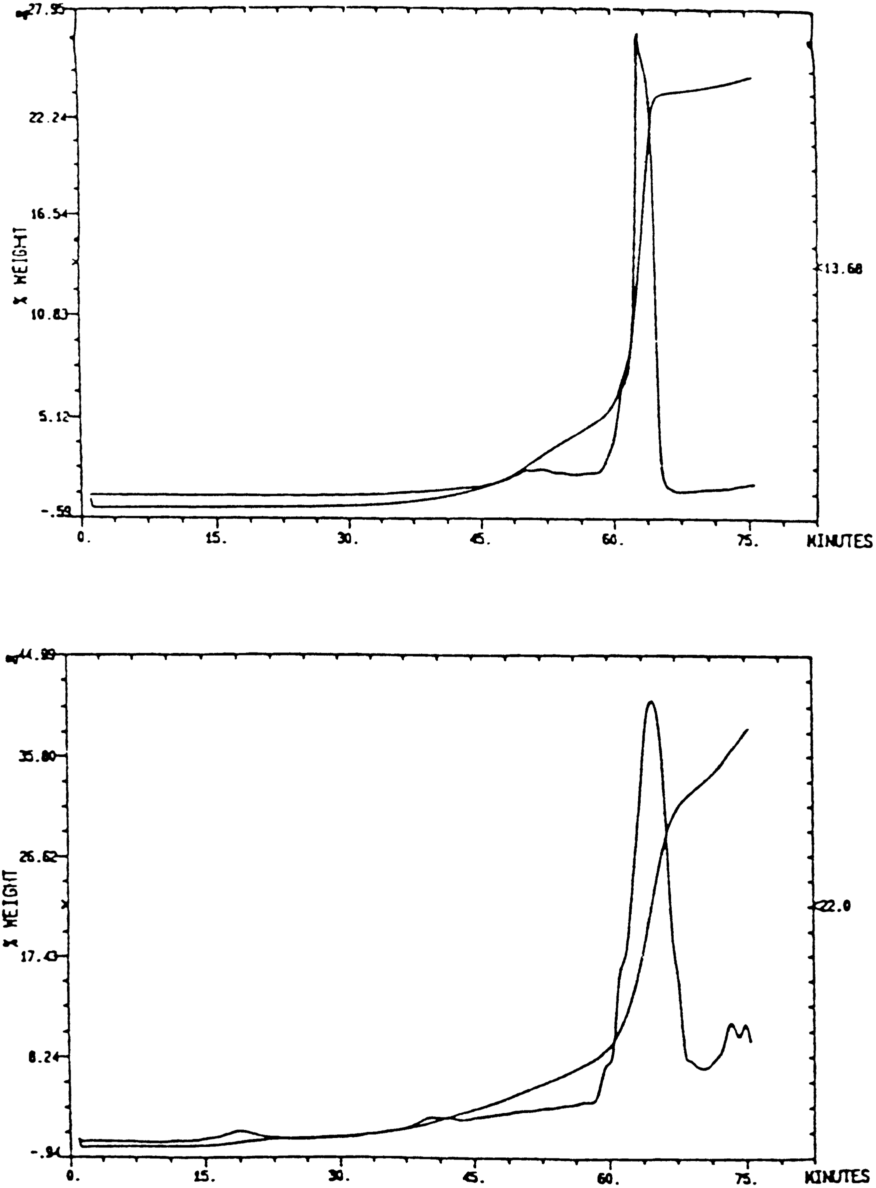


Figure 4. Comparison of carbon dioxide evolved in air from untreated wood (top) and fire retardant Dricon treated wood (bottom) by TGA-FTIR techniques. (Ordinates not to same scale.)

