EFFECT OF VARIOUS CHEMICALS ON THERMOGRAVIMETRIC ANALYSIS OF PONDEROSA PINE

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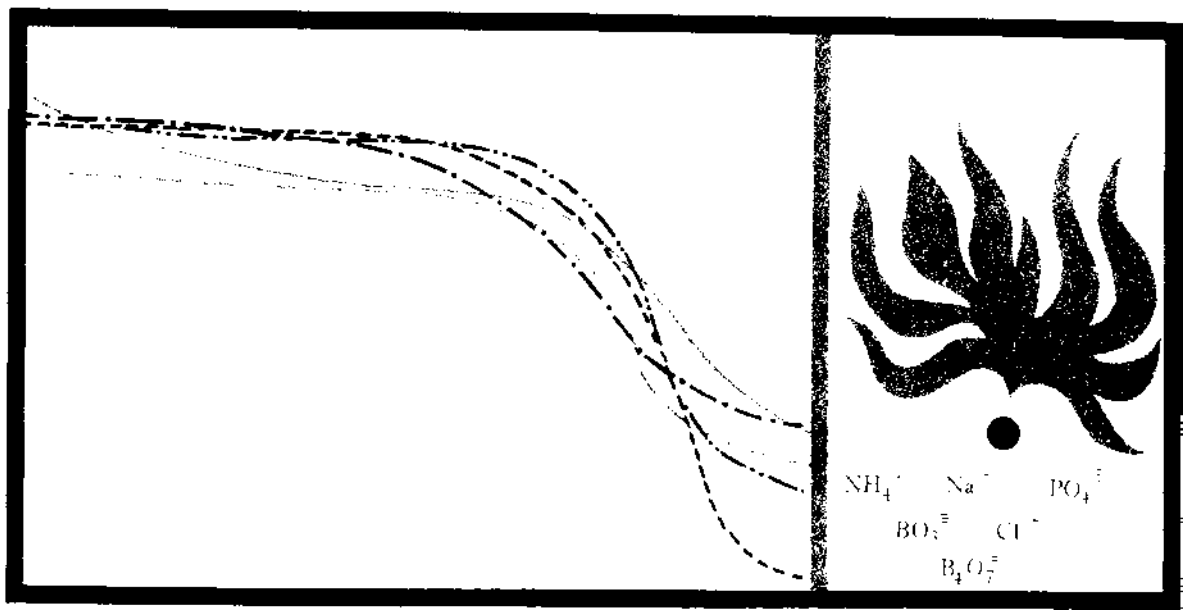

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SUMMARY

Thermogravimetric analyses of thin shavings of ponderosa pine, untreated andtreated with 33 chemicals, were performed in vacuum and in nitrogen within the temperature range of 25° to 400° C. The results were classified in accordance with the threshold decomposition temperature for the pyrolysis reaction of the wood samples and the degrees of volatilization at 250°, 300°, 350°, and 400° C.

The most desirable chemicals greatly increased the char formation of wood at 350° and 400° C., but did not lower the threshold temperature for pyrolysis or result in increased volatilization at 250° C. Boric acid, sodium tetraborate, ammonium pentaborate, calcium chloride, and tetrakis-(hydroxymethyl)-phosphonium chloride were in this class. In the next most desirable group, 11 chemicals increased the char formation at 400° C., accompanied by the lowering of the threshold temperature and an increase in volatilization at 250° C. The other chemicals studied had slight or no effect on the char yield, with some increasing volatilization at 250° C. while others did not.

The results of the present thermogravimetric analyses agree remarkably well with previous fire tube data on chemical treatments for wood.

Of the various theories of flame-retardant action, the, present thermogravimetric data support only chemical theories for the explanation of the action of impregnated chemicals. In general, effective fire-retardant chemicals undergo pyrolysis in the same temperature range as that of wood and form reactive components that alter the pyrolysis reactions of wood. However, a few apparently stable chemicals, which are effective fire retardants, also increase char formation or are reactive in some other manner not yet revealed.

The chemical action of effective retardants clearly involved dehydration of cellulose and lignin, and this apparently occurred in the very first stages of pyrolysis. It perhaps involves the protection of the glucoside linkage of cellulosic and -C-O-C- links of lignin, which appears to be the very first point of attack in the pyrolysis of untreated wood, and a stimulation of the attack on the peripheral hydroxyl and methoxy groups.

EFFECT OF VARIOUS CHEMICALS ON THERMOGRAVIMETRIC ANALYSIS OF PONDEROSA PINE[1]

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INTRODUCTION

The principal chemicals currently used for the fire-retardant treatmerit of wood have been known for their fire-retardant characteristics for over 60 years, and these characteristics were determined largely as a result of empirical tests. Because of the large number of organic and inorganic chemicals and combinations now available, empirical testing for fire-retardant effectiveness appears to be impractical. Therefore, this research has been undertaken as one of the several studies to determine the values for the basic thermal and chemical parameters for the pyrolysis and combustion of wood, and how these parameters are changed for wood treated with known fire-retardant salts. From inforination on how these fire-retardant chemical treatments perform in changing the pyrolysis and combustion processes for wood, it may then be possible more systematically to select improved fire-retardant chemicals, based on their known chemical and physical properties, rather than by empirical tests.

[1] Work here reported was financed in part by a grant of the National Science Foundation

[2] Maintained at Madison, Wis., in cooperation with the University of Wisconsin

A previous study[3] was made of thermogravimetric and differential thermal analysis on the pyrolysis of eight chemical treatments of ponderosa pine. These results appeared to be consistent with a theory[4] that neutral salts formed of strong acids with strong bases, and stable at temperatures of active pyrolysis of wood, are likely to be poor flame retardants; while salts that readily decompose to form either a strong acid or a strong base may be good flame retardants, although the mechanism of their action may differ greatly, depending on whether the effective reagent is an acid or a base. The present study extends the treatments investigated by the thermogravimetric technique to 33 chemicals. These chemicals are divided into four classes (1, 2, 3, 4) according to the degree to which they cause volatilization of wood at temperatures of 250° and 400° C.

APPARATUS

A commercial thermogravimetric balance (fig. 1) was used for the analyses of this study. In this apparatus, the sample to be pyrolyzed was suspended on a glass rod that passed vertically up through an oil dampening cell, through a transducer coil, and to a calibrated weighing spring at the top of the column, as shown schematically in figure 2. The entire column assembly was within a glass enclosure that could either be evacuated or supplied with a gas flowing at a controlled rate. The lower portion of the glass enclosure, the specimen pyrolysis chamber, could be quickly enclosed by an electric furnace that was programed to rise in temperature at a predetermined linear rate from 3° to 36° C. per minute. The temperature attained by the sample was measured by a thermocouple located in the pyrolysis chamber about 5 millimeters below the sample. This temperature was recorded on the X-axis of the X-Y recorder of the balance apparatus.

