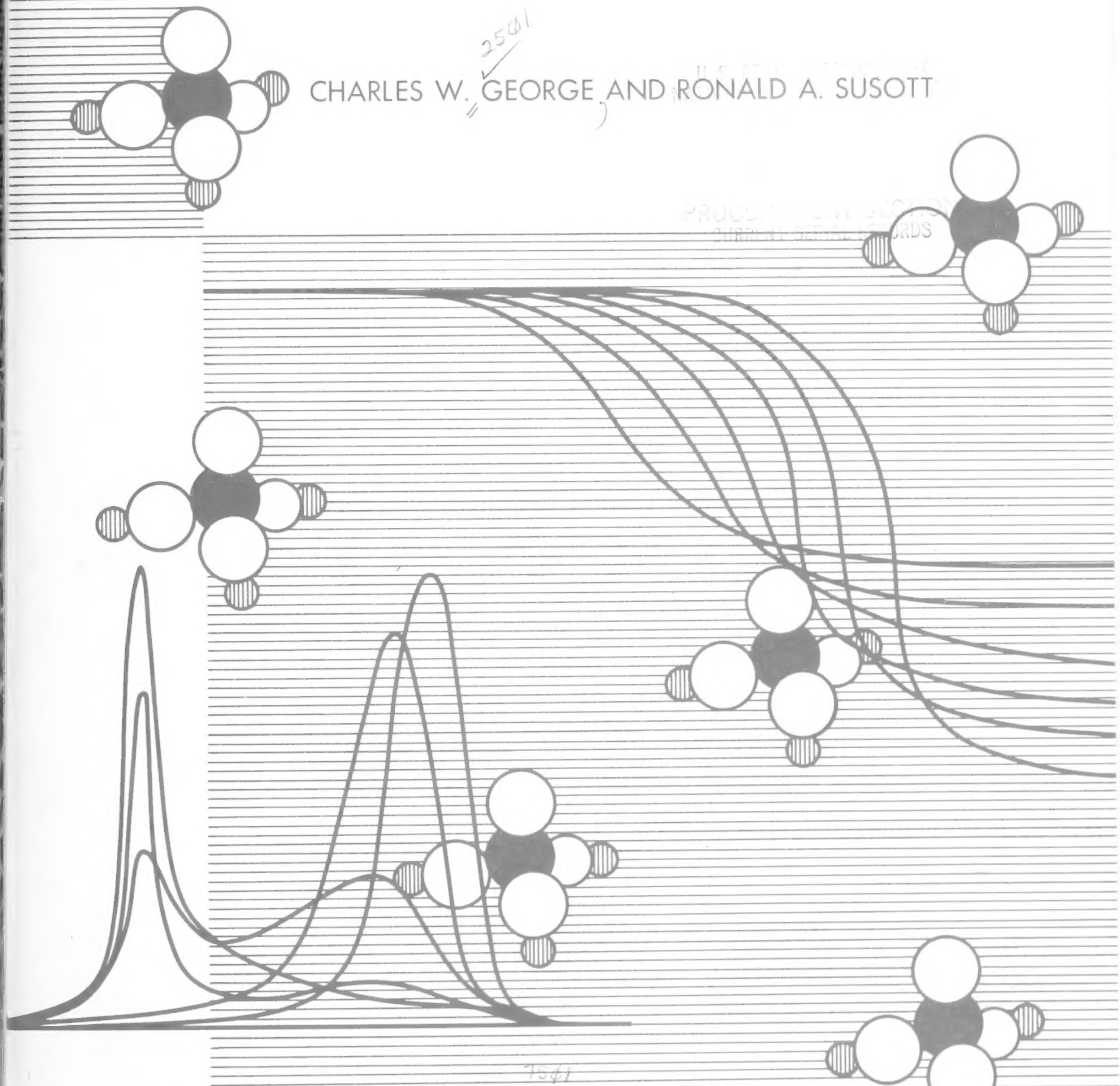
Effects of Ammonium Phosphate And Sulfate On The Pyrolysis And Combustion Of Cellulose

CHARLES W. GEORGE AND RONALD A. SUSOTT



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INTERMOUNTAIN FOREST AND RANGE EXPERIMENT STATION
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ABSTRACT

Differential thermal, thermogravimetric, and derivative thermogravimetric analyses were used to study the effects of two important fire retardant chemicals--ammonium phosphate and ammonium sulfate--on the pyrolysis and combustion of cellulose. To aid in the interpretation of treated cellulose thermograms, the thermal behavior of the fire retardant chemicals was investigated.

