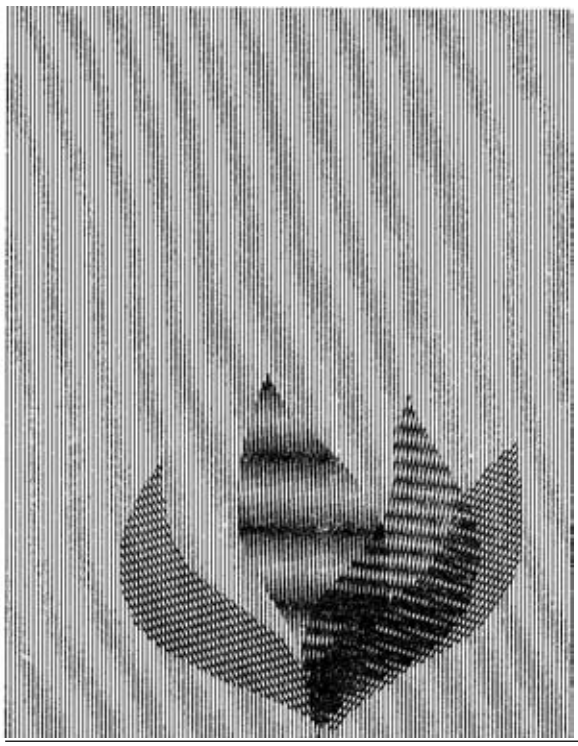
U. S. FOREST SERVICE
RESEARCH PAPER
FPL 80
OCTOBER 1967



EFFECT OF FIRE-RETARDANT AND OTHER INORGANIC SALTS ON PYROLYSIS PRODUCTS OF PONDERSOA PINE AT 250° AND 350°C.

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SUMMARY

Basic information was obtained on the pyrolysis reaction and products formed when wood treated with fire-retardant and other salts was pyrolyzed at 250° and 350° C. This information will be useful in the systematic evaluation and selection of improved fire-retardant treatments for wood.

Fourteen inorganic chemicals were used to treat wood shaving samples, which were then pyrolyzed in vacuum at 250° and 350° C. The pyrolysis products of untreated wood and chemically treated wood were separated into four fractions by vacuum distillation. The fractions were: a char residue, low vapor pressure tars, water, and "noncondensable" gases. The flammability of wood is normally associated with the volatile tar fraction.

When treated and untreated wood were pyrolyzed at 350° C., the chemicals increased the yield of the char, water, and gas fractions at the expense of the flammable tar fraction. This effect was greater for chemicals that are usually considered to be fire-retardant than for non-fire-retardant chemicals. Also, at a pyrolysis temperature of 350° C., very small amounts of chemical (on the order of 1 percent of the treated sample weight) markedly affected pyrolysis, increasing yields of char, water, and gases, and decreasing tars.

When treated wood was pyrolyzed at 250° C., most chemicals reduced the tar and char fractions of the pyrolysis products and increased the water fraction. An important exception was diammonium phosphate, which produced a higher proportion of tars in the pyrolysis products than was observed for untreated wood. The relation of these data to the fire-retardant characteristics of diammonium phosphate may be explained on the basis of the low temperature at which the tars were released (250° C.), and the fact that the tars were diluted with a relatively large amount of water vapor. Thus the result was a non-flammable composition.

In general, small concentrations of the various chemicals were less effective at 250° C. than at 350° C. in altering the composition of the pyrolysis products.

EFFECT OF FIRE-RETARDANT AND OTHER INORGANIC SALTS ON PYROLYSIS PRODUCTS OF PONDEROSA PINE AT 250° and 350° C.

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INTRODUCTION

When a piece of wood is progressively heated, a temperature is reached where the wood structure begins to decompose. Reactions occur in the cellulose, hemicellulose, and lignin which produce true gases, mists of liquids dispersed in the gaseous phase, solid particles that are also dispersed, and a carbon-rich solid residue known as charcoal (3).[2] This thermal decomposition of the wood is termed "pyrolysis" and the substances that result are termed "pyrolysis products." When oxygen is present and the temperatures are sufficiently high to bring about ignition, the volatile pyrolysis products burn in flaming combustion and the char burns in glowing combustion.

Therefore, in studying fire performance of wood and its modification by fire-retardant chemicals, it is desirable that infarmation be obtained on the principal products of the pyrolysis of wood and how these are modified by chemical treatments. This basic approach to the relation between wood and fire may lend itself more readily tosearches for possible new fire retardants for wood than empirical fire test methods currently being used.

In previous work (4, 10), salt treatments provided a variety of effects on the volatilization of wood in pyrolysis over a temperature range of 150° to 400° C. At 250° C. certain salts greatly promoted volatilization as compared to the untreated wood; at 350° C., some of these same salts decreased volatilization. However, there were also salts that had little influence on the volatilizations at either 250° or 350°C., and others that decrease volatilization at only the high temperature.

At 350° C. it was also found (1) that the pyrolysis products, if quickly withdrawn from the pyrolysis zone, could be separated by vacuum distillation into four fractions: char residue, low vapor pressure tar, water, and "noncondensable" gases. Most salts tended to increase the proportions

[1] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.
[2] Underlined numbers in parentheses refer to Literature Cited at the end of this report.

of the char and water fractions and decrease the proportion of the tar fraction at this temperature as compared to untreated wood. The reduction in the tar fraction was greater for salts that are usually considered to be fire retardant than for non-fire-retardant salts. As the flammability of wood and cellulose is associated with the tar portion of the pyrolysis products, the possibility arises that the fire-retardant chemicals are effective because they reduce the quantity of tar produced during thermal decomposition. Because this work was limited to one temperature and to eight inorganic salts, it seemed desirable to study at least one additional (lower) temperature and several additional salts.

Finally, it was hoped that further study would clear up a point concerning the previous work. This point was the effect of the concentration of a given chemical on the weight distribution of the pyrolysis products. In some cases, when wood was impregnated with solutions containing as little as 1 percent of a chemical, the tar fraction of the pyrolysis products was lowered to about half of the value observed for untreated wood. The retention of chemical necessary to reduce the tar fraction was much lower, in most cases, than the retention needed to make wood "fire retardant" according to many empirical tests. Pyrolyzing impregnated wood at a temperature near the "threshold temperature" (where thermal decomposition begins) might shed some light on the interpretation of these observations.

One practical implication of the previous results is that, when the chemical mechanism of cellulose pyrolysis is studied, "purity" of the samples (or freedom from inorganic contaminants) is of prime importance. Indeed, some authors (2) have pointed out that present ideas about the decomposition of cellulose may be in error because the effects of minor impurities (ash).

EXPERIMENTAL PROCEDURE

Description of Test Specimens

The wood samples used in this work were 0.005-inch-thick ponderosa pine shavings whose surface measurements were approximately 1.25 by 5 inches. The first samples were cut from a dry wood block with a microtome knife, but then later the technique was modified to use a water-soaked block to reduce the wear on the knife.

The thin dimension of the shavings helps eliminate temperature gradients. This is desirable because the decomposition reactions of wood are highly temperature-dependent and, if a temperature gradient existed in the sample, the pyrolysis products would be a mixture of components associated with each point on the gradient. Thus it is hoped that these samples approximate the idealized case of a wood slab whose temperature is raised in a step-wise fashion from ambient temperature to the pyrolysis temperature (either 250° or 350° C.).