Every displacement of the glass supporting rod, corresponding to a change of weight of the test specimen, was transmitted from a smallmetal element (transducer armature) surrounding the rod to the transducer coil, which controlled the charting on the Y-axis of the X-Y recorder. Thus a continuous record could be maintained of the weight of the specimen in regard to the exposure temperature.

[3] Browne, F. L., and Tang, W. K. Thermogravimetric and differential thermal analysis of wood and of wood treated with inorganic salts during pyrolysis. Fire Research Abstracts and Reviews. Vol. 4, Nos. 1 and 2, pp. 76-91. (May 1962).

[4] Browne, F. L. Theories of the combustion of wood and its control. Forest Products Laboratory Report 2136, 69 pp., 1958.

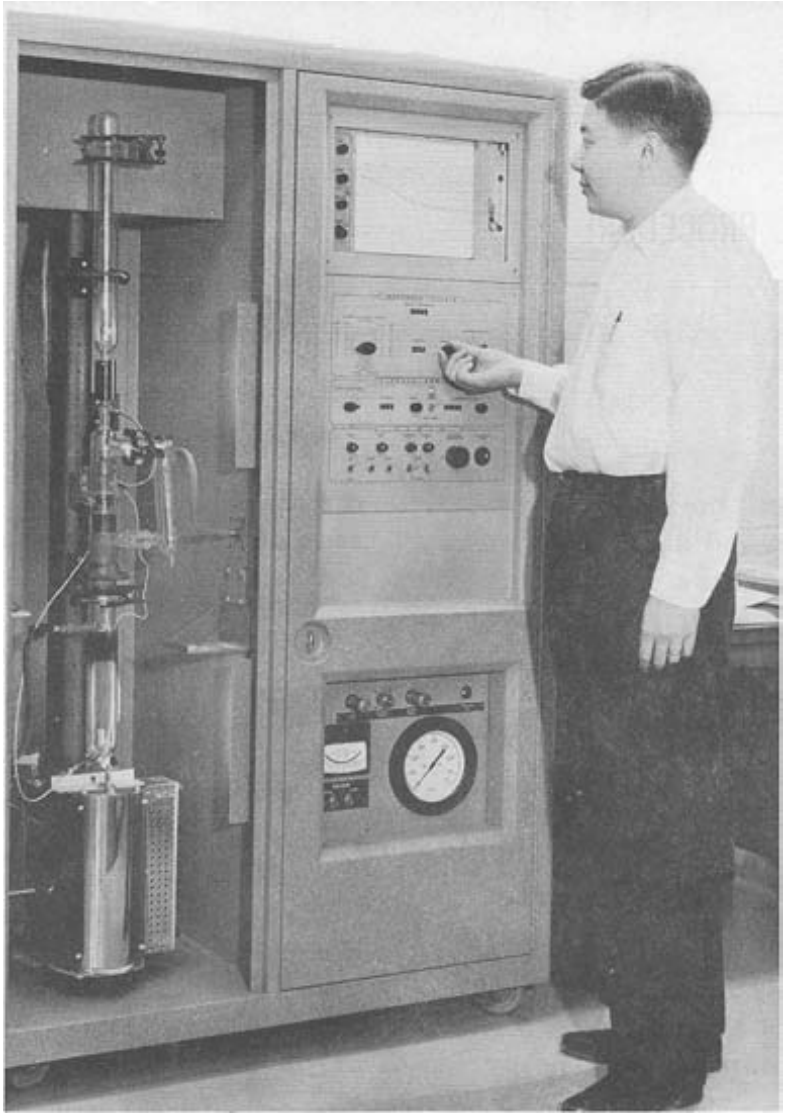

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Figure 1. -- Thermogravimetric balance used for dynamic thermogravimetric analyses of the pyrolysis reactions of treated wood samples.

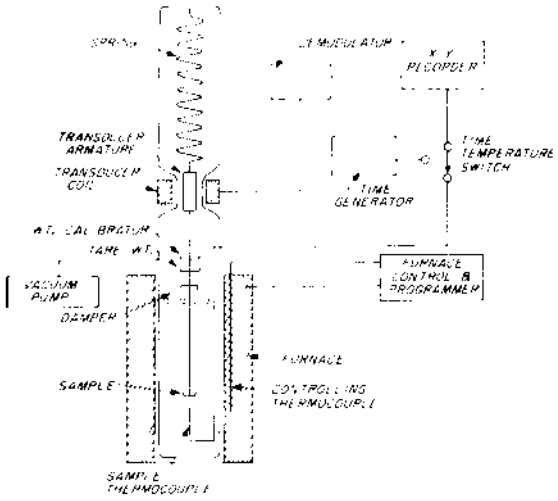

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Figure 2. --Schematic diagram of thermogravimetric balance.

EXPERIMENTAL PROCEDURE

For dynamic thermogravimetric analysis, the wood sample was suspended by the glass supporting rod from the balance spring, in a central position within the pyrolysis chamber. The Y-axis of the recorder was so calibrated that the full weight of the sample spanned 100 divisions of the chart, and the X-axis was set to span the range of sample temperatures to be studied.

The system was either evacuated or flushed with a controlled rate of nitrogen (2 liters a minute) to remove air from the sample and the pyrolysis chamber. The furnace was then raised into position, enclosing the pyrolysis chamber, and heating was started at a programed linear rate (3° or 6° C. per minute). The recording mechanism was set in motion.

Thermogravimetric data were recorded in the thermogravimetric balance under two different conditions: (I) In commercial oxygen-free nitrogen at atmospheric pressure, flowing at 2 liters per minute, and with the furnace set to rise in temperature at 6° C. per minute, starting from room temperature and going to at least 400° C. ; and (2) in a vacuum of 0.4 to 0.6 millimeter of mercury and with the furnace set to rise at 3° C. per minute from room temperature to at least 400° C.

The treated wood samples were shavings of ponderosa pine, 0.16 millimeter thick and weighing between 0.04 and 0.25 gram. Chemical treatment of the samples was by immersion of the dry shavings (80° F. and 30 percent relative humidity) in anaqueous solution of the desired chemical, repeatedly evacuating and then restoring atmospheric pressure, and drying by exposure to air at 30 percent relative humidity at 80° F. Wood samples were treated with 33 chemicals as listed in table 1.

To correct the pyrolysis curves of the treated wood samples for the weight loss attributable to the water of crystallization of the treating chemicals and decomposition of the chemicals, fragments of porous alundum crucibles of convenient size were dried and weighed; these fragments were allowed to absorb concentrated aqueous solutions of chemicals, dried to constant weight at 30 percent relative humidity at 80° F., weighed again, and then exposed in the thermogravimetric balance in the same manner as the treated wood samples.