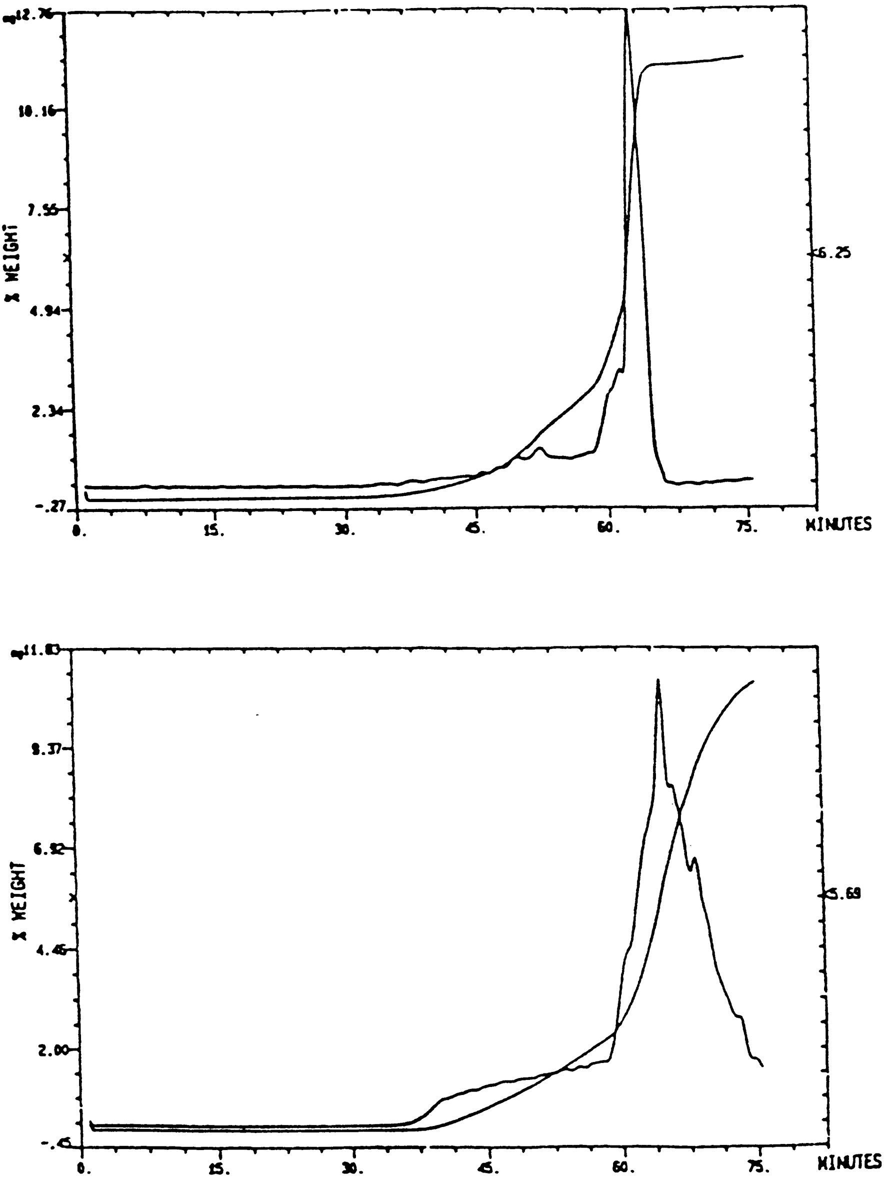


Figure 5. Comparison of carbon monoxide evolved in air from untreated (top) and Dricon fire retardant treated wood (bottom) by TGA-FTIR techniques. (Ordinates not to same scale.)

weight loss was monitored versus time. The gas phase consisted of air bubbled through water at room temperature (25 °C). Six temperatures were selected for investigation: 130, 140, 150, 160, 170 and 180 °C in order to obtain rate of weight loss data. Each sample was run at temperature for approximately 1 to 5 days. The data were analyzed via first order kinetics as suggested by Stamm [10]:

$$\ln(\text{Residual Weight\%}) = -kt + \ln(100\%) \tag{1}$$

RATE CONSTANTS

A typical plot of the logarithm of the residual weight percent versus time is shown in Figure 6.

Examination of these plots indicated that several reactions were occurring in these wood samples. The first was associated with about a 2% weight loss, the second corresponded to 10 to 15% loss and the third