The sample geometry is also important because it aids in the uniform distribution of treatment salts throughout the specimen cross section. Furthermore, it is desirable to duplicate the type of specimen used in the previous work from which this study follows (1).

Selection of Treating Chemicals

Previous work by Browne and Tang (4) showed that many inorganic salts may be separated into four groups or classes according to their effect on the thermogravimetric analysis (TGA) curves of wood (shown in fig. 1) as follows:

Group I--Reduce volatilization at 350° C. without increasing volatilization at 250° C.

Group II--Reduce volatilization at 350° C. but increase volatilization at 250° C.

Group III--Exert little effect on TGA volatilization either at 250° or 350° C.

Group IV-- Reduce TGA volatilization at 350 °C. very little, but increase volatilization at 250° C.

Therefore for this study, two chemicals were chosen to represent each of these four groups. In addition, several chemicals were chosen because they are components of commercial preparations used in the manufacture of fire-retardant-treated wood. In all, 14 chemicals were selected for use in the treatment of wood shaving specimens. They were:

Diammonium phosphate, sodium chloride. trisodium phosphate, ammonium chloride, potassium carbonate, calcium chloride, sodium tetraborate, potassium bromide, ammonium polyphosphate 11-37-0 (supplied by the Tennessee Valley Authority), zinc chloride, ammonium sulfate, ammonium sulfamate, boric acid, and phosphoric acid.

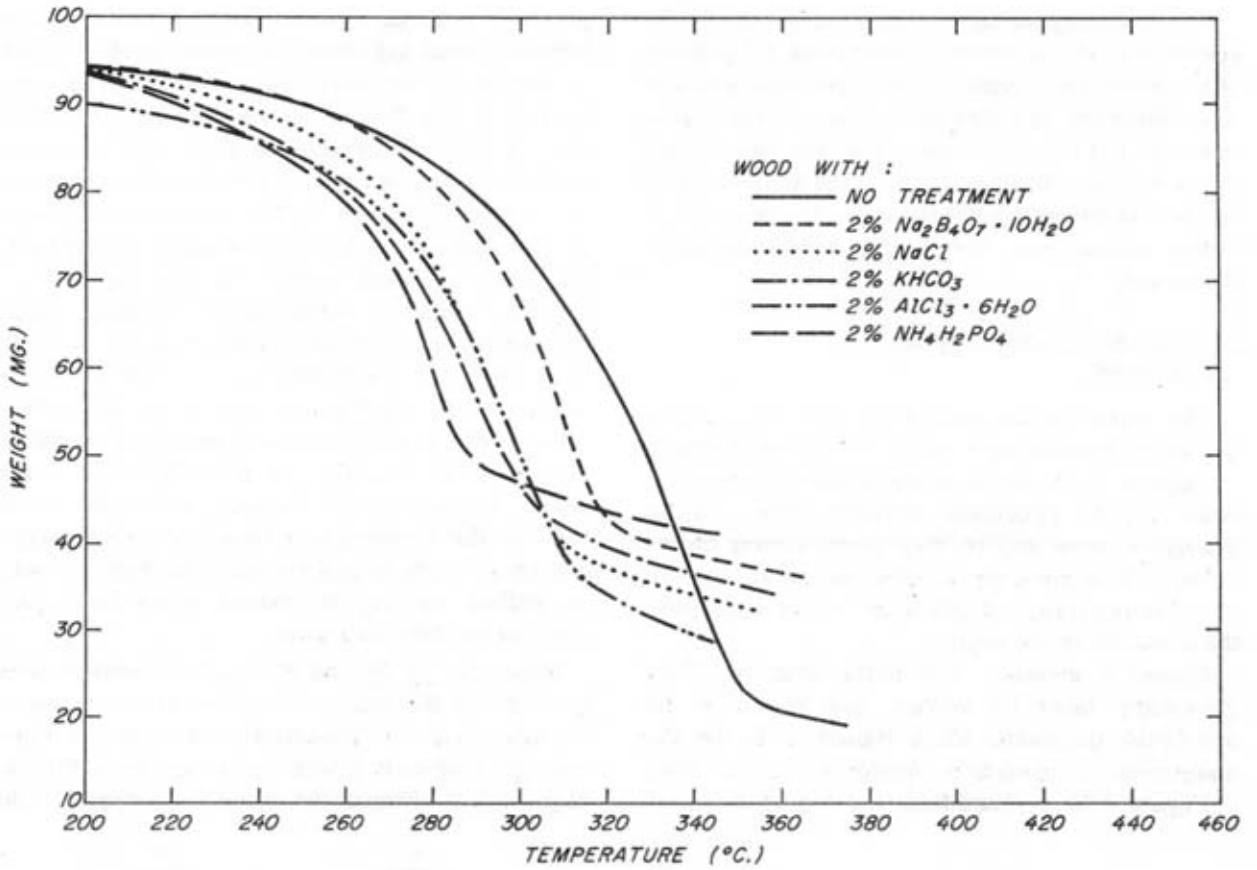

Figure I.--Typical results from the thermogravimetric analysis of wood untreated and salt-treated (taken from ref. 10). M 131 815

Treatment of Specimens

Previous work with the vacuum pyrolysis of wood at 350° C. (1) showed that, as the concentration of impregnated salt decreases, the proportions of the various fractions of volatile products tend to approach the values associated with untreated wood. For comparison with that previous work, the salts for this study were impregnated into the shaving samples in three water solution concentrations each: 15, 5, and 1 percent by weight.

To do this, batches of 50 samples each were placed in 4-liter dessicators to which a solution of either 15, 5, or 1 percent by weight of salt was then added. The salt solution was impregnated into the wood using the following pressure-vacuum procedure:

1. The atmospheric pressure above the solution containing the samples was reduced to about 2 inches of mercury for 30 minutes. This removed some of the entrained air from the wood

2. The dessicators were then opened to the atmosphere for 30 minutes.

3. Steps 1 and 2 were repeated three times. After completion of pressure-vacuum impregnation, the specimens were wiped free of surplus treatment solution prior to drying.

Untreated wood samples were also prepared by a similar procedure but using distilled water instead of salt solution.

To determine the amount of material transferred to the wood from the treatment solution, the specimens were individually weighed before and after impregnation. For both weighings, the samples were brought to moisture equilibrium at 80° F. and 30 percent relative humidity. When the added material is expressed as a percentage of the treated and conditioned sample weight, this figure is termed the "treatment level" of the samples. It should be noted that the "treatment level" merely expresses the gain in weight of the treated specimens without reference to the composition of the impregnated salt.

In calculating the treatment level of the treated specimens, it was assumed that about 1.5 percent of the untreated weight of the conditioned shavings was dissolved as water extractives by the treatment solution However, for the specimens prepared with shavings cut from the water-soaked blocks, no corrections were made for removal of water extractives during the second solution treatment.

Description of Experimental Equipment

The experimental equipment used to pyrolyze the wood shaving specimens in vacuum is shown in figures 2, 3, and 4. A vacuum is necessary to draw off the pyrolysis products from the hot pyrolysis zone before they react among themselves. The vacuum is also necessary in the room-temperature distillation which separates the products of pyrolysis.

Figure 2 shows a schematic diagram of the glassware used to collect and separate the pyrolysis products, while figure 3 shows the equipment in operation during a typical run.