An increase in the concentration of either flame retardant lowered the threshold temperature and activation energy required to initiate cellulose pyrolysis and combustion, generally decreased maximum weight loss rates, and caused an increase in the production of residue or char. Although these general similarities were found, there were distinct differences in the temperatures at which the rates changed when treated with the same quantity (on a molar fraction basis) of retardant chemical. The difference in which these chemicals alter pyrolysis and combustion is due to a difference in the availability of the inorganic fraction involved in the reaction or to a difference in the reaction mechanism, or both.

The study demonstrated that direct comparison of retardant chemicals on the basis of their thermal effects on pyrolysis and combustion at one treatment level could lead to erroneous interpretation and improper classification.

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INTRODUCTION

For the past 10 years, ammonium phosphate $(NH_4)_2HPO_4$ and ammonium sulfate $(NH_4)_2SO_4$ have been used as primary ingredients in forest fire retardant formulations. These chemicals, when applied to forest fuels, are known to alter or inhibit thermal degradation and combustion reactions. Because of the reduced flammability of chemically treated fuels, the use of such fire retarding chemicals has become an important tool in wildfire suppression. Knowledge of the reactions or mechanisms taking place and their relation to flammability will assist in a systematic selection of fire retardant chemicals and may lead to more effective methods of application.

Recent studies performed at the Northern Forest Fire Laboratory have indicated significant differences in the effects ammonium phosphate and ammonium sulfate have on flammability as measured indirectly by such parameters as rate of spread, fire intensity, radiant energy, flame height, and residue.[1] We do not know whether these differences in effects are due to the chemicals' physical differences, a difference in their thermal decomposition and availability, or to a difference in the actual mechanism by which they alter fuel degradation.

Truax, Harrison, and Baechler (1956) noted that both compounds were effective in retarding flaming combustion, but ammonium phosphate was superior in retarding glowing combustion. Browne and Tang (1963), on the basis of thermogravimetric analyses in a nitrogen atmosphere, found that the compounds have similar effects on the volatilization of wood and the threshold temperature for pyrolysis, although a difference in their volatilization rate was exhibited. Tang (1967) in a similar study found that ammonium phosphate had the same effects as ammonium sulphate on the pyrolysis of wood and cellulose but had little effect on the volatilization rate of lignin; the cellulose portion of wood was found to have the highest volatilization rate. The volatilization rate for wood seemed to be a combination of the effects on alpha-cellulose and lignin. Tang and Eickner (1968), using differential thermal analysis, compared the effects of 2-percent by weight ammonium sulfate and a 2-percent by weight ammonium phosphate treatment on pyrolysis and combustion of wood, cellulose, and lignin. Little difference was noted in thermograms and relative maximum heat intensities and it was concluded that these parallel results probably were produced by a similar mechanism.

Past research (Shafizadeh 1968; Kilzer and Broido 1965) has indicated that combustion adds secondary and competitive reactions to initial degradation reactions. It is likely that the occurrence of flaming combustion causes cellulose as well as the retardant chemicals to undergo different reactions and at different rates. Although relationships undoubtedly exist between the pyrolysis and combustion of cellulose and the role retardant chemicals play in altering related reactions, it may not be possible to predict combustion characteristics on the basis of pyrolysis characteristics. Thermal analysis in oxygen, or in an air atmosphere, may or may not accurately represent flaming and glowing combustion.

The purpose of the study was to provide extensive thermal analysis data that could be used to categorize the effects of these retardant chemicals on the pyrolysis and combustion of cellulose.[2]

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[1] Charles W. George and Aylmer D. Blakely. Study of the effects of diammonium phosphate and ammonium sulfate on flammability. 1968. (Unpublished report on file at the Northern Forest Fire Laboratory, USDA Forest Serv., Missoula, Montana.)

[2] For the purpose of this paper, pyrolysis is defined as the degradation of a material in an inert atmosphere or vacuum. Combustion refers to the process taking place when the initial material, as well as its degradation products, are in contact with oxygen or air.

EXPERIMENTAL PROCEDURE

The two flame retardants selected for investigation in this study were ammonium phosphate $(NH_4)_2HPO_4$ and ammonium sulfate $(NH_4)_2SO_4$. In determining the effect these additives have on the pyrolysis and combustion of cellulose, differential thermal (DTA), thermogravimetric (TGA), and derivative thermogravimetric (DTG) analyses were used.

