

THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS
OF WOOD AND OF WOOD TREATED WITH INORGANIC SALTS
DURING PYROLYSIS¹

A Progress Report

by Frederick L. Browne, chemist
and Walter K. Tang, chemical engineer

Forest Products Laboratory, Forest Service, U.S. Department of Agriculture²

Burning of wood is preceded by pyrolysis to form gases and vapors and a solid residue of charcoal; some of the gases and vapors can burn in flames when mixed with air, and the charcoal can burn in air by glowing without flame. Empirically it has long been known that flaming combustion can be retarded by impregnating wood with suitable materials, such as certain inorganic salts. Although a number of theories of flame-retardant action have been proposed (6),³ the mechanism of wood's combustion and the effect of chemical treatment on it remain uncertain. It appears most likely that the best flame retardants act by altering favorably the preliminary step of wood pyrolysis.

The present research was undertaken to study the mechanism of wood pyrolysis and the effect of chemicals on it by the methods of thermogravimetric and of differential thermal analysis. Results so far indicate that the methods are promising but that much further work will be needed before their significance can be fully established.

In dynamic thermogravimetric analysis, wood samples were weighed and the weight recorded continuously and automatically as a function of the temperature attained by the sample while it was being heated in a stream of nitrogen with the temperature rising steadily at a linear rate. Such graphs disclosed the threshold temperature for active pyrolysis, the range of temperature within which most of the pyrolysis occurred, and the yield of char (or extent of volatilization) when pyrolysis was practically completed.

In static thermogravimetric analysis, the sample weight was recorded as a function of time at constant temperature at each of a series of temperatures from about the threshold for active pyrolysis to a temperature at which pyrolysis became inconveniently

¹The work here reported was financed in part by a grant from the National Science Foundation and in cooperation with the Koppers Company, Pittsburgh, Pa.

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

³Numbers in parentheses refer to literature cited at the end of this report.

rapid. Such graphs served as a basis for calculating reaction rate constants and activation energies for an early stage of pyrolysis. In differential thermal analysis the difference in temperature between wood or treated wood and a reference material was recorded continuously as a function of the sample temperature while both sample and reference material were being heated with the furnace temperature rising steadily at a linear rate. Such graphs revealed the occurrence of endothermic or exothermic reactions at the various levels of temperature and a rough estimate of the relative extent of evolution or absorption of heat.

Apparatus

A thermogravimetric balance made by the American Instrument Company was used (2). The sample to be pyrolyzed was suspended from a calibrated spring, all 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 reaction chamber, could be quickly encompassed by an electric furnace that was either preheated to a desired constant temperature or else was programmed to rise in temperature at a predetermined linear rate. Movement of the balance spring was picked up by a transducer and demodulator and the impulse transmitted to the y-axis of an x-y recorder. The x-axis could be set to record the temperature attained by the sample as measured by a thermocouple located about 5 millimeters below the sample in the reaction chamber; or, by the flick of a switch, the x-axis could be set to record time instead of temperature. When the x-axis was set to record temperature, there was provision also for a discontinuous record of time in the form of pips scribed in the curve at intervals of 1, 5, or 20 minutes.

By a simple modification, the thermogravimetric balance was adapted for differential thermal analysis. A switch was provided to disconnect the impulse from the transducer and demodulator of the weighing system and to substitute for it the input from a differential thermocouple with one junction in the sample and the other junction in a reference material. Sample and reference material were contained each in its own glass tube with stopper carrying a thermocouple well and inlet and outlet tubes through which either vacuum or a stream of nitrogen could be applied. The nitrogen entered the tube through a glass sleeve at a point slightly above the level of the sample or reference material and discharged, together with any volatile products, from the top of the tube. Sample tube and reference tube slipped into wells drilled in a metal cylinder, which in turn fitted into the cylindrical chamber of the electric furnace of the thermogravimetric balance, now become a differential thermal balance.

Preparation of Samples

The size and shape of wood samples may affect the rate of pyrolysis and the yield of products because the diffusion of heat into the interior of the sample and the escape of volatile products from the interior enter into the overall process. Within thick samples the temperature at any instant varies more than in thin samples; the yield of char is greater for thick than for thin samples because volatile products formed at first undergo secondary pyrolysis, yielding tar coke to add to the wood charcoal if the volatile

products cannot escape fast enough. When delayed escape of volatile products is significant, pyrolysis in vacuum proceeds faster and yields less char than pyrolysis at atmospheric pressure.

Since the present purpose was to study as nearly the initial stage in pyrolysis as possible, it was necessary to minimize the effects of diffusion of heat and volatile products. Use of veneer (shavings) 0.16 millimeter thick, cut from green or re-soaked wood with a tool designed especially for the purpose, accomplished the objective remarkably well. This is demonstrated in figure 1, in which the curve for dynamic thermogravimetric analysis in nitrogen at atmospheric pressure nearly coincided with a curve for pyrolysis in a vacuum. Similar experiments with samples in the form of dowels about 1 centimeter in diameter showed that in nitrogen the pyrolysis proceeded much less rapidly and the yield of char at the end of active pyrolysis was much greater than in vacuum.

Ponderosa pine sapwood samples 0.16 by 46 by 47 mm. have been used for most of the tests so far. Samples were conditioned at 27° C. and 30 percent relative humidity. Those to be impregnated with a salt were immersed in aqueous solution of suitable concentration to provide the desired degree of treatment, evacuated for 30 minutes, left immersed at atmospheric pressure for approximately 2 hours, removed, wiped to remove excess solution, dried, and conditioned at 27° C. and 30 percent relative humidity. The quantity of salt retained by the wood was calculated as the difference between the equilibrium weights before and after treatment corrected for a loss of approximately 1.5 percent of water-soluble components of the wood to the treating solution, as determined by similarly impregnating matched wood specimens with distilled water and reconditioning them.

For differential thermal analysis, ponderosa pine sapwood was ground to particles less than 0.25 mm. in diameter. Samples to be treated were placed on a glass filter, repeatedly washed with aqueous solution with the aid of suction, drained with suction for about 30 minutes, dried, and conditioned at 27° C. and 30 percent relative humidity.

Inorganic Salts Tested

Tests have been made so far with the inorganic salts listed in table I, together with the residual weight left at 200°, 250°, and 400° C., respectively, when a sample of the salt was subjected to dynamic thermogravimetric analysis under the conditions described farther on for examination of wood treated with the salt.