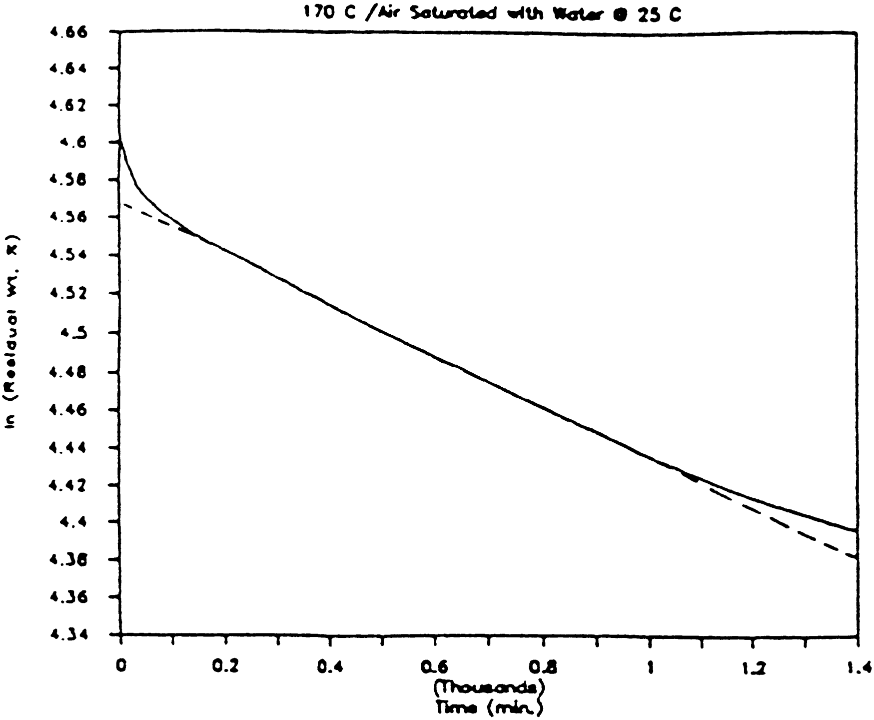


Figure 6. Weight loss: MAP-SYP versus time.

Table 1. Experimental rate of weight loss versus temperature for untreated SYP and MAP, GUP and Dricon-treated SYP ($K \times 10^6$ min.$^{-1}$).

Temp., °C	Untreated	MAP	GUP	Dricon
130	1.39	14.1	2.10	2.21
140	na	28.5	3.10	na
150	4.79	39.5	7.91	7.85
160	8.49	88.3	13.4	13.7
170	14.5	133	na	23.2
180	24.8	334	na	42.8

na = not available.

with an additional 10 to 15% loss. All of these events are acid catalyzed dehydration reactions.

The first event, presumably the degradation of soluble hemicelluloses, is rapid and difficult to observe experimentally. Probably, the second event corresponds to dehydration/depolymerization of cellulose, and the third to the complete dehydration of cellulose to carbonaceous material. This latter reaction is frequently typified by the granular "sawdust" sample turning into black powder on reaction. Since strength loss is readily related to the second event, i.e., the dehydration/depolymerization reactions, only the kinetics for this reaction will be addressed. The rates for these weight loss data are given in Table 1.

ARRHENIUS PARAMETERS

Application of the Arrhenius equation: $k = Ae^{-Ea/RT}$ or $\ln k = -Ea/RT + \ln A$ to the rate data for the 25°C bubbler gave rise to Figure 7, where the slope is equal to the Ea divided by the constant, R, and the intercept is the $\ln A$.

In theory, since all reactions are phosphate catalyzed, they follow the same dehydration mechanism and therefore the slopes, Ea/R, should be identical. However, the intercepts, $\ln A$, vary as the "acidity" of the specific fire retardant. The results (Table 2), show nearly identical slopes and varying intercepts.

IMPACT OF ACIDITY

The amount of acidity influences the Arrhenius constant, A or $\ln A$, but this amount of acidity can also be related to the strength of the acid or the acid equilibrium constant, K_a. For example, for a weak acid, HA, the equilibrium constant is:

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{2}$$

Since $[H^+] = [A^-]$, one can substitute and solve for the acidity or hydrogen ion:

$$[H^+] = \{K_a[HA]\}^{1/2} \tag{3}$$

This expression then can be used to find the available free hydrogen ion which serves as the acid catalyst in the thermal degradation. Obviously the more catalyst, the more degradation.