Figure 4 is a simplified drawing of the temperature control system for the furnace. The furnace itself has three sections, each of which is heated by its own resistance coil. The controlled power from the recorder-controller (fig. 3, left) is applied to each coil according to the setting on a variac between the controller and the coil, figure 4. The variacs are shown at the bottom of the control panel in figure 3. By using a cutout switch, it was possible to set the controller output power manually while the temperature at each section of the furnace was read on the recorder. In this way, the variacs were adjusted so that, when the center section of the furnace was controlled at either 250° or 350° C., the variation in temperature along the horizontal furnace axis was about ±2° C. The furnace was mounted on a wheeled carriage which moved on rails so that it could be pulled up to, or moved away from, the combustion tube with ease.

Stopcocks M, K, and F (fig. 2) allowed various portions of the vacuum manifold to be evacuated or opened to the atmosphere through the stopcock E. Stopcock J was connected to a McLeod gage which showed the system pressure. Cold

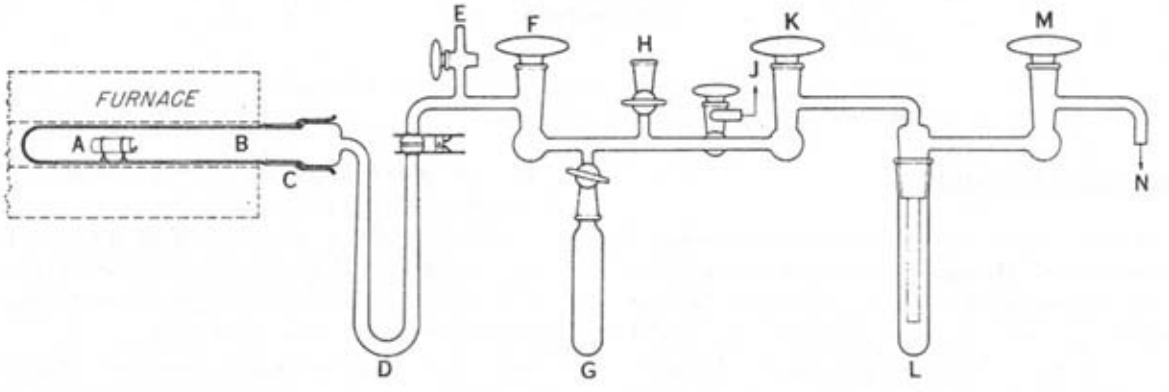

Figure 2.--Schematic drawing of equipment for collecting pyrolysis products of wood. The furnace covers the combustion tube as it would during the pyrolysis step of a typical run:

A. Wood shaving sample
B. Pyrolysis tube
C. Connection between tar trap and combustion tube sealed with O-ring
D. Tar trap
E. Vent to atmosphere
F. Stopcock
G. Water trap
H. Connection for obtaining volatile samples
J. Outlet to McLeod pressure gage
K. Stopcock
L. Protective cold trap for vacuum pump
M. Stopcock
N. Outlet to vacuum pump

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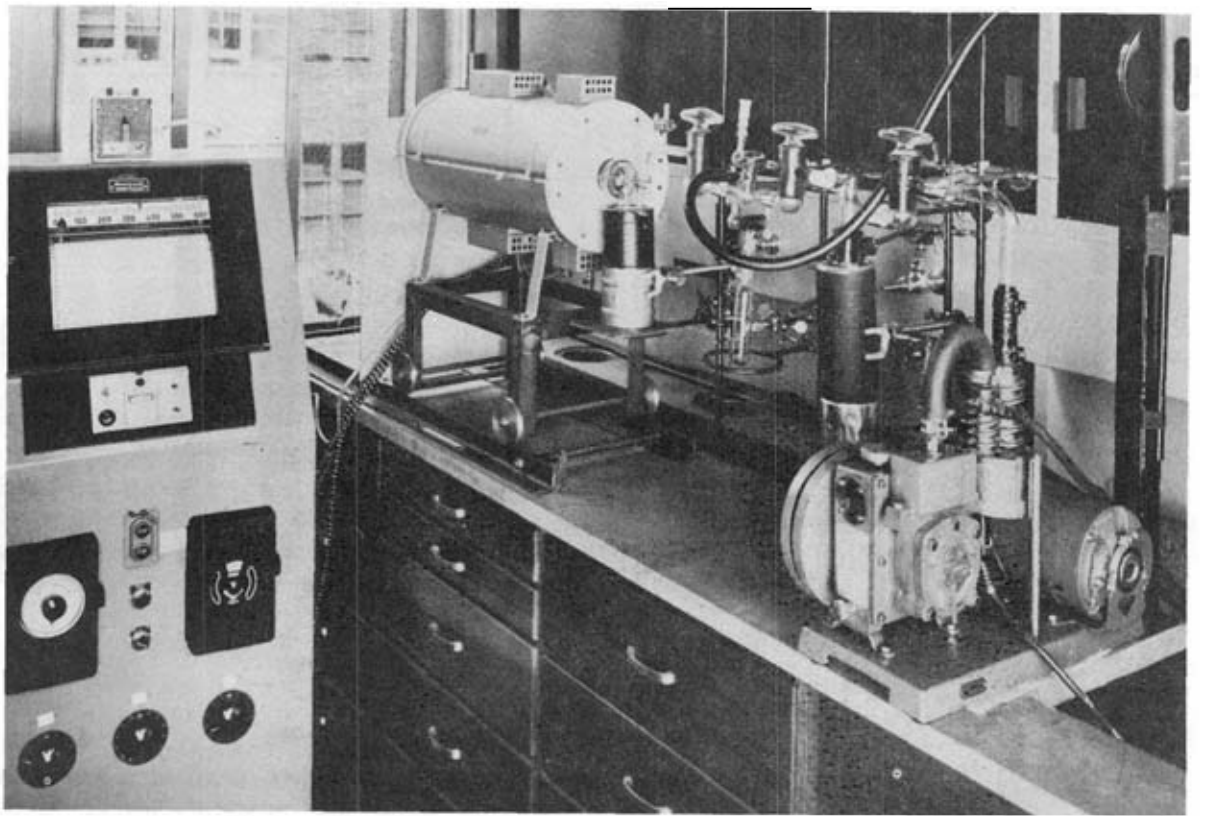

Figure 3.--Controller, furnace (center), and vacuum cold trap equipment used for collecting the pyrolysis products of wood. The furnace is in position to cover and heat the combustion tube as in the pyrolysis step of a typical run.

M 125 471

trap L was kept at -196° C. with liquid nitrogen at all times when the vacuum pump, connected at N (and shown in the right foreground in figure 3), was running. This was done to protect the pump oil from contamination. H was aport through which volatile samples could be removed from the system, although it was not used during any of the work described in this report.

The trap D, called the "tar trap," was sealed to the combustion tube B with a rubber O-ring at C. The trap G is known as the "water trap." Traps G and D, which were used to collect certain products of the pyrolysis carried on in the combustion tube B are shown in detail in figure 5.

Run Procedure

In the procedure for pyrolysis of the wood specimen and subsequent vacuum distillation of the pyrolysis products, first the furnace was moved to its remote position so the combustion tube B (fig. 2) was uncovered and at room temperature. Stopcock H was kept closed as no gas samples were withdrawn. Then:

1. The thin wood shaving specimen was placed on a wire holder in the combustion tube and the tar trap D was used to connect the combustion tube to the vacuum manifold. The shaving was positioned in the tube at A so that it would be in the center (control) section of the furnace. The furnace control system was set at either 250° or 350° C.