Data in handbooks state that those of the salts that contain water of crystallization lose it before the temperature reaches 200° C. The ammonium phosphates and ammonium chloride begin to decompose before they reach a melting point. Ammonium sulfamate melts at 132.9° C. and begins to decompose to ammonia and sulfamic acid at 160° C. Ammonium sulfamate and ammonium chloride are distinctly volatile and sublime completely at temperatures well below 400° C. Ammonium chloride changes from the α to the β form with a heat effect at 184° C. The four remaining salts do not melt, decompose, or sublime before reaching temperatures at which active pyrolysis of wood has been completed.

sapwood veneer 0.16 mm. thick. The lignin was sulfuric acid lignin from aspen in the form of fine powder. The α -cellulose was from southern yellow pine in the form of a thin felted mass. The differences in origin and form of the samples do not impair qualitative comparison of the three materials in view of the great differences in the course of their pyrolyses.

The loss in weight of 5 percent for cellulose and of 6 percent for wood and lignin recorded at 200° C. in figure 2 had actually been attained already at 100° C. and represented moisture in the samples initially. Further loss in weight attributable to pyrolysis began near 220° C. for both wood and lignin, but not until 275° C. for cellulose. On the other hand, pyrolysis of cellulose proceeded very rapidly as temperature rose still further, whereas the pyrolysis of lignin accelerated very slowly. Cellulose pyrolysis was essentially complete at 400° C. with a yield of char of only 15 percent, which decreased to 9 percent at 800° C. Lignin at 400° C. still was 70 percent unvaporized and, at 800° C., was 45 percent unvaporized.

The relatively sudden collapse of cellulose within a narrow range of temperature and the slower disintegration of lignin over a broad band of temperature perhaps are explicable from the nature of their macromolecules. Cellulose, as a repeating polymer of a single monomer of moderate size, may well follow a shorter and less involved path to complete pyrolysis than the more intricate macromolecule of lignin with its more varied constitution of aromatic nuclei connected by straight-chain links. The indication that the threshold temperature of pyrolysis is lower for lignin than for cellulose seems at first to conflict with much of the literature (6), which holds that the hemicellulose in wood pyrolyzes most readily, the cellulose less so, and the lignin least readily; but the apparent conflict is easily reconciled, because only a small fraction of the lignin has been lost at temperatures at which the cellulose is already completely pyrolyzed.

Figures 3 and 4 present similar thermogravimetric curves for ponderosa pine treated with all the salts listed in table 1 except monobasic ammonium phosphate, which is omitted from the figures because its performance was almost identical with that of dibasic ammonium phosphate. When the salts contained water of crystallization, the initial loss in weight before 200° C. was increased correspondingly. If the curves were adjusted to start from the anhydrous weight as 100 percent, the curves for wood treated with sodium borate and sodium phosphate would as nearly coincide with the curve for untreated wood up to 300° to 350° C. as the curve for treatment with sodium chloride actually does. On the other hand, the curves for the three ammonium salts and for potassium carbonate reveal distinctly faster pyrolysis than that of untreated wood in a region between approximately 200° and 300° C.

Beyond about 350° C. the weight of char from wood treated with any one of the salts exceeded the weight of char from untreated wood. The char from some but not all of the treated samples still contained the injected salt or products of its decomposition. To learn the yield of wood charcoal on completion of active pyrolysis of the treated samples, correction must be made for any inorganic residue in the char. Such residue at any temperature up to 400° C. was estimated by thermogravimetric analysis of each salt by itself. The procedure involves the assumption that the salt loses weight at the same rate and to the same extent in the presence as in the absence of actively pyrolyzing wood, an assumption that may require more careful examination at a later stage in the research.

Hunt, Truax, and Harrison (8), on the basis of laboratory tests by the fire-tube method, described the salts marked I in the last column of table 1 as "chemicals that have a considerable effect in retarding flame in light absorptions and a marked effect in heavy absorptions." They did not test ammonium sulfamate, but subsequent tests at the Forest Products Laboratory place it in group I. Salts of group II were described as "chemicals that have a very minor effect in retarding flame in light absorptions but a marked effect in heavier absorptions," salts of group III as "chemicals that have a moderate effect in retarding flame when present in wood in large quantities" and salts of group IV as "chemicals that have a noticeable but not important effect in retarding flame even when present in wood in large amounts."

Experimental Procedure

For thermogravimetric analysis, a sample of 0.16-mm. veneer weighing between 0.25 and 0.5 gram was suspended from the balance spring in a central position in the pyrolysis chamber. The y-axis of the recorder was so calibrated that the full weight of the sample just spanned 100 divisions of the graph paper and the x-axis was set to span the range in sample temperature to be studied. The system was evacuated and then flushed with nitrogen three times to remove air with its oxygen from the sample and the pyrolysis chamber.

For dynamic thermogravimetry the furnace, still unheated, was raised into position enclosing the pyrolysis chamber, heating was started at the programmed linear rate (usually 6° C. a minute), flow of nitrogen through the system was established at the desired rate (usually 2 liters a minute), and the recording mechanism was set in motion. The recorder scribed the decrease in sample weight in percent of its initial weight against the temperature attained by the sample and also indicated the lapse of time by pips scribed at 5-minute intervals.

For static thermogravimetry the furnace was brought to a constant temperature selected in advance and was then raised to enclose the pyrolysis chamber. The recorder was set in motion when the furnace reached its position with the x-axis of the recorder charting sample temperature together with 1-minute pips until the constant furnace temperature was nearly reached (usually in 13 to 15 minutes), after which the x-axis was switched to record time instead of temperature.

For differential thermal analysis the sample tube was packed with about 5 g. of ground wood and the reference tube was packed to an equal depth with aluminum oxide. Alternatively, for certain tests the sample tube contained chemically treated wood and the reference tube untreated but otherwise similar wood. With tubes in position, the furnace was set to rise in temperature at the rate of 12° C. a minute until it reached 600° C. The recorder charted the difference in temperature between sample and reference material against the temperature attained by the sample.

Results by Dynamic Thermogravimetry

Figure 2 records the portion of the dynamic thermogravimetric curves between 130° and 400° C. obtained for wood, lignin, and α -cellulose. The wood was ponderosa pine

From the yield of char as indicated by the curve in figure 3 or 4, corrected for the content of salt or its decomposition product, and from the content of dry wood easily calculable from the weight at 150° C., the extent of volatilization of the dry wood substance originally present in the sample was calculated for sample temperatures of 250° and 400° C. and is recorded in table 2, together with the temperature at which active pyrolysis began, the content of anhydrous salt in the sample before pyrolyzing, and the practical classification of the salt for flame retardance.