Samples

The cellulose samples used in this experiment were prepared from high purity Munktell's chromatographic cellulose powder (smaller than 170 mesh) containing less than 0.02-percent ash. After the cellulose was dried in a desiccator over silica gel, the moisture content was determined using thermogravimetric analysis. The desired percent by weight chemical was obtained by adding a stock solution of known concentration to a previously weighed sample of the cellulose. The weight of cellulose was corrected for 2.6-percent moisture content and weight percents expressed on a dry basis. Each sample was prepared by combination of the desired chemical and cellulose (the total equaled 1 gram) and addition of 10 milliliters of distilled water. After thorough mixing, the samples were dried to approximately 2-percent moisture content in an oven at 32° C. Twenty samples between 0- and 25-percent treatment of both ammonium phosphate and ammonium sulfate were prepared. Both chemicals were analytical reagent grade. An untreated sample was prepared by adding 10 milliliters of distilled water to 1 gram of cellulose and drying as for the treated samples.

Differential Thermal Analyses

Differential thermal analysis (DTA) data were taken using a DuPont 900 Thermal Analyzer.[3] The standard temperature cell (ambient to 500° C.) was used for all treated cellulose samples. The intermediate temperature cell (ambient to 850° C.), similar to the standard cell, was used only to obtain thermograms of the inorganic compounds.

The sample of 10 (±1) milligrams was placed in macrocapillary tubes, 4 millimeters in diameter. Glass beads were used as the inert reference material. Chromel-alumel thermocouples were used to determine the differential temperature of the sample and reference material. A heating rate of 25° C. per minute was used for all analyses.

Pyrolysis of all samples was studied using nitrogen to provide the inert atmosphere. After the cell had been purged by evacuation and addition of N_2, a flow rate of 1 liter N_2 per minute was established. An atmosphere of moisture-free air was used for studying combustion. In order to increase the contact between the sample and reactive gas, a fluidizer requiring a lower flow rate (100 cubic centimeters per minute) was used for tests in air.

Thermogravimetric and Derivative Thermogravimetric Analyses

Thermogravimetric analyses (TGA) were made using the DuPont 950 Thermogravimetric Analyzer while recording weight and temperature signals on the DuPont 900. Ten-milligram samples were placed in a tared aluminum pan with a chromel-alumel thermocouple about 1 millimeter above the center of the sample to record sample temperature. The sample weight was adjusted to the 100-percent chart line following initial water loss near 150° C. so that all sample weights would be on a percent-weight-remaining and moisture-free basis.

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[3] The use of corporation names in this publication is for the information and convenience of the reader. Such use does not constitute an official approval by the U.S. Department of Agriculture of any product to the exclusion of others which may be suitable.

Figure 1.--Thermal analysis apparatus for obtaining DTA, TGA, and DTG thermograms.

Pyrolysis was studied in a nitrogen atmosphere at a flow rate of 100 cubic centimeters per minute. A similar flow rate of air was used in investigations of combustion. For samples pyrolyzed in nitrogen, the percent of weight remaining as a function of sample temperature was monitored. For combustion analysis, an alternate method of recording data was needed due to the highly exothermic character of the reaction. The oven temperature and sample temperature were monitored for several blank runs using a Moseley Autograf 7100B two-pen strip-chart recorder. After correlating the two readings, the percent of weight remaining as a function of sample environment temperature could be calculated. In this way, decomposition in nitrogen and air could be compared in terms of similar environmental temperatures instead of sample temperatures. Endotherms and exotherms in N_2 had a negligible effect making sample and sample environment temperature essentially equivalent.)

Derivative thermogravimetric analyses (DTG) were obtained simultaneously with TGA by differentiating the mass signal from the DuPont 950 using a Cahn 2030 Time Derivative Computer.[4] Calibration was accomplished using a constant weight loss rate, provided by a Knudsen diffusion cell containing a 50 μl sample of 95 percent ethanol. The Knudsen cell was placed in the furnace at 40° C. and TGA-DTG curves recorded. The Moseley two-pen recorder was used to record both the DTG curves and sample or sample environment temperature so a comparison of rate of weight loss and temperature could be made.

The apparatus used for obtaining DTA, TGA, and DTG data is shown in figure 1.

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[4] This derivative computer provided a noisefree response that was not significantly different in time to the weight loss response.

RESULTS

Thermal Behavior of $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$

An understanding of the thermal behavior of flame retardants will assist in interpretation of the effects they have on the pyrolysis and combustion of cellulose. A and B, page 11, show DTA and TGA thermograms of $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ in an atmosphere of air. No significant change in their thermal behavior in nitrogen was found. Changes in the heating rate (between 5° and 30° C. per minute) and gas flow rate (50 to 150 cubic centimeters per minute) caused minor shifts in the thermograms.