2. With the stopcock E closed but with stopcocks M, K, and F open, the system pressure was reduced by a mechanical vacuum pump, connected at N, to a point where it was less than 10 microns (less than 0.010 mm. of mercury).

3. A Dewar flask containing liquid nitrogen (-196° C.) was placed around the tar trap D. The furnace was then drawn over the combustion tube long enough to assure complete pyrolysis of the specimen (usually 2 hours was allowed). During this pyrolysis, the system pressure was kept at about 10 microns so that the pyrolysis products were quickly withdrawn from the hot

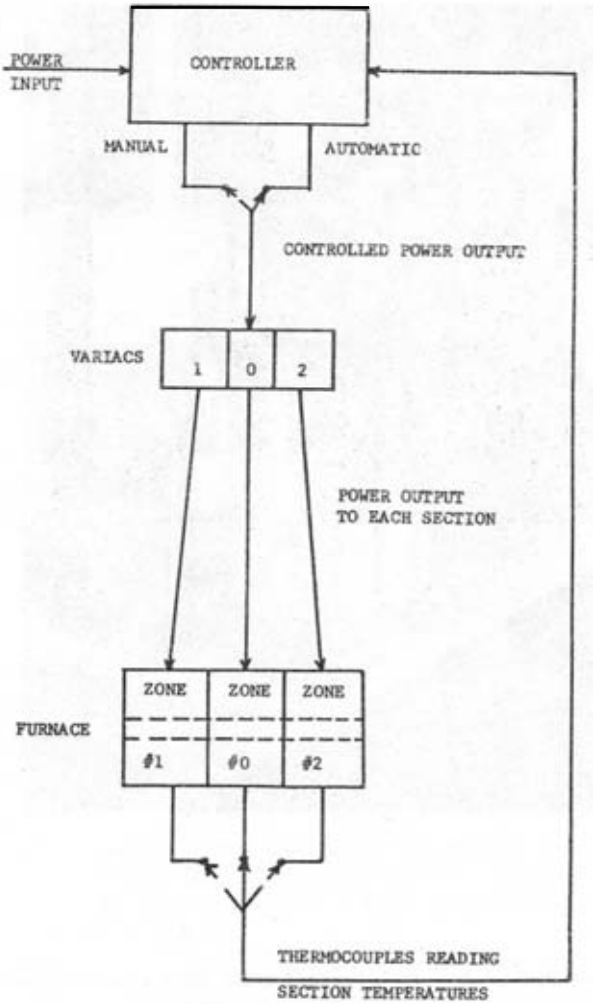

Figure 4.--Simplified drawing of furnace temperature control system. M 125 474

furnace and cooled in the tar trap D.

4. The stopcocks K and J were then closed. This sealed off part of the manifold including the tar trap, water trap, and combustion tube containing the charred sample. Stopcock J must be closed because the rubber tubing used to connect the McLeod gage to the vacuum manifold was permeable to carbon dioxide from the atmosphere.

5. Next, the Dewar flask containing liquid nitrogen was lowered from around the "tar trap" D and raised to cover the "water trap" G. The tar trap was allowed to came to room temperature. Under these conditions, all the pyrolysis products whose vapor pressure is greater than 10 microns at room temperature vaporize in the tar trap and are condensed in the water trap. Thus, all of the relatively low

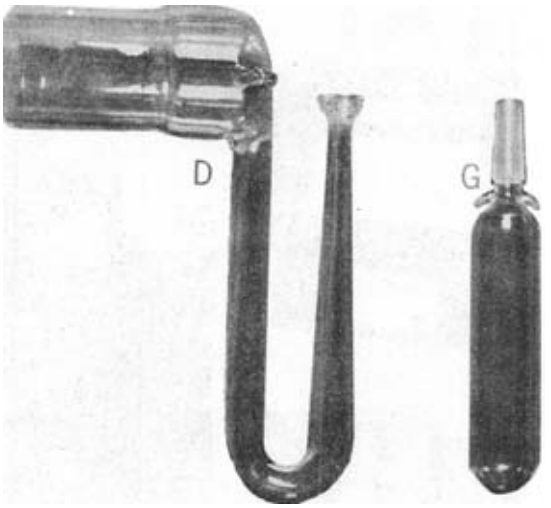

Figure 5.--Traps used to collect the tar and water fractions:

D. Tar trap
G. Water trap M 125 472

vapor-pressure products (tar) were left in the tar trap, while the relatively higher vapor-pressure components were distilled to the water trap. Usually about 1/2 hour was allowed for this vacuum distillation step.

6. The Dewar flask containing the liquid nitrogen was then removed from the water trap G and, simultaneously, the stopcock E was opened to the atmosphere. The water trap was allowed to come to room temperature in order that carbon dioxide might vaporize. About 1/2 hour was allowed for the water trap to come to room temperature equilibrium

Using this procedure the products of the vacuum pyrolysis of wood were separated into four fractions: first, the char fraction which remains in the combustion tube; second, the relatively high-boiling residue (termed "tar") left in the tar trap; third, the relatively low-boiling products (mostly water) left in the water trap; and fourth, the gases which have not been condensed in any of the traps.

In general. three replications were performed for each concentration of each salt at both temperatures of 250° and 350° C. However, the work was simplified because the first eight of the listed salts had been run previously at three concentrations using a pyrolysis temperature of 350°C. (1).

Method of Calculation of Pyrolysis Products

When the above procedure is used to pyrolyze treated wood and collect the pyrolysis products, the material contained in each fraction can be considered as coming from two distinct sources: the wood itself and the treatment salt contained in the specimen. The methods of calculation involve first determining the amount of each fraction based on the treated sample weight, then deducting the portion of each fraction that is due to the treatment salt, so that results can be expressed on a salt-free wood basis. The salt-free wood basis facilitates comparison of the effect of the various treatment chemicals.

To begin, the weight of each fraction from a sample of treated wood was determined by direct weighing. The char fraction was obtained by weighing the wood specimen before and after a run. Tar and water fractions were obtained by weighing the appropriate traps before and after the pyrolysis procedure described above. Using the weights of the fractions thus obtained, the results of each pyrolysis were expressed as a percentage of the treated and conditioned but unpyrolyzed specimen weight.

To obtain the portion of each fraction contributed by the treatment salt, inert alundum disks were soaked in saturated solutions of the various chemicals and pyrolyzed according to the above procedure. The disks were conditioned at 80° F. and 30 percent relative humidity and weighed before and after soaking so that the weight of absorbed chemical could be determined. From the weight of treatment salt in each fraction, along with the previously calculated "treatment level" of the samples, it was possible to determine the amount of chemical in each fraction. The weight of material from the treatment salt was then deducted from the total weight of each fraction to give the weight of that fraction due to wood alone (on a salt-free wood basis).

In these methods of calculation two important assumptions are involved. The first is that the inert alundum disks take up material of the same composition from the saturated salt solutions as does wood from the treatment solutions. This is probably a pretty good assumption. A second assumption is that the pyrolysis of treatment chemical to endproducts is identical, whether the chemical is absorbed on an alundum disk or on wood. In some cases, this last assumption results in negative values being obtained for the weights of some of the fractions obtained from salt-treated wood.