Table 1.--Composition of treated samples immediately before thermogravimetric analysis

Chemical with which the wood was impregnated	For test[1] in nitrogen atmosphere			For test[1] in vacuum		
	Dry wood	Anhydrous chemical	Moisture	Dry wood	Anhydrous chemical	Moisture
	Pct.	Pct.	Pct.	Pct.	Pct.	Pct.
Class 1: Volatilization much reduced at 400°C., increased little at 250°C.:						
Boric acid, H3BO3	88	5	7	91	4	5
THPC, tetrakis-(hydroxymethyl)-phosphonium chloride, $(HOCH_2)_4PC$)	70	24	6	73	24	3
Sodium tetraborate, $Na_2B_4O_7 \cdot xH_2O$	75	11	14	82	9	9
Ammonium pentaborate, $NH_4B_5O_8 \cdot xH_2O$	73	20	7	78	20	2
Calcium chloride, $CaCl_2 \cdot xH_2O$	64	18	18	72	19	9
Class 2: Volatilization much reduced at 400°C., but much increased at 250°C.:						
Magnesium chloride, $MgCl_2 \cdot xH_2O$	78	6	16	74	10	16
Aluminum chloride, $ALCl_3 \cdot xH_2O$	77	16	7	78	15	7
Diammonium phosphate, $(NH_4)_2HPO_4$	85	11	4	80	15	5
Lithium chloride, $LiCl \cdot xH_2O$	60	14	26	71	14	15
Ammonium sulfate, $(NH_4)_2SO_4$	76	18	6	79	19	2
Ammoniumbromide, NH_4Br	77	17	6	79	19	2
Monammonium phosphate, $NH_4H_2PO_4$				81	17	2
Zinc chloride, $ZnCl_2 \cdot xH_2O$	71	19	10	76	19	5
Ammonium iodide, NH_4I	76	18	6	78	16	5
Ammonium chloride, NH_4Cl	75	19	6	79	18	3
Ammonium sulfamate, $NH_4 \cdot SO_3 \cdot NH_2$	78	17	5	79	16	5
Class 3: Little reduction in volatilization at 400°C. or increase at 250°C..						
Ammonium fluoride, NH_4F	89	3	8	89	3	8
Ammoniumformate, NH_4OOCH	93	0	7	98	0	2
Sodium sulfate, $Na_2SO_4 \cdot xH_2O$	74	20	6	78	22	0
Monosodium phosphate, $NaH_2PO_4 \cdot xH_2O$	78	17	5	78	19	3
Potassium chloride, KCl	77	17	5	77	19	4
Barium chloride, $HaCl_2 \cdot xH_2O$	75	16	9	79	17	4
Sodium chloride, NaCl	79	14	7	76	19	5
Potassium nitrate, KNO_3	76	19	5	80	20	0
Cesium chloride, CsCl	76	19	5	78	20	2
Potassium bromide, KBr	75	20	5	77	21	2
Potassium iodide, KI	81	13	6	84	16	0
Strontium chloride, $SrCl_2 \cdot xH_2O$	79	11	10	86	11	3
Class 4: Little reduction in volatilization at 400°C., but much increase at 250°C.:						
Trisodium phosphate, $Na_3PO_4 \cdot XH_2O$	75	15	10	77	17	6
Potassium fluoride, $KF \cdot xH_2O$	81	9	10	88	8	4
Tetramethyl ammonium chloride, $(CH_3)_4NCl$	72	21	7	78	20	2
Sodium formate, NaOOCH	75	18	7	80	18	2
Potassium carbonate, $K_2CO_3 \cdot xH_2O$	74	19	7	78	17	5

[1]Two samples were used for thermogravimetric analysis in both nitrogen and vacuum.

RESULTS

The composition of the wood samples is listed in table 1 in percentages of dry wood, anhydrous chemical, and moisture at the start of the thermogravimetric analysis. The thermogravimetric analysis curve's for the treated wood samples are shown in figure 3 and after correction for chemical and moisture content in figure 4. The corrected thermogravimetric data for the extent of volatilization of the treated wood samples at 250°, 300°, 350°, and 400° C. are summarized in table 2. Table 3 presents the thermogravimetric data for the chemicals alone in pyrolysis at 250°, 300°, 350°, and 400° C. in nitrogen at atmospheric pressure, and again in vacuum. The methods of sample calculations to correct treated wood sample weight and weight losses for chemical and moisture content are given in Appendix I.

With a few exceptions the thermogravimetric curves (figs. 3 and 4) showed a gradual initial drop in weight to a plateau, between about 100° and 150° C. , before the curves began to benddownward again at the point regarded for the present purpose as the threshold temperature for pyrolysis of the wood. The loss in weight at the plateau of the curve for pyrolysis in nitrogen was taken as the initial moisture content of the treated samples, moisture content meaning the hygroscopic moisture present plus any water of crystallization in the treating chemical. For samples tested in vacuum, the plateau on the thermogravimetric curve usually indicated a lower moisture content than that of samples tested in nitrogen. The difference came from a rapid loss of moisture while the sample was being evacuated, before the balance could be adjusted to make the scale of the weight axis of the chart precisely span the initial weight of the sample.

Typical examples of the method of calculating the composition of the wood samples are given in part A of Appendix I.

The thermogravimetric curves for treated wood samples (fig. 3) record the weight of the wood char, contaminated with any unvolatilized portion of the treating chemical or any of its decomposition products. For the various chemicals such contamination may amount to all the anhydrous chemical present as with sodium chloride, none of the chemical as with ammonium chloride, or some portion in between. If many comparisons are to be made among chemicals or among various retentions of the same incompletely volatile chemical, means must be found to subtract the contaminating chemical from the solid residue so that the