Untreated wood began to pyrolyze actively at 220° C., was volatilized at 250° C. to the extent of 4 percent only, but at 400° C. volatilization attained 76 percent. Wood treated with one of the ammonium salts began to pyrolyze at much lower temperatures, 150° or 180° C., was much more extensively volatilized than untreated wood at 250° C., but was much less extensively volatilized than untreated wood when active pyrolysis was essentially completed at 400° C. Treatment with potassium carbonate advanced the onset of wood pyrolysis slightly (to 210° C.), increased volatilization of wood at 250° C. significantly, but somewhat less than the ammonium salts, but did not diminish the volatilization of wood at 400° C. so much as the ammonium salts did. The three sodium salts failed to alter the temperature at which wood pyrolysis began and increased the volatilization of wood at 250° C. little if at all. At 400° C., however, sodium tetraborate restricted volatilization of wood about as much as the ammonium salts did, whereas sodium phosphate and sodium chloride permitted nearly as much volatilization of wood as occurred with untreated wood.

Apparently, the extent to which a salt might lower the temperature at which pyrolysis began depended on the nature of the salt but not, within wide limits, on the quantity of salt in the wood. On the other hand, those salts that increased volatilization of wood at 250° C. seemed to effect greater increase the greater the concentration of the salt. The salts that are highly effective flame retardants seemed to decrease the volatilization of wood at 400° C. to a greater extent the higher the concentration in the wood before heating, even though some of them, such as ammonium sulfamate and ammonium chloride, had been driven off completely before the temperature reached 400° C.

Sodium tetraborate differed from the other salts of group I for flame retardance in that it failed to lower the temperature at which pyrolysis began or to increase the volatilization of wood at 250° C. Sodium borate did, however, decrease the volatilization of wood significantly at 400° C.

Results by Static Thermogravimetry

The effort to study the kinetics of wood pyrolysis by static thermogravimetry presented problems that have not yet been solved satisfactorily.

The pyrolysis of wood usually has been considered amenable to treatment as a pseudo first-order reaction (1, 3, 5, 11, 17). The rate of loss in weight was therefore recorded at each of a succession of temperatures not too far above the threshold temperature for active pyrolysis, and the logarithm of the as yet unvolatilized fraction of the wood ultimately volatilized at the given temperature was plotted against the time since heating began. The weight loss of as much as 35 percent during the period of some 15 minutes required for the sample to attain the constant furnace temperature had to be ignored. Beyond this point, the charts took the form of straight lines from the slopes

of which velocity constant for each temperature was calculated. The slope of plots of the logarithm of the velocity constants against the reciprocal of the absolute temperature, which proved linear, yielded the activation energies given in table 3.

Results by Differential Thermal Analysis

Curves for differential thermal analysis of wood, α -cellulose, and lignin made with aluminum oxide for reference, are given in figure 5. All three substances presented endothermic nadirs at 130° C. that came chiefly from dehydration. Near 250° C. the curves entered the exothermic region. Lignin then showed a marked exothermic peak at 415° C. whereas cellulose, after reaching a very feeble exothermic peak at 310° C., fell rapidly to a sharp endothermic nadir at 350° C. succeeded by a strong exothermic peak at 470° C. Schwenker (16) observed a weak exothermic peak at 328° C. and a strong endothermic nadir at 372° C. for cotton fabric (alkali-scoured) but no appreciable temperature differential between 400° and 500° C. Both Schwenker (16) and Keylwerth and Christoph (9) found that the weak exothermic peak at 310° C. became strongly exothermic when the pyrolysis took place in air.

The curve for wood revealed the influence of both lignin and cellulose in that the sharp nadir in cellulose at 350° C., which was completely lacking in lignin, in wood became a valley between exothermic peaks at 340° and 440° C. Kollmann (10) and Tang (18) observed this valley in experiments in which the rate of rise in temperature at the center of a "thick" piece of wood was observed while the piece was being heated in a furnace at constant temperature. Keylwerth and Christoph gave the designations β_1 and β_2 to the peaks at 340° and 440° C., respectively.

Comparison of the thermogravimetric with the differential thermal data shows that, with lignin, loss in weight due to active pyrolysis began when the reaction became exothermic and proceeded fastest in the most strongly exothermic region. Weight loss of cellulose began in the feebly exothermic region about 310° C., but most of the weight loss occurred in the endothermic region, with its nadir at 350° C. With wood, nearly all of the loss in weight took place in the exothermic region preceding the valley between the β_1 and β_2 peaks; beyond the valley there was little further weight loss, despite a more strongly exothermic condition, until the peak at 440° C. was passed.

Figure 6 presents differential thermal analyses of wood treated with salts against untreated wood as the reference material in order to reveal the effect of the salts on the absorption or evolution of heat in the various regions of temperature. Figures 7 and 8 present the differential thermal analyses for untreated wood and for wood treated with the salts when the reference material is inert aluminum oxide, together with the corresponding thermogravimetric analyses.

Salts that contained water of crystallization caused an endothermic nadir at about 150° C. (fig. 6). (The small nadir at 150° C. for sodium chloride may be due to a slight increase in moisture in the treated wood, as can be observed in figure 4.) The three ammonium salts showed a common nadir near 220° C. that possibly was due to dissociation of ammonia and its possible reaction with wood. Decomposition of the ammonium phosphate to the pyro- and metaphosphates and decomposition and sublimation of ammonium sulfamate and ammonium chloride may account for most of the heat

effects between 220° and 450° C. Presumably ammonium sulfamate and ammonium chloride are volatilized completely before 400° C. The sodium and potassium salts, after their water of crystallization is lost, are believed to remain undecomposed and nonvolatile up to temperatures well beyond the present interest. All of the salts, however, exhibited an exothermic peak somewhere between 325° and 385° C.

Comparison of figures 6 and 8 shows that the three ammonium salts exerted a predominantly endothermic effect in the zone of temperature within which nearly all of the volatilization of wood took place. They also suppressed the exothermic peak β_1 of untreated wood or, in the case of ammonium phosphate, perhaps shifted it from 340° to 285° C. and shifted the β_2 peak from 440° to about 400° C. One is tempted to attribute the effectiveness of the three ammonium salts to these characteristics, which were not shared by such ineffective salts as sodium phosphate and sodium chloride. It must be recognized, however, that the characteristics in question were not exhibited by the effective flame retardant, sodium borate, or the somewhat effective retardant, potassium carbonate. All of the sodium and potassium salts exerted a predominantly exothermic effect in the region of chief volatilization of wood, made the β_1 peak more strikingly exothermic, and left the β_2 peak relatively unaltered.