RESULTS

The results of pyrolyzing wood shaving samples according to the previously described procedure are given in tables 1 and 2. The data found in these tables are the arithmetic mean of three determinations for each treatment level of each salt. The results are expressed on a salt-free wood basis using the data given in table 3 for the pyrolysis products from the inorganic salts. Data for sodium tetraborate, calcium chloride, diammonium phosphate, ammonium chloride, sodium chloride, potassium bromide, trisodium phosphate, and potassium carbonate pyrolyzed at 350° C. are taken from reference 1.

DISCUSSION

Char Fraction

At 350° C.--Considering the effect of the inorganic salts on the char fraction (nonvolatile residue) is equivalent to examining the effect of the salts on the total volatilization of wood. The results in table 1 indicate that, at a pyrolysis temperature of 350° C., all of the salts tended to increase the yield of char (decrease the amount of volatilization) in comparison to untreated wood. Some chemicals, however, did this to a greater extent than others. Notable are calcium chloride, ammonium polyphosphate, zinc chloride, ammonium sulfate, boric acid, ammonium sulfamate, and phosphoric acid; for these chemicals the yield of char was greater than 50 percent of the pyrolysis products at 350" C. This compares to a char yield of about 20 percent €or untreated wood. The two salts that are usually considered to be the least fire retardant when applied to wood, sodium chloride and potassium bromide, gave the lowest yield of char among the chemicals used, except for ammonium chloride,

The effect of the concentration of chemical in the wood shaving is also interesting in relation to the yield of char in the pyrolysis products, In most cases, decreasing the amount of chemical present in proportion to wood tended to decrease the amount of char formed toward the amount associated with untreated wood. Again, the salts

Table 1.--Major products of 350° C. pyrolysis of ponderosa pine shavings treated with inorganic salts

Treatment			Products				
Salt	Treatment solution composition	Treatment level	Char	Tar	Water	Gas	Tars / total volatiles
	Percent	Percent	Percent	Percent	Percent	Percent	Percent
Untreated wood	--	--	19.83	54.90	20.87	4.41	68.48
Sodium tetraborate ($Na_2B_4O_7$)	15	24.12	43.06	14.90	31.92	10.11	26.17
	5	4.28	48.39	11.75	30.42	9.43	22.77
	1	(1)	44.13	20.39	29.33	6.15	36.50
Calcium chloride ($CaCl_2$)	15	54.75	56.52	14.35	3.57	25.55	33.00
	5	23.55	46.03	22.23	20.38	11.36	41.19
	1	4.21	28.77	38.68	23.60	8.95	54.30
Di-ammonium phosphate [$(NH_4)_2HPO_4$]	15	24.13	45.14	14.30	37.53	3.02	26.07
	5	6.69	45.49	16.76	32.01	5.73	30.75
	1	0.51	33.85	35.21	25.07	5.87	53.23
Ammonium chloride (NH_4Cl)	15	26.31	29.84	35.16	27.00	8.00	50.11
	5	7.95	29.78	33.83	24.43	11.95	48.18
	1	4.23	27.33	43.17	23.63	5.87	59.41
Sodium chloride (NaCl)	15	27.79	26.20	35.21	24.53	14.06	47.71
	5	10.34	25.91	35.69	25.18	13.21	48.17
	1	4.55	26.77	34.94	29.99	8.31	47.71
Potassium bromide (KBr)	15	32.85	29.12	27.84	32.09	10.94	39.28
	5	17.06	28.10	29.72	31.97	10.21	41.34
	1	2.99	27.26	30.17	30.06	12.51	41.48
Tri-sodium phosphate (Na_3PO_4)	15	28.78	42.89	14.92	24.49	17.70	26.13
	5	9.41	40.24	15.82	30.72	13.22	26.47
	1	(1)	36.55	21.20	31.41	10.85	33.41
Potassium carbonate (K_2CO_3)	15	30.49	43.46	5.59	32.07	18.87	9.89
	5	5.54	44.43	9.51	31.82	14.23	17.11
	1	1.03	41.13	13.54	30.32	14.99	23.00
Ammonium polyphosphate	15	19.27	51.02	10.82	39.89	-1.73	22.09
	5	5.00	43.79	18.98	34.64	2.58	33.77
	1	1.11	37.74	26.83	34.22	1.20	43.09
Zinc chloride ($ZnCl_2$)	15	33.20	72.76	-7.83	32.83	2.24	--
	5	12.18	60.89	-4.50	35.87	7.74	--
	1	1.05	36.36	31.70	25.98	5.96	49.81
Ammonium sulfate [$(NH_4)_2SO_4$]	15	23.35	53.33	-7.82	48.06	6.43	--
	5	8.20	49.08	7.30	33.65	9.97	14.34
	1	(1)	35.34	26.88	30.47	7.31	41.57
Boric acid (H_3BO_3)	15	28.61	50.04	5.86	32.62	11.48	11.73
	5	3.90	46.20	10.74	33.89	9.17	19.96
	1	(1)	28.13	40.16	25.73	5.98	55.88
Ammonium sulfamate ($NH_4NH_2SO_3$)	15	22.08	57.67	-19.62	56.59	5.36	--
	5	6.27	49.85	2.56	33.41	14.18	5.10
	1	(1)	38.41	20.26	30.76	10.57	32.89
Phosphoric acid (H_3PO_4)	15	24.58	54.70	-0.21	36.43	9.08	--
	5	6.80	54.08	2.51	37.27	6.14	5.47
	1	(1)	39.06	20.57	33.31	7.06	33.75

[1] Cannot be determined from gain in weight data.

Table 2.--Major products of 250° C. pyrolysis of ponderosa pine shavings treated with inorganic salts