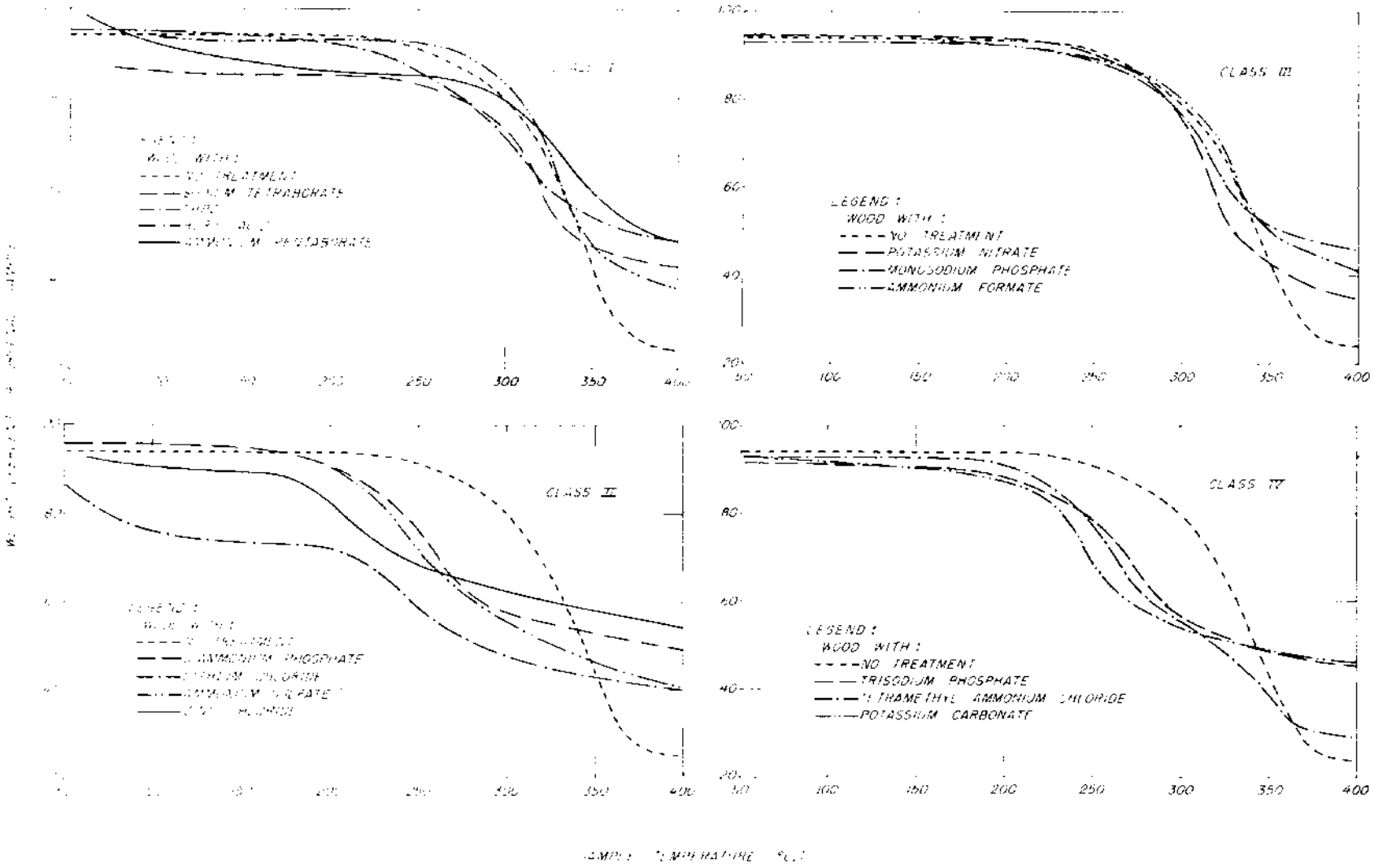

Figure 3.--Original thermogravimetric analysis curves of treated wood, heated in nitrogen at 6° C. per minute (including chemicals and initial moisture).

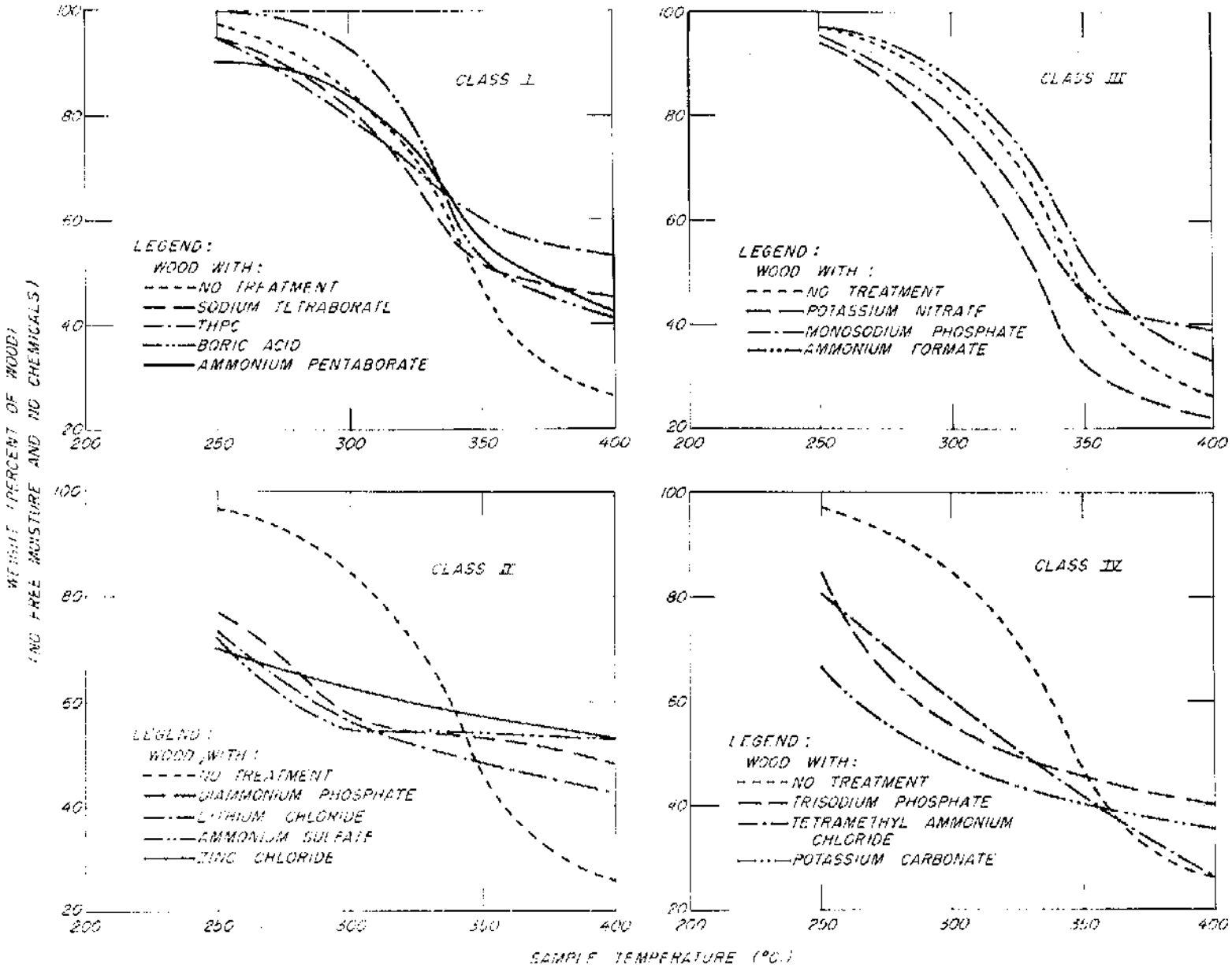

Figure 4.--Thermogravimetric analysis curves of treated wood, heated in nitrogen at 6° C. per minute (corrected for chemicals and moisture to show the true effect of chemicals on the volatilization of wood).