Conclusions

The methods of dynamic thermogravimetric analysis and differential thermal analysis offer promise of contributing significantly to study of the mechanism of wood pyrolysis and the action of chemical treatments on it. The possible use of static thermogravimetric analysis to study the kinetics of the reactions seems to present greater difficulty.

The threshold temperature for active pyrolysis of lignin and of wood was found near 220° C., whereas that of α -cellulose was near 275° C. In each case the threshold temperature occurred soon after an endothermic region of the pyrolysis yielded to a definite exothermic trend. Once started, however, the collapse of cellulose was rapid, was essentially complete before 400° C., left little char, and was associated with a marked endothermic nadir. Lignin, on the other hand, lost weight slowly, losing only one-fourth its weight by the time 400° C. was reached and only half at 800° C., and the pyrolysis appeared to be steadily exothermic. Wood exhibited the effects of its two chief constituents; the pyrolysis showed exothermic peaks at 340° and 440° C., with a valley between them that was due to the endothermic region of the cellulose.

The inorganic salts tested so far fall into three groups according to the effects they exhibited.

(1) Two ammonium phosphates, ammonium sulfamate, and ammonium chloride lowered the threshold temperature for active pyrolysis, markedly accelerated loss in weight between the threshold temperature and 250° C., exerted a markedly endothermic effect through the region of temperature in which most of the loss in weight of wood occurred, and kept to a minimum the amount of wood volatilized when pyrolysis was essentially complete at 400° C. These ammonium salts are recognized as highly effective flame retardants.

(2) Two salts of limited or negligible effectiveness as flame retardants, trisodium phosphate and sodium chloride, failed to lower the threshold temperature for active pyrolysis or to increase the volatilization of wood up to 250° C. very much, exerted a predominantly exothermic effect in the region of temperature in which most weight loss occurred, and allowed nearly as much wood to volatilize when pyrolysis was complete as was the case with untreated wood.

(3) The highly effective flame retardant, sodium tetraborate, behaved like the ineffective salts of the second group in the region of temperature up to 250° C. It resembled the effective salts of the first group, however, in holding down the extent of volatilization of wood when pyrolysis was complete at 400° C. Potassium carbonate, which is considered a moderately effective flame retardant, proved less effective than sodium tetraborate in reducing the extent of volatilization at 400° C. but showed a slight ability to stimulate volatilization of wood below 250° C. and to advance the threshold temperature of active pyrolysis.

A more extensive study of chemical treatments is needed before decisions can be reached but it may be mentioned that the salts of the first group are formed between a weak base and a strong acid, those of the second group between a strong base and a strong acid, and those of the third group between a strong base and a weak acid. It has been suggested repeatedly (4, 12, 13) that good flame retardants are likely to be substances that readily decompose to form a strong acid or to form a strong base. No doubt the mechanism of action may differ according as the effective reagent is an acid or a base (7, 14, 15).

References

1. Akita, Kazuo, Report of Fire Research Institute of Japan, vol. 9, no. 1-2, (1959).
2. American Instrument Company, Aminco Laboratory News, 16(3):5, 6 (1960).
3. Bamford, C. H., Crank, J., and Malan, D. H., Proc. Cambridge Phil. Soc. 42:166-82 (1946).
4. Bergström, Hilding, Jernkontorets Annaler 107:37-45, 309-50 (1923); 109:90-2 (1925).
5. Bowes, P. C., Fire Research Note No. 266, Department of Scientific and Industrial Research and Fire Offices' Commission, Joint Fire Research Organization (Great Britain) (1956).
6. Browne, F. L., Forest Products Laboratory Report No. 2136 (Dec. 1958).
7. Gottlieb, Irvin M., Textile Research Journal 26:156-68 (1956).
8. Hunt, G. M., Truax, T. R., and Harrison, C. A., Amer. Wood Preservers' Assoc. Proc. 28:71-93 (1932).
9. Keylwerth, R., and Christoph, N., Deut. Verband Materialprüfung, Materialprüf 2(8):281-328 (1960).

10. Kollmann, Franz, Holz als Roh- und Werkstoff 18(6):193-200 (1960).
11. Martin, S., Research and Development Technical Report, USNR DL-TR-102-NS081-001 (1956).
12. Metz, Ludwig, VDI-Verlag G.M.B.H., Berlin (1942).
13. Serebrennikov, P. P., Tzentralny Naouchno-Izslidovatel'ski Institut Lessnogo Khoziaistva Bulletin 2:43-66 (1934).
14. Schuyten, H. A., Weaver, J. W., and Reid, J. D., Advances in Chemistry Series No. 9, "Fire Retardant Paints" (1954); Ind. Eng. Chem. 47:1433-9 (1955).
15. Schwenker, R. F., Jr., and Pacsu, E., Ind. Eng. Chem. 50:91-6 (1958).
16. Schwenker, R. F., Jr., Paper No. 42, Division of Cellulose Chemistry, 138th National Meeting of the American Chemical Society, New York (Sept. 1960).
17. Stamm, A. J., Ind. Eng. Chem. 48:413-17 (1956).
18. Tang, Walter K., "Study of the Effect of Chemical Treatment on the Thermal Decomposition of Wood," Forest Products Laboratory Report (Aug. 1960).

Table 1. --Salts used to treat wood samples

Salt	Residual weight on dynamic thermogravimetric analysis			Classification for relative flame retardance
	at 200° C.	at 250° C.	at 400° C.	
	percent	percent	percent	
Dibasic ammonium phosphate, $(\text{NH}_4)_2\text{HPO}_4$	97	88	71	I
Monobasic ammonium phosphate, $(\text{NH}_4)\text{H}_2\text{PO}_4$	--	--	--	I
Ammonium sulfamate, $\text{NH}_4 \cdot \text{SO}_3 \cdot \text{NH}_2$	94	91.5	0	I
Ammonium chloride, NH_4Cl	99	95	0	I
Sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	52.8	52.8	52.8	I
Tribasic sodium phosphate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	43.1	43.1	43.1	III
Potassium carbonate, $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$	83.6	83.6	83.6	III
Sodium chloride, NaCl	100	100	100	IV

Table 2. --Dynamic thermogravimetric analysis of untreated wood and of wood treated with inorganic salts