Treatment			Products				
Salt	Treatment solution composition	Treatment level	Char	Tar	Water	Gas	Tars / total volatiles
	Percent	Percent	Percent	Percent	Percent	Percent	Percent
Untreated wood	--	--	90.76	1.96	5.87	1.41	21.21
Sodium tetraborate ($Na_2B_4O_7$)	15	23.63	93.95	0.62	4.90	0.53	10.25
	5	4.00	94.69	0.49	4.44	0.38	9.23
	1	(1)	94.70	2.07	5.32	-2.09	39.06
Calcium chloride ($CaCl_2$)	15	61.44	94.32	1.04	-8.54	13.18	18.31
	5	23.05	96.90	1.59	0.90	0.61	51.29
	1	5.96	95.00	4.03	3.89	-2.92	80.60
Di-ammonium phosphate [$(NH_4)_2HPO_4$]	15	23.48	57.02	8.82	33.25	0.91	20.52
	5	6.18	68.68	7.20	21.97	2.15	23.00
	1	0.84	82.19	5.00	11.96	0.85	28.07
Ammonium chloride (NH_4Cl)	15	25.23	86.86	0.53	9.93	2.68	4.03
	5	6.99	86.61	0.90	11.36	1.13	6.72
	1	3.13	90.15	0.28	8.62	0.95	2.84
Sodium chloride (NaCl)	15	27.79	88.40	1.43	7.59	2.58	12.33
	5	9.76	88.63	2.66	7.48	1.23	23.39
	1	3.72	90.31	2.29	5.44	1.96	23.63
Potassium bromide (KBr)	15	34.52	90.42	2.13	5.11	2.34	22.23
	5	17.99	90.77	1.99	4.92	2.32	21.56
	1	2.07	91.35	2.47	5.03	1.15	28.55
Tri-sodium phosphate (Na_3PO_4)	15	28.28	93.55	1.09	-0.57	5.93	16.90
	5	8.98	85.84	1.21	9.59	3.36	8.55
	1	(1)	88.97	0.79	8.73	1.51	7.16
Potassium carbonate (K_2CO_3)	15	29.65	83.03	0.38	7.38	9.21	2.24
	5	3.86	88.96	1.73	8.33	0.98	15.67
	1	(1)	91.37	2.97	6.55	-0.89	34.41
Ammonium polyphosphate	15	16.59	89.19	2.06	9.91	-1.16	19.06
	5	4.36	92.25	1.25	6.44	0.06	16.13
	1	(1)	92.98	1.61	5.46	-0.05	22.93
Zinc chloride ($ZnCl_2$)	15	32.48	71.30	-0.76	26.48	2.98	--
	5	11.33	72.40	2.38	23.99	1.23	8.62
	1	0.40	81.50	3.87	15.00	-0.37	20.92
Di-ammonium sulfate [$(NH_4)_2SO_4$]	15	24.10	69.97	-17.82	43.89	3.96	--
	5	6.62	67.81	-1.42	27.23	6.38	--
	1	(1)	69.31	1.62	21.70	7.37	5.28
Boric acid (H_3BO_3)	15	19.43	90.22	-4.40	8.48	5.70	--
	5	3.87	90.65	-0.47	8.27	1.55	--
	1	(1)	87.84	3.12	8.32	0.72	25.66
Ammonium sulfamate ($NH_4NH_2SO_3$)	15	21.46	69.55	-21.68	50.74	1.39	--
	5	6.16	67.70	-2.28	27.81	6.77	--
	1	(1)	69.53	3.18	21.22	6.07	10.44
Phosphoric acid (H_3PO_4)	15	24.20	61.91	1.23	30.42	6.44	3.23
	5	6.35	63.37	1.79	30.24	4.60	4.89
	1	(1)	69.75	4.47	20.28	5.58	14.78

[1] Cannot be determined from gain in weight data.

Table 3.--Major products of pyrolysis of inorganic salts at 250° C. and 350° C.

Salt	At 250° C.				At 350° C.			
	Char	Tar	Water	Gas	Char	Tar	Water	Gas
	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
Sodium tetraborate ($Na_2B_4O_7$)	58.58	2.47	43.22	4.27	59.93	1.39	31.30	7.38
Calcium chloride ($CaCl_2$)	51.90	0.06	53.40	5.36	47.07	1.78	47.02	4.13
Di-ammonium phosphate [$(NH_4)_2HPO_4$]	77.92	2.77	14.42	4.89	62.31	3.08	22.46	12.15
Ammonium chloride (NH_4Cl)	-2.24	100.03	5.87	-3.66	0.00	100.49	0.74	-1.23
Sodium chloride (NaCl)	99.45	1.47	0.98	-1.89	100.00	0.00	0.00	0.00
Potassium bromide (KBr)	99.28	0.38	3.88	-3.54	100.00	0.00	0.00	0.00
Tri-sodium phosphate (Na_3PO_4)	67.61	2.27	32.19	-2.08	66.94	-0.08	24.60	8.54
Potassium carbonate (K_2CO_3)	82.36	0.38	16.46	0.80	74.30	0.38	13.56	11.76
Ammonium polyphosphate	53.35	0.55	33.96	12.14	63.14	3.86	23.35	9.65
Zinc chloride ($ZnCl_2$)	57.29	8.66	32.05	2.00	8.54	65.89	29.79	-4.22
Di-ammonium sulfate [$(NH_4)_2SO_4$]	1.03	67.76	9.19	22.02	6.01	75.30	9.35	9.34
Boric acid (H_3BO_3)	29.44	43.22	33.64	-6.30	27.09	39.82	39.82	-6.73
Ammonium sulfamate ($NH_4NH_2SO_3$)	2.71	83.23	0.06	14.00	0.01	87.67	0.18	12.14
Phosphoric acid (H_3PO_4)	54.97	2.41	33.76	8.84	44.41	10.41	34.65	10.53

that are usually considered to be fire retardant when applied to wood showed the largest degree of sensitivity to concentration of the treating chemical, as measured by the yield of char. These include ammonium polyphosphate, zinc chloride, ammonium sulfate, boric acid, ammonium sulfamate, and phosphoric acid. Calcium chloride also showed a large dependence on concentration for char yield, although it is not usually considered as a fire-retardant salt in the commercial sense.

Relatively small amounts of some salts were needed to increase the yield of char over untreated wood when the shaving samples were pyrolyzed at 350° C. Thus, a treatment level of as little as 1 percent or less of these salts produced a char yield of 35-40 percent as compared to 20 percent for untreated wood. Indeed, in some cases the yield of char was markedly increased by an amount of treatment salt too small to be measured from the gain in weight of the samples after treatment with the salt solution.

At 250° C.--When the wood shaving samples were pyrolyzed at 250° C. in vacuum, the effect of the inorganic salts on the char fraction was not nearly as clearcut as at 350° C. Some salts tended to increase the yield of char, among them sodium tetraborate, calcium chloride, trisodium phosphate (in high concentrations) and ammonium polyphosphate. However, the increase was not great, possibly because only about 10 percent of the wood was volatilized even for untreated samples. At 250° C. other chemicals had little effect on the char yield or possibly decreased it slightly. These chemicals include ammonium chloride, sodium chloride, potassium bromide, trisodium phosphate, boric acid, and potassium carbonate (at low concentrations).

Many of the chemicals that are usually considered to be fire retardant, however, actually lowered the yield of the char fraction at 250° C. as compared to untreated wood. In effect, these salts increased the volatilization of treated wood as compared to untreated wood when both were pyrolyzed at 250° C. Chemicals which tended to decrease the char yield (increase the volatilization) were diammonium phosphate, zinc chloride, diammonium sulfate, ammonium sulfamate, and phosphoric acid.

It is rather surprising that these salts tended to increase the volatilization of wood during the early stages of pyrolysis (at low temperatures). Two factors probably tend to cancel out the possible flammability of increased volatiles at low temperatures for the fire-retardant salts: (1) the pyrolysis temperature is below the ignition temperature of the volatiles, and (2) the volatiles are not very rich in flammable tars.

The effect of the concentration of treatment salt on the char yield was not as easy to determine for pyrolysis at 250° C. as it was at 350° C. For most of the chemicals whose char yield is within a few percent of the value associated with untreated wood, the effect of the treatment level was not great.

Of the five chemicals which decreased the proportion of char in the pyrolysis products at 250° C., diammonium phosphate, zinc chloride, and phosphoric acid exhibited the expected behavior: as the treatment level was reduced, the char yield moved toward the value determined for untreated wood, For diammonium sulfate and ammonium sulfamate the trend of concentration effects was not clear. As at 350° C., some of the salts produced marked effects on the char fraction of wood pyrolyzed at 250° C. eventhoughthe salts were used in very low concentrations. Notable in this respect were diammonium sulfate, ammonium sulfamate, and phosphoric acid.