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Table 2.--The effect of chemicals on the volatilization of wood

Impregnating chemical	Volatilized in atmospheric pressure of nitrogen at-				Volatilized in vacuum at-			
	250°C.	300°C.	350°C.	400°C.	250°C.	300°C.	350°C.	400°C.
	Percent of dry wood				Percent of dry wood			
Class 1: Volatilization much reduced at 400°C., increased little at 250°C.:								
Boric acid	0	7	48	59	1	17	51	58
THPC, tetrakis-(hydroxymethyl)-phosphonium chloride	5	20	40	47	12	36	47	50
Sodium tetraborate	5	19	49	55	6	29	53	58
Ammonium pentaborate	10	16	44	58	9	17	46	60
Calcium chloride	13	37	48	55	18	40	54	60
Class 2: Volatilization much reduced at 400°C., but much increased at 250°C.:								
Magnesium chloride	16	33	50	57	23	38	47	53
Aluminum chloride	20	44	53	59	22	43	51	56
Diammonium phosphate	23	43	47	52	32	41	45	49
Lithium chloride	27	44	52	57	32	47	55	59
Ammonium sulfate	28	46	46	47	32	35	42	50
Ammoniumbromide	29	36	44	49	27	37	52	55
Monammoniumphosphate					30	42	47	52
Zinc chloride	30	38	43	47	31	34	26	33
Ammonium iodide	33	36	43	48	26	38	51	58
Ammonium chloride	35	40	57	58	15	27	63	68
Ammonium sulfamate	38	49	48	44	38	32	39	45
Class 3: Little reduction in volatilization at 400°C. or increase at 250°C.:								
Ammonium fluoride	0	10	44	75	5	24	75	82
Ammoniumformate	3	13	47	67	5	24	72	79
Sodium sulfate	4	19	61	72	8	32	78	83
Monosodium phosphate	5	20	55	61	8	35	62	63
Potassium chloride	5	21	59	65	10	51	66	70
Barium chloride	5	20	61	73	8	34	69	74
Sodium chloride	6	21	66	70	10	48	68	72
Potassium nitrate	6	25	68	78	10	58	77	81
Cesium chloride	7	31	61	65	14	58	65	69
Potassium bromide	7	27	62	67	10	48	67	71
Potassium iodide	7	39	58	61	12	58	64	68
Strontium chloride	9	35	59	65	11	44	56	62
Class 4: Little reduction in volatilization at 400°C., but much increase at 250°C.:								
Trisodium phosphate	15	45	54	60	22	46	55	59
Potassium fluoride	15	50	57	61	36	50	56	60
Tetramethyl ammonium chloride	19	40	58	74	28	31	71	73
Sodium formate	29	54	63	67	33	54	58	61
Potassium carbonate	33	52	59	64	29	52	58	67
UNTREATED WOOD								
	3	15	54	74	8	33	61	81

Table 3.--Extentto which the chemicals, dispersed in porous alundum, remained unvolatilized when subjected to thermogravimetric analysis in the same manner as the treated wood samples

Chemical (dispersed in alundum)	Chemical left after heating in atmosphere of nitrogen at-				Chemical left after heating in vacuum at-			
	250°C.	300°C.	350°C.	400°C.	250°C.	300°C.	350°C.	400°C.
	Percent of anhydrous chemical				Percent of anhydrous chemical			
Class 1								
Boric acid	59	58	57	57	45	45	44	44
THPC, tetrakis-(hydroxymethyl)-phosphonium chloride	79	67	58	51	75	62	52	45
Sodium tetraborate	100	100	100	100	100	100	100	100
Ammonium pentaborate	95	91	88	87	84	78	74	74
Calcium chloride	100	100	100	100	100	100	100	100
Class 2								
Magnesium chloride	100	100	100	100	100	100	100	100
Aluminum chloride	44	41	39	39	60	57	54	54
Diammonium phosphate	88	80	75	71	66	60	55	52
Lithium chloride	100	100	100	100	100	100	100	100
Ammonium sulfate	96	81	34	0	82	15	0	0
Ammonium bromide	16	0	0	0	0	0	0	0
Monammonium phosphate					66	60	55	52
Zinc chloride	98	96	94	86	93	69	2	0
Ammonium iodide	34	0	0	0	0	0	0	0
Ammonium chloride	95	78	35	0	0	0	0	0
Ammonium sulfamate	91	88	62	0	75	5	0	0
Class 3								
Ammonium fluoride	0	0	0	0	0	0	0	0
Ammonium formate	0	0	0	0	0	0	0	0
Sodium sulfate	100	100	100	100	100	100	100	100
Monosodium phosphate	92	89	88	87	91	86	83	82
Potassium chloride	100	100	100	100	100	100	100	100
Barium chloride	100	100	100	100	100	100	100	100
Sodium chloride	100	100	100	100	100	100	100	100
Potassium nitrate	100	100	98	96	100	99	96	93
Cesium chloride	100	100	100	100	100	100	100	100
Potassium bromide	100	100	100	100	100	100	100	100
Potassium iodide	100	100	100	100	100	100	100	100
Strontium chloride	100	100	100	100	100	100	100	100
Class 4								
Trisodium phosphate	100	100	100	100	100	100	100	100
Potassium fluoride	99	96	94	91	98	97	94	93
Tetramethyl ammonium chloride	97	60	0	0	95	20	0	0
Sodium formate	100	100	98	98	99	98	92	89
Potassium carbonate	100	100	100	100	100	100	100	100

char and the extent of volatilization of the dry woodinitially present can be estimated. Although this was not accomplished with a high degree of precision, a reasonable approximation was obtained by using chemically treated alundum samples. The water of crystallization in the chemical was determined from the plateau in the thermogravimetric curve and was subtracted from the difference in weight before and after treatment to determine the content of anhydrous chemical. Residues after pyrolysis at 250°, 300°, 350°, and 400°C. are then expressed in percentage of the initial anhydrous chemical (table 3). The method of calculation by which these results were used to correct the thermogravimetric data for treated wood samples is illustrated by examples in part B of Appendix I.