Salt present in the wood	Content of anhydrous salt in sample	Temperature of onset of active pyrolysis	Extent of volatilization of wood in sample	Classification of salt for flame retardance
	percent	° C.	percent at 250° C. : percent at 400° C.	
None (untreated wood)	0	220	4 : 76	---
Dibasic ammonium phosphate	40.5	180	35 : 48	I
.....Do.....	11.1	180	21 : 50	I
.....Do.....	2.4	180	11 : 57	I
Ammonium sulfamate	23.4	180	45 : 42	I
.....Do.....	16.6	180	44 : 50	I
Ammonium chloride	29.8	150	52 : 54	I
.....Do.....	18.6	150	34 : 57	I
.....Do.....	9.0	150	22 : 60	I
Sodium tetraborate decahydrate	11.0	220	4 : 53	I
.....Do.....	1.0	220	2 : 57	I
Tribasic sodium phosphate dodecahydrate	37.6	220	15 : 73	III
.....Do.....	3.2	220	9 : 64	III
Potassium carbonate sesquihydrate	29.2	210	36 : 65	III
.....Do.....	18.6	210	29 : 60	III
.....Do.....	6.7	210	18 : 60	III
Sodium chloride	31.1	220	6 : 69	IV
.....Do.....	13.5	220	6 : 70	IV

Table 3. --Activation energies computed from static thermogravimetric analysis of untreated and treated wood

Salt present in wood	Content of anhydrous salt in sample	Activation energy
	percent	kilocalories/mole
None (untreated wood)	0	35.8
Dibasic ammonium phosphate	10.8	31.9
Monobasic ammonium phosphate	15.1	33.1
Ammonium sulfamate	15.7	34.0
Ammonium chloride ¹	17.7	8.1 (1st step) 34.8 (2nd step)
Sodium tetraborate decahydrate	17.4	24.7
Tribasic sodium phosphate dodecahydrate	18.0	29.3
Potassium carbonate sesquihydrate	20.0	25.4
Sodium chloride	12.0	33.0

¹Figure 4 shows that pyrolysis in the presence of ammonium chloride occurs in two steps, for each of which the activation energy was computed.

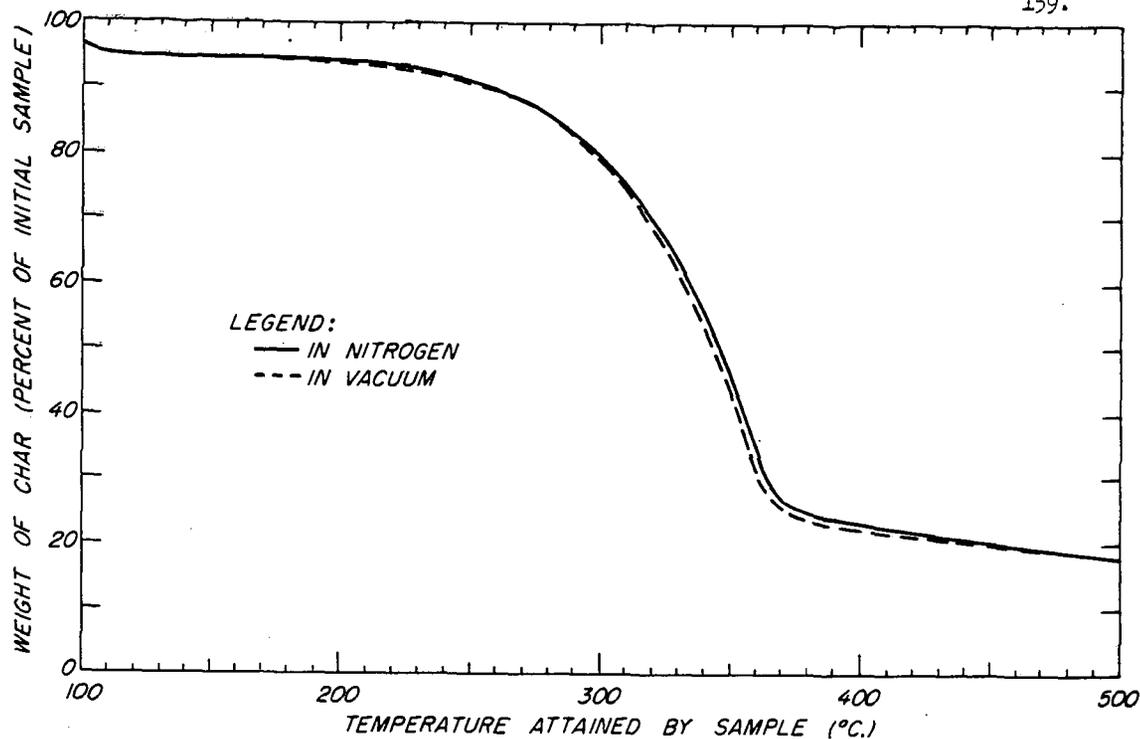


Figure 1.--Close agreement between curves for dynamic thermogravimetric analysis of thin veneer (0.16 mm thick) in nitrogen flowing at 2 liters a minute at atmospheric pressure and in vacuum of 10 Hg absolute.