Tar Fraction

At 350° C.--When the wood shaving samples were pyrolyzed at 350° C. all the chemicals tended to reduce the yield of tars. Since the char "burns" in place by glowing while the water fraction and "gas" fraction are not combustible, it can be seen that the flammability of wood is associated with the tar fraction. Most authors who have studied the thermal decomposition of wood and cellulose seem to agree that the flammability of the wood or cellulose is closely related to the formation of tar (6, 7, 8) and that the addition of chemicals to these materials inhibits tar formation (8, 9). At 350° C., the least fire-retardant chemicals, sodium chloride and potassium bromide, produced the highest tar yield, except for ammonium chloride. The effect of ammonium chloride, when compared to untreated wood, is difficult to interpret because this salt sublimes at 335° C. Thus it appears that many chemicals are effective fire retardants for wood through reduction of the

tar component of the volatile pyrolysis products of the wood.

The most effective chemicals in reducing the yield of tars at 350° C. were sodium tetraborate, diammonium phosphate (in high concentrations), trisodium phosphate, potassium carbonate, ammonium polyphosphate, zinc chloride, diammonium sulfate, boric acid, ammonium sulfamate (in high concentrations), and phosphoric acid (in high concentrations).

In some cases, negative values were reported for the tar fraction yield. This results from the assumption made in calculating the effect of the chemical treatments. The assumption was that the treating chemical was distributed into the four pyrolysis fractions in the same proportion whether wood was present or not. Obviously the pyrolytic interaction between wood and chemical was not this straightforward because a higher proportion of chemical was deposited in the tar trap when wood was not "mixed" with the chemical, resulting in negative tar yields. Negative tar yields could also be aggravated if the material collected in the tar trap were extremely hygroscopic.

The effect of chemical treatment level on tar yield at a pyrolysis temperature of 350° C. is easy to understand: as the treatment level is reduced, the tar yield is increased. This is reasonable because untreated wood has a tar yield of about 55 percent at 350° C. and a reduction in treatment level causes the tar yield of treated wood to increase toward the value associated with untreated wood, Sodium tetraborate and ammonium chloride, however, seem to show an optimum treatment level for tar yield suppression with the lowest tar production being at the intermediate treatment level. More work is needed to confirm this point. Also, very lowtreatment levels produced marked reduction in the yield of tars. Thus, an amount of chemical too small to measure from the gain in weight of the shaving specimens reduced the tar yield from about 55 percent of the pyrolysis products for untreated wood to about 20 percent in some treated wood.

At 250° C.--The variation in the proportion of tar in the pyrolysis products of wood pyrolyzed at 250° C. was not as easy to interpret as the variation at 350°C. Sodium chloride and potassium bromide had little effect on the tar fraction at 250° C. Other chemicals reducing the proportion of tar at this temperature were sodium tetraborate, calcium chloride (in high concentrations), ammonium chloride, trisodium phosphate, potassium carbonate (in high concentrations), zinc chloride, diammonium sulfate, boric acid, ammonium sulfamate, and phosphoric acid (in high concentrations). As at 350° C., the negative values observed for the tar fraction-yield of some chemicals at 250° C. may be explained either by the interaction of chemical and wood or by the fact that the material measured in the tar fraction obtained from pyrolysis of the chemical alone was quite hygroscopic.

Anomalous behavior was noted for diammonium phosphate: this salt tended to increase the tar fraction yield at 250° C. as compared to untreated wood. Since diammonium phosphate is usually considered to be a good fire retardant when applied to wood, it must be assumed that either the total amount of the tar was diluted with the water vapor present in the pyrolysis products or that 250° C. was well below the ignition point of the tars.

The effect of the concentration of treating chemical on the tar yield at 250° C. was difficult to estimate in many cases. For the most part, the amount of the tar fraction was so low that only minor differences appear as the treatment level was varied. Thus for calcium chloride, ammonium chloride, sodium chloride, potassium bromide, trisodium phosphate, potassium carbonate, and ammonium polyphosphate the trend of tar fraction yield as it is influenced by concentration is not clear. For potassium carbonate, zinc chloride, calcium chloride, boric acid, and phosphoric acid, however, small amounts of chemical might actually increase the tar yield, but further work is needed to clarify this point. For sodium tetraborate, zinc chloride, and diammonium sulfate, a reduction in the treatment level of salt appears to make the tar fraction yield approach the value associated with untreated wood.

Water Fraction

At 350° C.--Most of the chemical treatments for wood shavings pyrolyzed at 350° C. tended to increase the yield of the water fraction in comparison to untreated wood, The only salt that did not increase the water fraction yield was calcium chloride, especially when used in relatively high concentrations. The increase in the water fraction yield over untreated wood was

not as great at 350° C., however, as the decrease in the tar fraction yield at this pyrolysis temperature.

Many of the chemicals, including sodium tetraborate, diammonium phosphate, ammonium chloride, sodium chloride, potassium bromide, trisodium phosphate, potassium carbonate, zinc chloride, and boric acid increased the water fraction yield from about 21 percent for untreated wood to about 25–35 percent for treated wood. Only ammonium polyphosphate, diammonium sulfate, ammonium sulfamate, and phosphoric acid tended to increase the water fraction yield to a marked degree, the greatest increase being found for diammonium sulfate and ammonium sulfamate, Ranking the chemicals according to the water fraction yield did not appear to have any relationship to the ranking of the chemicals as fire retardants for wood.

In most cases, too, concentration effects were similar to those observed for the char fraction; as the treatment level was reduced, the water fraction yield tended to approach the yield obtained for untreated wood. Exceptions to this generalization are sodium chloride, trisodium phosphate, zinc chloride, boric acid, and phosphoric acid, Sodium chloride and trisodium phosphate seemed to have an inverse water yield to treatment level relationship: as the treatment level was reduced, the water fraction yield increased, For zinc chloride, boric acid and phosphoric acid, an intermediate treatment level rather than a high or low level appeared to give the greatest water fraction yield although further work should be done to verify this point.

Rather low concentrations of treatment chemical had a measurable effect on the water fraction yield, in some cases the treatment level being too small to measure from the gain in weight of the wood specimens after impregnation. Chemicals having an effect on the water fraction at low concentration were sodium tetraborate, ammonium polyphosphate, diammonium sulfate, boric acid, ammonium sulfamate, and phosphoric acid.

At 250° C.--All the chemicals except calcium chloride, sodium tetraborate, and potassium bromide tended to increase the water fraction yield for wood pyrolyzed at 250° C. The largest increases in water fraction were noted for diammonium phosphate, zinc chloride, diammonium sulfate, ammonium sulfamate, and phosphoric acid. Intermediate increases were noted for ammonium chloride, sodium chloride, trisodium phosphate (at low concentrations), potassium carbonate, ammonium polyphosphate, and boric acid. If sodium tetraborate, ammonium polyphosphate, and boric acid are excepted, it seems that all the chemicals usually considered to be good fire retardants increased the yield of water in the pyrolysis products of wood heated at 250° C.

The effect of chemical concentration in relation to the variation of the water yield at 250° C. differed from chemical to chemical. For chemicals such as sodium tetraborate, ammonium chloride, sodium chloride, potassium bromide, potassium carbonate, and boric acid, whose yield of water vapor at 250° C. was close to that of untreated wood, the variation with chemical concentration was not great. On the other hand, those chemicals that increase the water yield to 25 percent or more behaved typically: as the treatment level was reduced the water yield decreased toward the value associated with untreated wood.