In all the tables of this report, the chemicals are classified in four classes according to their effect on volatilization of wood in the early and late stages of pyrolysis. Other work at the Forest Products Laboratory has shown that, at temperatures below the "exothermic point" or onset of fast pyrolysis for untreated wood (about 270° C.), some chemicals greatly hasten volatilization in the early stage of pyrolysis, whether or not they decrease the ultimate volatilization significantly when the pyrolysis reaches completion, either above or below the "exothermic point." Other chemicals hasten the early volatilization little, if at all, whichever effect they may have on the ultimate volatilization. Thermogravimetric curves reveal the effect of the chemicals on the rate of pyrolysis at moderate temperatures, such as 250° C., just as theyreveal the effect when the loss in weight nearly ceases as the temperature nears 400° C.

Thus the four classes of chemicals recognized, which are essentially the same as those reported previously, [3] may be described as follows:

1. Chemicals that reduce the volatilization at 400° C. on the thermogravimetric curve with little increase in volatilization at 250° C.

2. Chemicals that reduce volatilization at 400° C. but increase volatilization at 250° C. significantly.

3. Chemicals that exert relatively little effect on volatilization either at 250° or 400° C.

4. Chemicals that decrease volatilization at 400° C. very little but significantly increase volatilization at 250° C.

Since the four classes merge gradually into one another, the lines of separation are necessarily rather arbitrary.

Presumably chemicals of classes 1 and 2 are good flame retardants, but those of class 1 have the advantage of avoiding the hazard, to which those of class 2 are subject, of slowly damaging wood at temperatures that may occasionally be encountered in service. Distinction between classes 3 and 4 may be of little significance for selecting flame retardants but, in practical wood treatment, mixtures of chemicals are often chosen, some

Table 4.--Effect of chemicals on the threshold temperature for pyrolysis and results of fire-tube test for comparison

Impregnating chemical	Threshold temperature: In atmosphere of nitrogen	Threshold temperature: In vacuum	Fire-tube test: Fraction volatilized: With low retention	Fire-tube test: Fraction volatilized: With high retention	Fire-tube test: Group assignment
	°C.	°C.	Pct.	Pct.	
Class 1					
Boric acid	260	215	71.5	21.2	II
THPC	200	200	.....	.....	.....
Sodium tetraborate	200	220	74.5	11.8	I
Ammonium pentaborate	270	270	70.8	34.2	III
Calcium chloride	210	190	71.0	17.2	II
Class 2					
Magnesium chloride	190	185	49.0	15.0	I
Aluminum chloride	230	215	73.0	15.7	II
Diammonium phosphate	180	140	57.8	15.0	I
Lithium chloritie	190	190	64.8	18.8	I
Ammonium sulfate	170	160	72.5	20.2	II
Ammonium bromide	150	105	61.0	18.5	II
Monammonium phosphate	.....	140	59.8	17.8	I
Zinc chloride	170	150	63.2	17.2	II
Ammonium iodide	150	120	.....	.....	.....
Ammonium chloride	150	90	30.8	18.8	I
Ammonium sulfamate	165	150	.....	.....	.....
Class 7					
Ammonium fluoride	200	215	.....	.....	.....
Ammoniumformate	170	170	.....	.....	.....
Sodium sulfate	200	200	77.0	61.2	IV
Monosodium phosphate	190	190	.....	.....	.....
Potassium chloride	210	200	71.2	61.8	IV
Barium chloride	195	205	74.8	64.7	IV
Sodium chloride	220	200	70.0	59.5	IV
Potassium nitrate	195	190	71.8	66.8	IV
Cesium chloride	210	190	.....	.....	.....
Potassium bromide	205	190	.....	.....	.....
Potassium iodide	190	180	60.2	48.3	III
Strontium chloride	175	180	72.0	45.5	III
Class 4					
Trisodium phosphate	190	190	63.5	46.5	III
Potassium fluoride	180	180	.....	.....	.....
Tetramethyl ammonium chloride	180	180	.....	.....	.....
Sodium formate	150	150	.....	.....	.....
Potassium carbonate	195	185	[1]61.8	[1]37.7	[1]III
UNTREATED WOOD					
	210	210	82.8	82.8	.....

[1]Fire-tube data are for sodium carbonate since potassium carbonate was not tested.

of which provide properties other than fire resistance. Among the chemicals in class 4, for example, the alkali fluorides impart resistance to fungal decay.

Table 4 reports the threshold temperatures for pyrolysis of wood treated with the various chemicals. Threshold temperature is the point on the thermogravimetric curve at which the plateau interpreted as loss of moisture ends and the weight begins to fall off again more rapidly, presumably because volatilization of wood has begun. The threshold temperature so observed for untreated wood, 210° C., is considerably below the "exothermic point" at which pyrolysis is commonly considered to become rapid.

To compare results by thermogravimetric analysis with the results of older fire-tube data,[5] table 4 includes the weight losses or fraction volatilized at "low"and at "high" retention of the chemicals common to both the thermogravimetric and the fire-tube experiments, together with the groups to which the chemicals were assigned on the basis of the fire-tube data.

DISCUSSION

The chemicals fitted reasonably well into the four classes with respect to the data on volatilization of the wood in table 2, whether the results in nitrogen at atmospheric pressure or the results in vacuum were considered. For classes 1 and 3 the volatilization at 250° C. always was less than 15 percent in nitrogen or 20 percent in vacuum, and for classes 2 and 4 always 15 percent or more in nitrogen and 20 percent or more in vacuum (except for ammonium chloride). For classes 1 arid 2 the volatilization at 400° C. always was less than 60 percent in nitrogen and, except for ammonium chloride, not greater than 60 percent in vacuum. For classes 3 and 4 the volatilization at 400° C. always was 60 percent or more except for the one case of trisodium phosphate, where it was 59 percent.

The exceptional position of ammonium chloride in vacuum may be attributed to its complete escape by sublimation, as shown in table 3, before pyrolysis of the wood had gone very far, so that it failed to exert as much effect as otherwise would have been possible. Other salts that sublime at relatively low temperature, ammonium bromide and iodide, likewise exhibited notably less reduction in the volatilization of wood at 400° C. (table 2) in vacuum than they did at atmospheric pressure. Ammonium formate probably owes its position in class 3 rather than in class 1 or 2 to the fact that it sublimes so readily even at. room temperature that, although the wood samples received substantial impregnation, very little chemical was left in the

[2] Hunt, G. M., Truax, T. R., and Harrison, C. A. Experiments in fireproofing wood--third progress report. Proc. Amer. Wood-Preserver's Assn. 71-93, 1932.

wood after the equilibration preceding thermogravimetric analysis.

Aluminum chloride misses class 1 in table 2 by a narrow margin that may well be due to uncertainties in the calculations arising from the ease with which aluminum chloride, especially whenmoisture is present, loses hydrogen chloride at temperatures very little above room temperature. Thus the data in table 2 indicating less weight loss for aluminum chloride in vacuum than at atmospheric pressure are clearly anomalous. It may well be that aluminum chloride belongs in class 1 rather than in class 2.