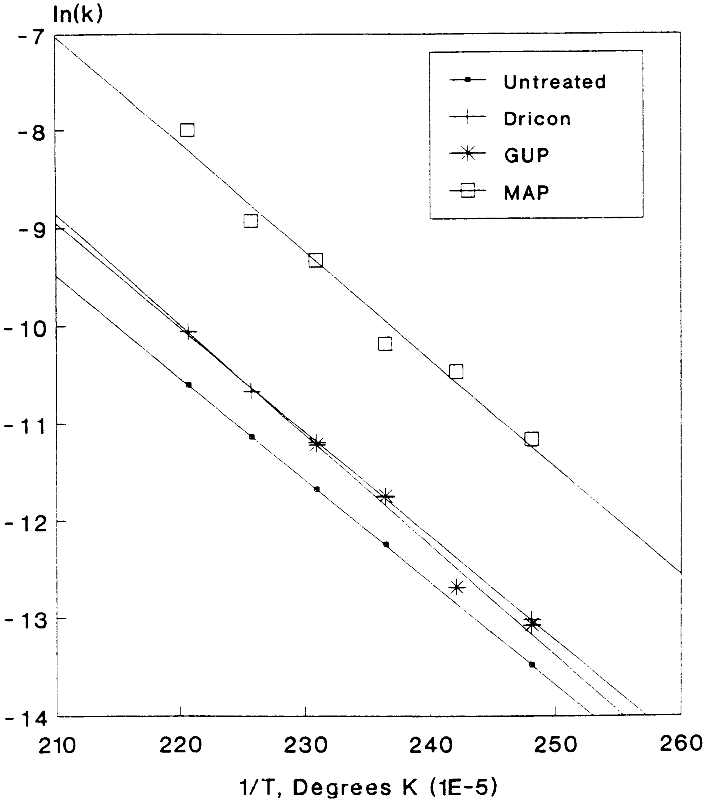


Figure 7. Arrhenius plot for fire retardants: weight loss in SYP.

Table 2. Arrhenius parameters for untreated SYP and Dricon-, GUP- and MAP-treated SYP.

	Ea, Kcal/mole	ln (A)
Untreated	20.95	12.52
Dricon	21.50	13.64
GUP	22.64	14.92
MAP	22.15	16.24
Average	21.81	

The aqueous acid equilibrium constants were measured via titration and the values are given in Table 3.

For purposes of concentration in wood, the amount of fire retardant can be expressed as moles per 100 grams of SYP (in lieu of the more normal moles per liter for aqueous samples). Substituting the concentration in Equation (3), the free hydrogen ion concentration for MAP, GUP and Dricon treated SYP is obtained and reported in Table 4.

The empirical relationship of the free ions or acidity and the Arrhenius constant, A, can be obtained by plotting these free ions from Table 4 versus the logarithm of the Arrhenius constant (ln As from Table 2) as in Figure 8.

Although the plot suggests a curve the portion encompassing the three fire retardant chemicals is nearly a straight line. Thus regression analysis was used and gave a slope of 2.19×10^4 with intercept of 13.46. The following equation can be used to determine the Arrhenius constant for phosphate containing fire retardants:

$$\ln A = (2.19 \times 10^4)[H^+] + 13.46 \tag{4}$$

where $[H^+]$ represents the free hydrogen ion for the retardant.

The rate constants for any temperature can be calculated by incorpo-

Table 3. Acid equilibrium constants for fire retardant chemicals.

	K_a
MAP	1.58×10^{-7}
GUP	3.63×10^{-8}
Dricon	7.94×10^{-10}

Table 4. Free hydrogen ion concentration—FR chemicals in SYP moles H^+ per 100 grams SYP.

	Moles/100 g SYP	"Free Ions" × 10^5
MAP	0.106	12.9
GUP	0.103	6.11
Dricon	0.161	1.13

ration of the above Equation (4) into the Arrhenius equation and using the energies of activation in Table 2:

$$\ln k = -21{,}810/R(T + 273) + \ln A \tag{5}$$

Relative agreement for rate constants was found for calculated (Table 5) and the above experimentally determined values (Table 1). Further