Noncondensable Gas Fraction

At 350° C.--When the wood shaving samples were pyrolyzed at 350° C. the effect of all the chemicals except ammonium polyphosphate was to increase the yield of "noncondensable" gases in the pyrolysis products. The noncondensable gas fraction (or simply the gas fraction) probably contains a large measure of carbon dioxide and is the least precisely measured of the four pyrolysis fractions reported herein. Accurate measurement was difficult because the gas fraction was determined as the difference between the original (unpyrolyzed) sample weight and the sum of the weights of the other three fractions. Nevertheless, certain observations can be made from the gas fraction data.

The chemicals which caused the greatest increase in the gas fraction yield were calcium chloride, trisodium phosphate, and potassium carbonate. Also showing sizable increases in the gas fraction were sodium chloride, potassium bromide, and ammonium sulfamate. Moderate increases were shown for the remainder of the chemicals used.

For sodium tetraborate, calcium chloride,

trisodium phosphate, sodium chloride, and boric acid, the effect of concentration was similar to that observed at 350° C. for the char, tar, and water fractions: as the concentration of treatment salt was reduced, the value of the gas fraction yield approached the value associated with untreated wood, For potassium bromide, a low concentration tended to increase the gas fraction yield to a high value: for potassium carbonate, zinc chloride, diammonium sulfate, ammonium sulfamate, phosphoric acid, ammonium polyphosphate and ammonium chloride, the trend of concentration effects on the gas fraction yield are not clear. For diammonium phosphate, it appears that the concentration of treatment salt had an inverse effect because the gas fraction yield increased as the proportion of salt to wood was reduced. More work is needed on diammonium phosphate-treated wood to confirm this point.

At 250° C.--Gas fraction data for wood shavings pyrolyzed at 250° C. were again somewhat more difficult to interpret than similar data at 350° C. Even for untreated wood, the gas fraction represents only about 1.5 percent of the unpyrolyzed sample weight. At 250° C., it appears that sodium tetraborate, ammonium polyphosphate, and perhaps diammonium phosphate decreased the gas fraction yield while calcium chloride, trisodium phosphate, potassium carbonate, diammonium sulfate, boric acid, ammonium sulfamate, and phosphoric acid increased this quantity. The largest increases were noted for calcium chloride, potassium carbonate, diammonium sulfate, and phosphoric acid. The remaining salts had little effect on the gas fraction when the pyrolysis temperature was 250° C.

In many cases, because of the small quantities involved, concentration effects were difficult to determine at 250° C. The most interesting variations in the gas fraction with treatment level were noted for potassium carbonate, zinc chloride, diammonium sulfate, boric acid, and ammonium sulfamate.

Considering potassium carbonate, zinc chloride, and boric acid, it appears that high concentrations of chemical increased the gas fraction yield above the value observed for untreated wood; but as the proportion of chemical to wood was reduced, the gas fraction of the pyrolysis products was reduced. At low treatment levels of these three chemicals, a smaller gas fraction was observed than for untreated wood at 250° C.

For diammonium sulfate and ammonium sulfamate, it appears that high salt treatment levels gave the lowest gas fraction yield values, but these values are still higher than those for untreated wood. However, when the proportion of chemical to wood was decreased, the gas fraction values increased to quantities well above the value associated with untreated wood. There is no ready explanation for the behavior of these last two salts.

Tars as a Fraction of Total Volatiles

At 350° C.--This quantity reflects the composition of the volatiles in that it measures the portion of the total volatiles that consist of flammable tars. All of the chemicals at 350° C. tended to reduce the tar portion of the volatiles, although some accomplished a greater reduction than others. For those cases in which the tar fraction had negative values (as discussed earlier), it was not possible to calculate the tar component of the volatiles in a meaningful way but the quantity was assumed to be very low. The smallest reduction in the tar component of the volatiles was observed for the salts that are usually considered to be least fire retardant when applied to wood: sodium chloride and potassium bromide. Ammonium chloride was also of limited value in reducing the tar component of the volatiles, but this chemical sublimes at 335° C. under atmospheric pressure so one might expect that its effectiveness would be reduced. The chemicals that reduced tar in the volatiles the most at 350° C. were potassium carbonate, zinc chloride, diammonium sulfate, ammonium sulfamate, and phosphoric acid.

Concentration effects were relatively pronounced for the tar component of the volatile products. As the treatment level of chemical was reduced, the fraction of tars in the volatile products of wood tended to increase (i.e., move toward the value associated with untreated wood). Again, the only exceptions were sodium tetraborate and sodium chloride. For sodium tetraborate, an intermediate treatment level gave the lowest value of the tar portion of the volatiles.

Variation of the tar component of the volatiles with treatment level is probably not significant for sodium chloride.

At 250° C.--With the exception of calcium chloride and diammonium phosphate, all other treating chemicals tended to reduce the tar fraction of the volatiles at 250° C. Calcium chloride actually increased the tar portion of the volatiles to a sizable degree. The data for diammonium phosphate are interesting because this salt is usually regarded as a very effective fire-retardant treatment for wood. The tar fraction data (as discussed previously) showed that at 250° C. diammonium phosphate actually increased the tar fraction yield as compared to untreated wood. However, when the data were recalculated to show the tars as a fraction of the total volatiles, it was evident that the volatiles from diammonium phosphate-treated wood contain about the same proportion of tars as do those from untreated wood. Thus one effect of the increased volatilization of diammonium phosphate-treated wood was to dilute the increased tars,

Chemicals that were effective in reducing the tar portion of the volatiles were potassium carbonate (in high concentrations), zinc chloride, diammonium sulfate, boric acid, ammonium sulfamate, and phosphoric acid.

Examination of the data calculated for the tars as a fraction of the total volatiles shows that, with the exception of ammonium chloride and trisodium phosphate, the tar portion of the volatiles increased as the proportion of chemical to wood (treatment level) was reduced. In some cases, notably sodium chloride, potassium, bromide, potassium carbonate, and boric acid, a very small quantity of chemical added to the wood tends to increase the tar content of the volatiles above the value associated with untreated wood.

CONCLUSIONS

1. When untreated wood and wood treated with inorganic chemicals are pyrolyzed in vacuum at 350° C., the chemicals increase the yield of char, water, and "noncondensable" gases and decrease the yield of flammable tars. Chemicals that are usually considered to be fire-retardant treatments for wood accomplish these changes to a greater degree than non-fire-retardant chemicals.

2. As the proportion of chemical to wood is reduced at 350° C., the distribution of pyrolysis products tends to change toward the distribution associated with untreated wood.

3. Small concentrations of chemical (on the order of 1 percent or less) markedly alter the process of pyrolysis of wood at 350° C. so that the pyrolysis products contain less of the flammable components.

4. When wood that has been treated with inorganic chemicals is pyrolyzed at 250° C., most chemicals decrease the yield of flammable tars and char and increase the yield of water vapor as compared to untreated wood. An exception is diammonium phosphate (a good fire-retardant treatment for wood). This salt actually increases the flammable tar fraction of the pyrolysis products of wood at 250° C. The effectiveness of diammonium phosphate as a fire retardant for wood possibly may be explained by observing that (a) 250° C. is probably below the ignition temperature of the tars and (b) the tars are diluted by a sizable quantity of water vapor.

5. When wood shavings were pyrolyzed at 250° C., the effect of varying the proportion of chemical to wood (varying the treatment level) was not nearly as clearcut as when wood was pyrolyzed at 350° C.

6. Very small concentrations of chemical do not lower the yield of flammable pyrolysis products at 250° C. as they do at 350° C.

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