Results in nitrogen rarely differed significantly from those in vacuum. Such small differences as there were often were in the direction of slightly greater volatilization in vacuum than innitrogen. As pointedout in a previous publication,[3] the agreement between thermogravimetric data in nitrogen and in vacuum comes from the use of wood shavings that are thin enough to avoid appreciable differences in temperature between the surface and interior of the sample and to let primary volatile products escape before they could undergo much secondary pyrolysis. With thick specimens there usually would be distinctly greater volatilization in vacuum than at atmospheric pressure.

The presence of THPC and calcium chloride in the highly desirable class 1, which appears to offer effective flame retardance without materially impairing the performance of wood at moderate temperatures, proves that the favorable properties can be imparted by chemicals other than the compounds of boron. Class 1 chemicals, however, probably are much less numerous than class 2 chemicals.

For some time it seems to have been gene rally accepted[4] that effective flame retardants lower the threshold temperature for rapid pyrolysis and for charring. The class 1 chemicals, however, demonstrate that such effect, although common enough, is not an essential property of good flame retardants. It is possible to impart resistance. to flaming combustion without impairing the stability of wood at moderate temperatures.

Other chemical effects of effective flame retardants commonly reported in the literature,[4] notably increased yield of char (decreased volatilization) and of aqueous condensate, decreased yield of tar, and shift of the "exothermic point" to higher temperature, find confirmation in the present data, as well as in a previous study.[3]

The present data may well be discussed in relation to the theories of the mechanism of flame retardance that have been advanced in the literature which are:

1. Coating theories

    a. Exudation of melted chemical coats the wood fibers and retards escape of flammable vapors and access of oxygen.

b. Chemicalsthat foam or intumesce on heating similarly trap vapors and bar oxygen.

2. Thermal theories

a. Coatings or foams insulate the wood against penetration of heat.

b. A diametrically opposed theory that coatings or treatments that increase thermal conductivity carry heat away fast enough to prevent attainment of the ignition temperature.

c. Absorption of heat by endothermal reactions of the chemical keep the temperature below the point of ignition.

3. Gas theories

a. Nonflammable gases released by the chemical dilute the flammable gases from the wood too much for a flammable mixture with air to be formed.

b. The chemical evolves a gas that acts as a chain breaker for the free–radical chain reactions on which flaming depends.

4. Chemical theories--the chemical directly alters pyrolysis of wood

a. Since thorough dehydration of cellulose leaving only carbon is an ideal reaction for the purpose, useful chemicals are likely to be highly hydrophilic and soluble in water.

b. Since strong acids and strong bases tend to attack cellulose, salts of strong acids with weak bases or of weak acids with strong bases, which dissociate readily when heated, are likely to be effective.

c. More specifically, the action of acids and bases is postulated as a condensation at the hydroxyl groups of cellulose (or lignin) with splitting off of water followed by pyrolysis to regenerate the acid or base, leaving carbon.

d. Still broader application of the theory of acids and bases is gained on the basis of the electron donor–acceptor theory (Lewis theory) of acids and bases with intermediate formation of carbonium ions or carbanions.

e. Many of the effective flame retardants contain groups capable of hydrogen bonding, such as –O, –OH, or $-NH_2$ groups, hence by their hydrogen bonding they may tend to hold the carbon atoms of cellulose and lignin together in char instead of allowing their escape in volatile fragments. A variant of the theory relies on

polyfunctionality of phosphates, borates, sulfates, etc., to accomplish the same purpose.

Although the coating theories, the thermal insulation theory, and sometimes perhaps the thermal conductivity theory are certainly valid for fire-retardant paints, it is equally certain that they do not apply to such class 1 chemicals as calcium chloride or such class 2 chemicals as ammonium sulfamate or aluminum chloride, and it is exceedingly doubtful that they could apply even to the borates or the phosphates.

For the thermal absorption theory and the gas dilution theory, great importance has long been attached to those chemicals that contain much water of crystallization. Although such chemical may increase the moisture in treated wood greatly even after equilibration at 30 percent relative humidity, as shown in table 1, both thermogravimetric analysis and the differential thermal analysis previously reported[3] show that the water is lost and its endothermal effect dissipated before pyrolysis of the wood begins. The loss of all moisture before the wood begins to decompose is indicated in the thermogravimetric curve by the usual plateau in the region of 100° to 150° C. and in the differential thermal curve by the termination of the initial endothermal dip before serious weight loss from pyrolysis of the wood sets in. Thus thermal absorption from evaporation of hydrate water, which certainly delays rise in temperature of wood exposed to heat, reaches completion and ceases before it can have an appreciable effect on pyrolysis and combustibility of wood.

Water of crystallization from the chemical is also an important source of nonflammable vapor in the gas dilution theory, but its escape so far in advance of the onset of pyrolysis indicates that the water vapor is no longer present to act as a diluent when flammable gases and vapors are being evolved from the wood. Other diluting gases that have been mentioned are ammonia, carbon dioxide, sulfur dioxide, and hydrogen chloride. All of the ammonium salts tested are possible sources of ammonia or of the vaporized salt itself; ammonium sulfamate may supply some sulfur dioxide as well, and aluminum chloride evolves hydrogen chloride. None of the chemicals tested gives rise to carbon dioxide at temperatures reached in this work. Ammonium fluoride and ammonium formate are so volatile that they escaped almost completely while the samples were being prepared and the samples pyrolyzed essentially like untreated wood. If they are not too readily volatile, the ammonium salts are good flame retardants, but the data of table 2 show that their effectiveness can be accounted for adequately by the way in which they reduce the supply of volatile material from the wood before the surrounding atmosphere is reached. Other chemicals that release no diluting gases other than an early emission of water, such as sodium tetraborate and the chlorides of calcium, magnesium, lithium, and zinc,

are equally effective flame retardants, provided that they likewise reduce the supply of volatile material from the wood sufficiently.

Among the chemicals of classes 1 and 2 only ammonium bromide and ammonium iodide are known to furnish gases that serve effectively to break the free-radical chain reactions of flaming combustion. Although the flame suppression of gaseous bromides and iodides has been well demonstrated, the effectiveness of ammonium bromide and iodide when impregnated in wood seems to be due chiefly to their reduction of the volatilization of the wood. This is especially so since such chemicals as lithium chloride, zinc chloride, and ammonium sulfate, which give rise to no chain breakers, do an equally good job of reducing wood volatilization and imparting flame resistance.

Thus the data from this study strongly support the chemical theories as the major source of flame-retardant action for chemicals impregnated in wood. Table 4 shows that all chemicals in classes 3 and 4 that have been evaluated by the fire-tube method? were placed in the ineffective groups III or IV, and all but one of those in classes 1 and 2 were in the effective fire-tube groups I or II. The one exception, ammonium pentaborate, behaves like the tetraborate used in the fire-tube tests; rated in group III for the fire-tube data, the pentaborate was almost on the borderline between groups II and III and would have been in group II if the fraction volatilized with high retention had been under 30 instead of 34.2 percent.