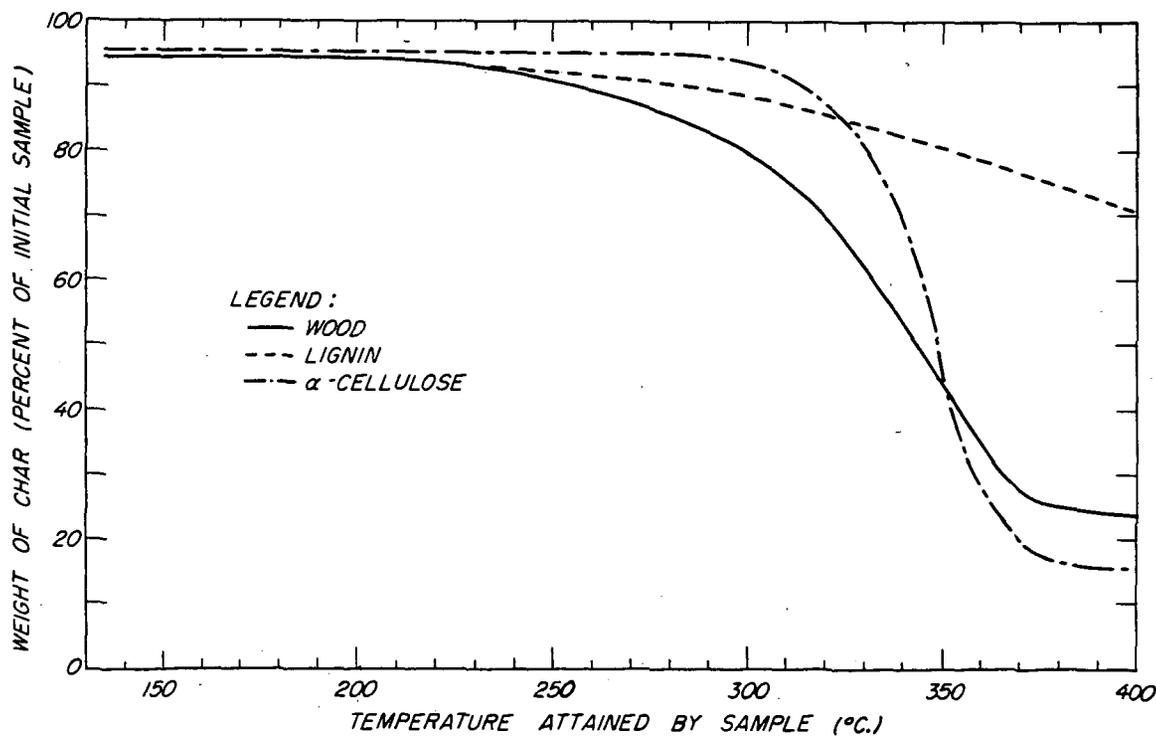


Figure 2.--Portion of dynamic thermogravimetric curves between 130° and 400° C., with temperature rising 6° a minute, for wood, lignin, and α -cellulose.

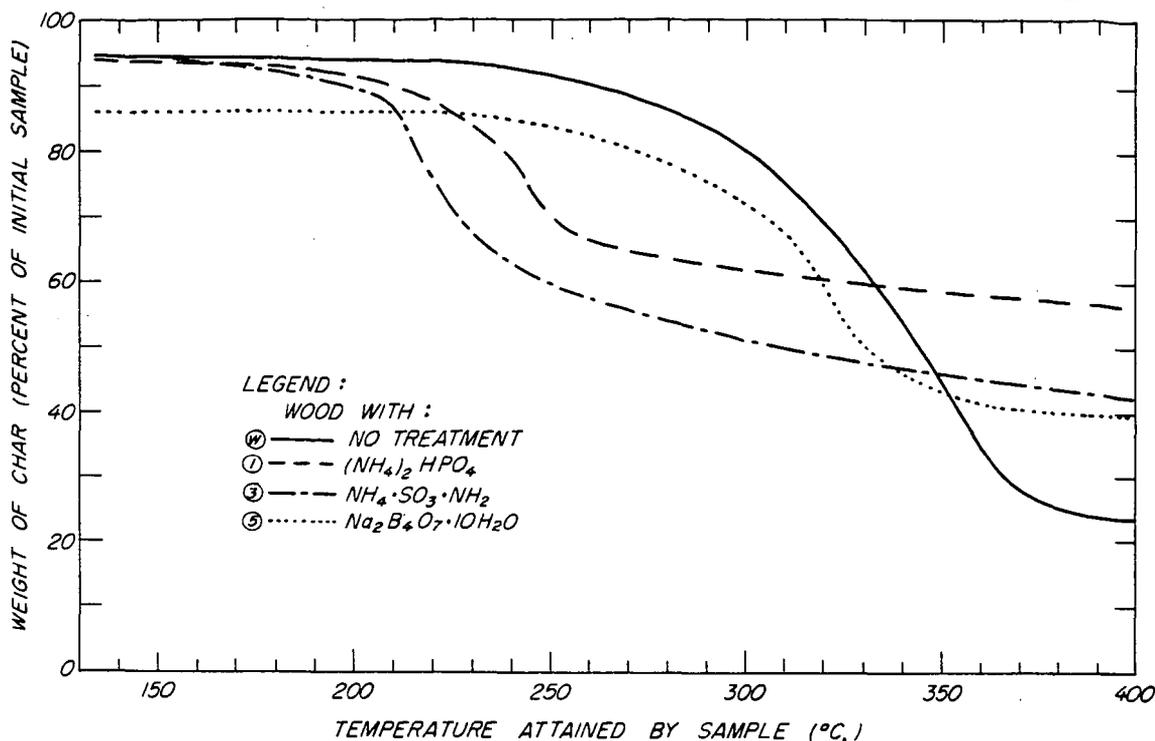


Figure 3. --Portion of dynamic thermogravimetric curves between 130° and 400° C., with temperature rising 6° a minute, for untreated wood and for wood treated with dibasic ammonium phosphate, ammonium sulfamate, or sodium tetraborate, respectively, at the maximum retention of salt indicated in table 2.

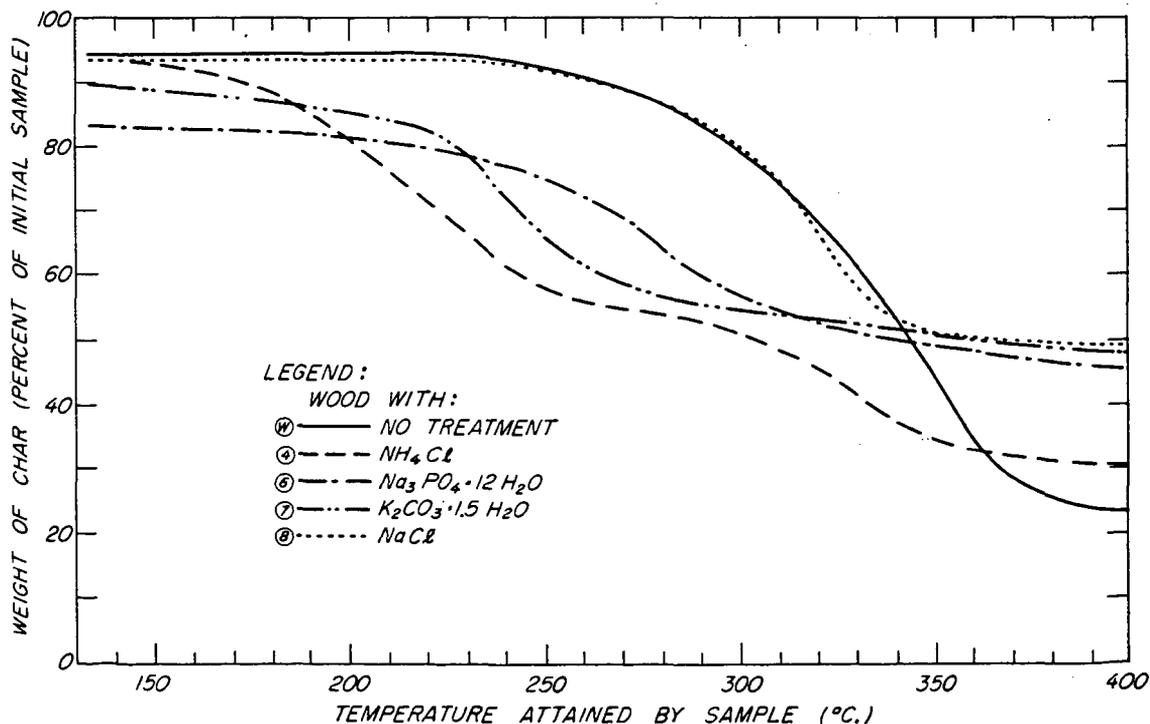


Figure 4. --Portion of dynamic thermogravimetric curves between 130° and 400° C., with temperature rising 6° a minute, for untreated wood and for wood treated with ammonium chloride, tribasic sodium phosphate dodecahydrate, potassium carbonate sesquihydrate, or sodium chloride, respectively, at the maximum retention of salt indicated in table 2.