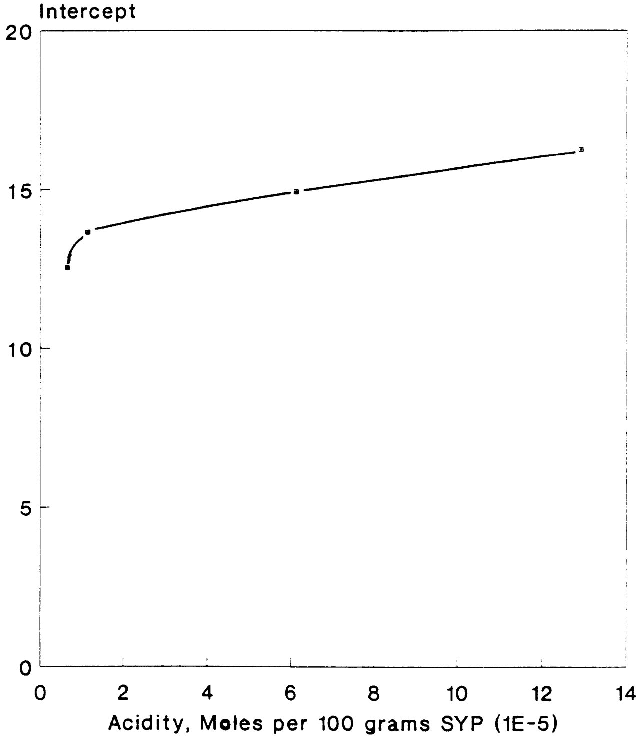


Figure 8. Arrhenius intercept versus acidity: weight loss data in SYP.

Table 5. Calculated rate of weight loss versus temperature for MAP-, GUP- and Dricon-treated SYP ($k \times 10^6$ min.$^{-1}$).

	k		
Temp., °C	MAP	GUP	Dricon
130	20.7	4.68	1.57
140	39.9	9.01	3.03
150	74.4	16.8	5.65
160	134	30.5	10.3
170	238	53.9	18.1
180	410	92.8	31.2

work is underway to refine these relationships such that better correlation is obtained.

Thermal Degradation

Strength Analysis/Weight Loss

Thermal experiments were performed by placing larger samples of SYP, MAP-SYP and Dricon-SYP in a humidity chamber set at 77°C and 79% relative humidity (248 mm Hg water vapor pressure). Samples were removed periodically and examined for weight and strength loss. The experiments were conducted for 77 days and the data represent some two dozen samples of plywood per individual data value.

The weight loss data from these pieces of plywood were examined as above; however, only a single first order rate for weight loss was observed. The strength loss samples for bending (large) and tension (small) samples were treated separately. The results of these calculations are shown in Table 6.

Using the derived empirical relationship for weight loss, which contains the acidity and quantity of fire retardant, the following rates of

Table 6. Experimental rate constants for weight loss, 77°C and 248 mm Hg water vapor ($k \times 10^4$ days $^{-1}$).

Sample Type	SYP	MAP-SYP	Dricon-SYP
Small—1″ × 24″	1.64	10.90	4.90
Large—3″ × 24″	1.45	7.90	5.55
Average	1.54	9.10	5.22

Table 7. Calculated weight loss: 77°C and 24 mm Hg water vapor ($k \times 10^4$ days^{-1}).

SYP	MAP-SYP	Dricon-SYP
0.116	2.54	0.381

weight loss were calculated. For the untreated SYP sample the measured Arrhenius constant was used.

The differences between experimental and calculated range between three and thirteenfold and may be due to the differences in water vapor between the experimental and calculated values, i.e., 248 and 24 mm Hg, respectively.

The importance of water vapor has been speculated on by Woo and Schniewind [11] and the above data suggests that water vapor should be incorporated as a first order reactant. Therefore, a 10-fold difference in water (248 mm vs. 24 mm), corresponds to a 10-fold multiplication of the Table 7 values. This gives better agreement.

Strength Loss

Strength testing of these samples versus time showed losses in various strength properties. Analysis of these strength data, using first order kinetics, gave rates of strength loss consistent with previously discussed weight loss rates and, as Stamm [10] predicted, about 10 times slower.

The normalized strength loss rate data show that SYP has a rate of 1, Dricon-SYP a rate of 3–7, and MAP-SYP a rate of 12–15 depending upon the particular strength property. These results along with additional data will be a topic for a future paper.

CONCLUSION

The relative ranking of the treatments by strength testing is consistent with the small scale isothermal weight data. Also the same mag-

Table 8. Rate constants for strength loss at 77°C and 79% RH ($k \times 10^3$ days^{-1}).

Type	SYP	MAP-SYP	Dricon-SYP
Tension Stress	1	15	7
MOR	1	12	3

nitude differences were found between the two data sets. Therefore the use of isothermal TGA with appropriate controls as a predictor of strength performance seems reasonable.

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