Comparison of tables 2 and 3 reveals a markedtendency for the chemicals of classes 1 and 2 to decompose beyond the loss of water of crystallization, or to sublime in the temperature region within which most of the pyrolysis of wood occurs, namely, 250° to 400° C. Of 15 chemicals in these two classes, 11 are thus reactive; by contrast, among 10 inert chemicals of class 3 (ignoring the excessively volatile ammonium fluoride and formate) only 2 chemicals exhibit any weight loss up to 400° C., (potassium nitrate shows only an insignificant loss and monosodium phosphate shows only the loss of 2 molecules of water, most of which came off before 250° C. was reached). The facts strongly suggest that the chemicals most likely to alter the pyrolysis of wood are those that themselves undergo pyrolysis at the same time as the wood.

The suggestion previously advanced[4] that effective fire-retardant chemicals are necessarily hydrophilic enough to be soluble in water cannot be confirmed by present data because the experiments so far have not included any chemicals that are not soluble in water.

The theory that effective chemicals are usually salts either of a strong acid with a weak base or of a weak acid with a strong base finds little support in table 2. Among the effective chemicals are boric acid (a very weak acid acting alone), lithium, calcium, and magnesium chlorides (salts of a strong acid with a strong

base), sodium tetraborate (a salt of a strong base and a weak acid), and ammonium sulfate and aluminum chloride (salts of a strong acid and a weak base). On the other hand, all the chemicals of the inert class 3 except the two excessively volatile ammonium salts are combinations of a strong acid with a strong base. Perhaps salts of a strong acid with a strong base usually are too stable to become reactive in the temperature range critical for wood pyrolysis, and the essential condition is contemporaneous reactivity of chemical and wood.

Study of the yields of major products on pyrolysis of treated wood at 350° C. indicates that chemicals of all four classes exert a dehydrating action revealed in a marked increase in the yield of water. The dehydrating action is not confined, however, to strong acids or strong bases present at the pyrolyzing temperature because it is shared fully by such stable chemicals as sodium tetraborate in class 1, trisodium phosphate and potassium carbonate in class 4, and sodium chloride in class 3. The effective chemicals clearly act by decreasing the yield of tar and increasing that of char.

The applicability of the electron acceptor–donor theory is rendered doubtful by the indication that reactivity in a critical range of temperature rather than formation of strong acids or strong bases is the dominant consideration.

The effective chemicals certainly are characterized by the ability to increase the yield of char on pyrolysis but the data throw little light on the theory that high yield of char comes from a capacity of the chemical for hydrogen bonding or for polyfunctional reactions. Carbon has such pronounced susceptibility to coordinate bonding with itself that it would seem that a bridging agent should be unnecessary if only any interference with carbon's own propensity to polymerize is avoided.

The fact that so many highly effective chemicals are themselves volatile enough to escape completely before temperatures are reached at which untreated wood pyrolyzes rapidly suggests that the effective chemicals accomplish their result primarily by redirecting the very first stage of wood pyrolysis. The tar formed in large amount on pyrolysis of pure alpha–cellulose is said to be almost entirely levoglucosan. If so, the initial step in pyrolysis is splitting of the glucosan linkages of the cellulose macromolecule without dehydration. The effective chemicals perhaps delay or suppress splitting at the glucosan linkage and stimulate dehydrating reactions at the peripheral hydroxyl groups. Those that stimulate dehydration too much fall in class 2 because they lower the threshold temperature for pyrolysis. The less numerous but more desirable chemicals of class 1 possibly act more by protecting the glucoside linkages than by overstimulating dehydration. It is more difficult to visualize the action on the more complicated lignin macromolecules but it, too, has -C-O-C- linkages and peripheral hydroxyl and methoxy groups.

APPENDIX I

Examples of the calculation of (A) composition of samples at the start of thermogravimetric analysis and (B) the percentage of the dry wood volatilized at four stages of the pyrolysis of samples treated with zinc chloride:

Part A - –Calculation of Composition of Samples

Since ponderosa pine equilibrated at 30 percent relative humidity at 80° F. contains moisture to the extent of 6 percent of the dry wood (5.7 percent of the total weight), the initial weight of the sample divided by 1.06 gave the weight of the dry wood present. For the sample pyrolyzed in nitrogen, the moisture in the treated wood sample was read from the plateau in the thermo–gravimetric curve (fig. 3). The content of anhydrous chemical was obtained by adding the percent of dry wood and moisture and subtracting the total from 100 percent.

For the sample pyrolyzed in vacuum, the moisture content at the start of pyrolysis was read from the plateau in a thermogravimetric curve, but the moisture content of the equilibrated sample before starting to evacuate was taken as the same as the corresponding sample for pyrolysis in nitrogen. On such assumption the content of the dry wood in the sample for vacuum pyrolysis was corrected for the loss of moisture during the evacuation of the apparatus. The content of the anhydrous chemical was then obtained by difference between these values and 100 percent.

Steps	Analysis in nitrogen	Analysis in vacuum
1. Weight before impregnation, gram.	0.4036	0.4271
2. Weight of dry wood (line 1 ÷ 1.06), gram	.3808	.4029
3. Weight after impregnation, gram	.5348	.5586
4. Percent of dry wood (line 2 ÷ line 3 X 100). . .	71	72
5. Moisture (100– plateau in TGA curve), percent	10	5
6. Factor by which content of dry wood is increased because of loss of moisture during evacuation	. . . . .	$\frac{100-5}{100-10} = 1.055$
7. Dry wood at start of pyrolysis, percent	71	76
8. Percent anhydrous chemical in sample, 100 - (line 7 + line 5)	19	19

Part B --Calculation of Percent of Dry Wood Volatilized at Various Stages of Pyrolysis

Steps	Analysis in nitrogen at-				Analysis in vacuum at-			
	250°C.	300°C.	350°C.	400°C.	250°C.	300°C.	350°C.	400°C.
9. Residue, chemical alone, from alundum samples, percent	98	96	94	86	93	69	2	0
10. Chemical left in treated sample (line 8 X line 9 ÷ 100), percent	19	18	18	16	18	13	0	0
11. Residue, treatedwood(TGA curve), percent:	69	62	58	54	71	63	56	51
12. Wood char left (line 11 - line 10), percent	50	44	40	38	53	50	56	51
13. Wood volatilized (line 7 - line 12), percent	21	27	31	33	23	26	20	25
14. Wood volatilized as percent of dry wood initially present (line 13 ÷ line 7 X 100)	30	38	44	46	30	34	26	33