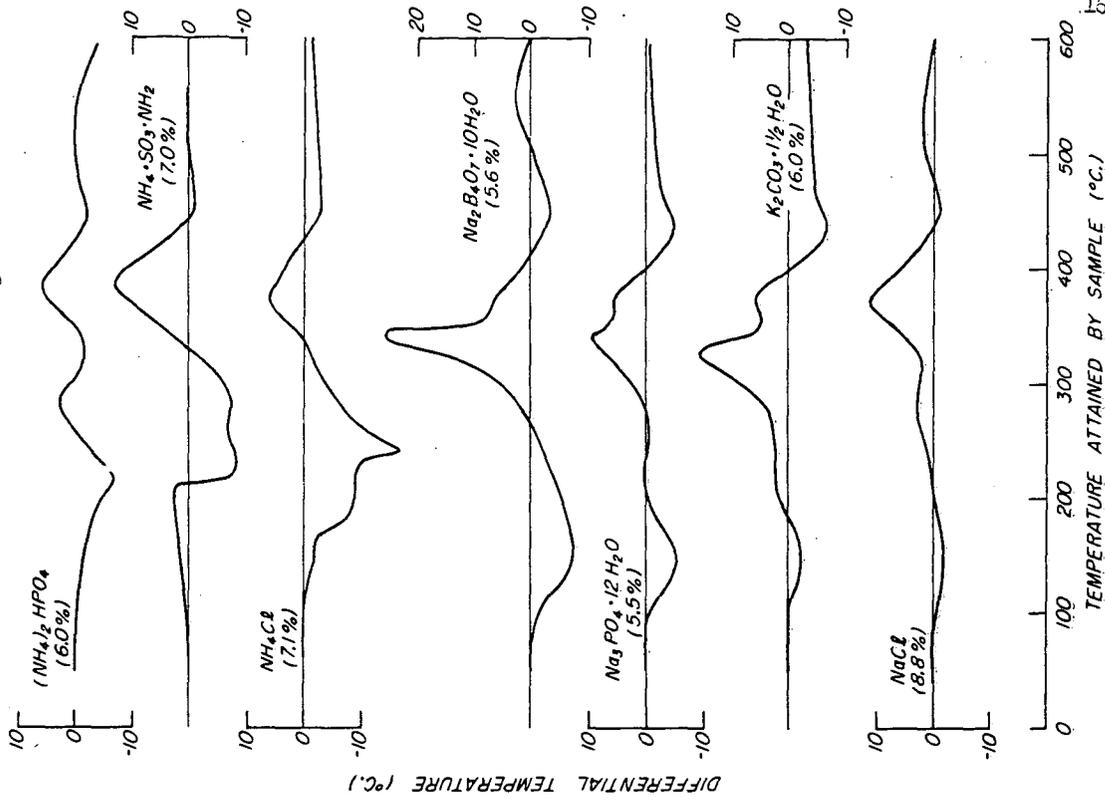


Figure 6. -- Differential thermal analyses of wood containing salts (at the concentration indicated within parentheses) with untreated wood used as the reference material.

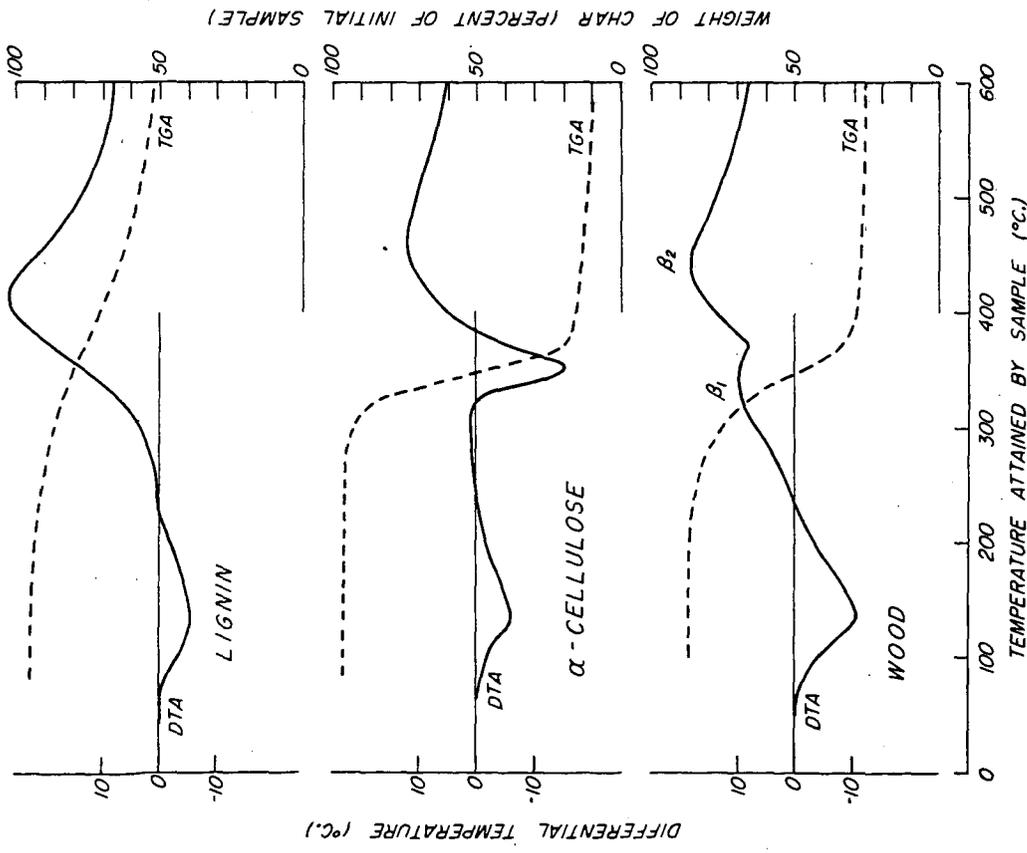


Figure 5. -- Curves for differential thermal analysis (DTA) of lignin, α -cellulose, and wood (solid lines, scales at left, reference material aluminum oxide) with the curves for dynamic thermogravimetric analysis (broken lines, scales at right) superimposed.

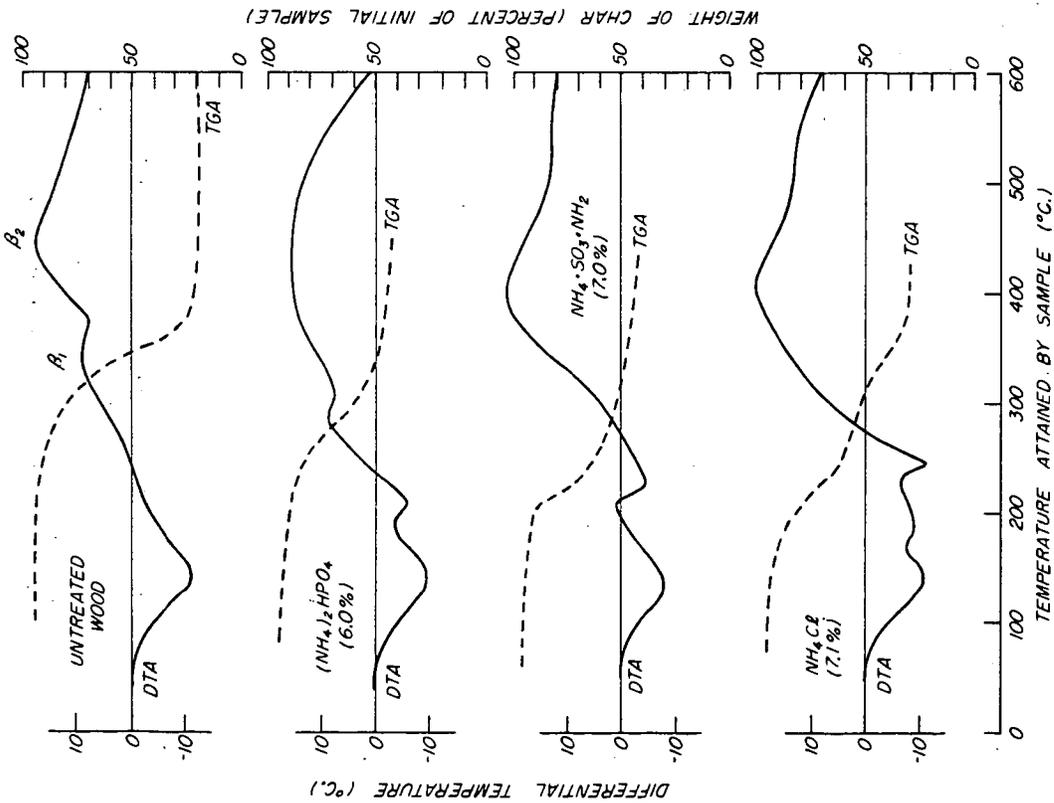


Figure 7. --Curves for differential thermal analysis (DTA) of untreated wood and of wood treated with salts that decompose thermally below 400° C. (solid lines, scales at left, reference material aluminum oxide) with curves for dynamic thermogravimetric analysis (TGA) superimposed (broken lines, scales at right).

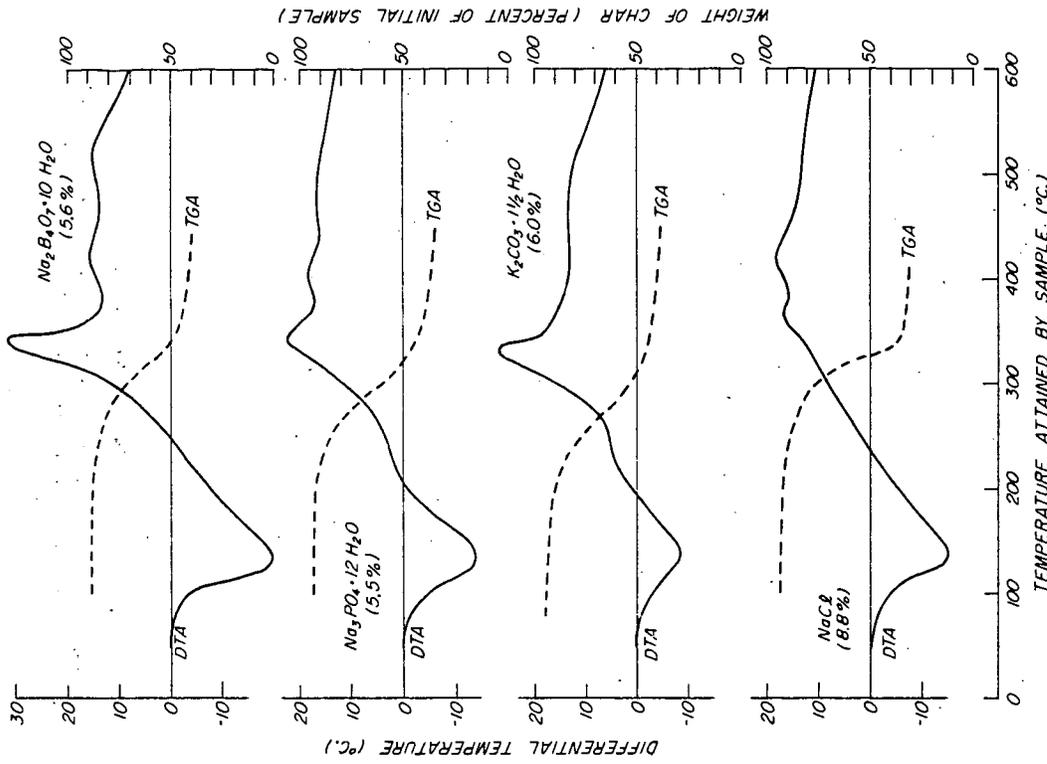


Figure 8. --Curves for differential thermal analysis (DTA) of wood treated with salts that, except for loss of water of crystallization, do not decompose below 400° C. (solid lines, scales at left, reference material aluminum oxide) with curves for dynamic thermogravimetric analysis (TGA) superimposed (broken lines, scales at right).