The small endotherm at 166° C. in the thermogram for $(NH_4)_2HPO_4$ is caused by decomposition and partial conversion to $NH_4H_2PO_4$. The second endotherm at 190° C. is produced by melting of the $NH_4H_2PO_4$. TGA curves indicate about 13 percent weight loss by 185° C. and is noted by a slight plateau. This weight loss corresponds closely to loss of the first mole of NH_3. A nearly linear weight loss of the remaining sample (equivalent to $NH_4H_2PO_4$) is observed up to 550° C. where the remaining sample is rapidly volatilized. Weight loss following loss of the first mole NH_3 indicates a complex decomposition consisting of more products than simply NH_3 and H_3PO_4 and probably accounts for the difference in melting point between $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$. It is likely that polymerization of the phosphate occurs with formation of water:

$$2H_3PO_4 \xrightarrow{> 190^\circ\ C.} H_2O + H_4P_2O_7$$

and

$$H_4P_2O_7 \longrightarrow 2H_2O + P_2O_5$$

Although the temperatures at which these reactions occur depend on sample size, configuration, etc., the general reaction equations are in agreement with equations given by Van Wazer (1958, p. 503) and Tang and Eickner (1968).

Thermal analysis of monoammonium phosphate helped substantiate these possibilities. DTA of $NH_4H_2PO_4$ shows melting and decomposition to begin at 190° C. (A, page 11). The TGA curve was identical to the TGA curve for $(NH_4)_2HPO_4$ after loss of its first mole of NH_3.

In $(NH_4)_2SO_4$, the only endotherm occurs at 360° C. and is due to melting and decomposition. The TGA curve shows initiation of weight loss near 225° C. with the rate being nearly constant until 350° C. where rapid decomposition begins. The weight loss at this point (20 percent) is less than necessary for loss of the two moles NH_3. This can be explained by the likely simultaneous decomposition of $(NH_4)_2SO_4$ and H_2SO_4, a possible initial product in addition to NH_3. The absence of the peak in the DTA curve near 225° C. indicates either the NH_3 is weakly associated or the heat exchange at this point is very small in comparison to the large endotherm at 360° C.

Differential Thermal Analyses

DTA thermograms for the pyrolysis of cellulose at several treatment levels of ammonium phosphate and sulfate on cellulose are shown on page 12; those leading to combustion are shown on page 13. The peak temperatures of primary endotherms and exotherms for pyrolysis and combustion are given in tables 1 and 2.

A major difference in thermograms for the pyrolysis of the two cellulose treatments is indicated. As $(NH_4)_2HPO_4$ is added to cellulose and pyrolyzed in nitrogen (page 12), the strong endotherm at 364° C. in untreated cellulose gradually shifts to lower temperatures. However, as the $(NH_4)_2SO_4$ concentration is increased to 0.50 percent, a new endotherm appears near 250° C.; this endotherm dominates the DTA curves at higher concentrations. The endotherm near 210° C. for $(NH_4)_2HPO_4$ treatments of cellulose greater than 4.00 percent is attributed to the inorganic fraction. Monoammonium phosphate $NH_4H_2PO_4$, which could be formed as the sample was dried, has an endotherm near 210° C. (A, page 11). An endotherm due to the presence of $(NH_4)_2SO_4$ is not readily discernible.

The DTA thermograms for combustion in air (page 13) of both $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ treated cellulose are dominated by a strong exotherm from about 300° to 450° C. The endotherm near 250° C. for $(NH_4)_2SO_4$ treated samples is apparent at a concentration of 0.70 percent, and above, but is small compared to the latter exotherm. A prominent difference between the effects of the two chemicals on the combustion of cellulose is that $(NH_4)_2SO_4$ causes a larger exotherm (note the difference in the ΔT scale used, pages 12 and 13).

Thermogravimetric and Derivative Thermogravimetric Analyses

The cellulose samples, treated with $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ in concentrations from 0 to 25 percent by weight were investigated for thermal behavior in air and nitrogen by TGA and DTG. After initial water loss and setting of sample weight to 100 percent, the TGA curves are horizontal until pyrolysis (pages 14, 15) and combustion (pages 16,17) begin. As the chemical percent is increased, there is a lowering of the pyrolysis and combustion threshold temperature. The threshold temperature was determined using the DTG curves and arbitrarily denoted as the temperature required to produce a weight loss rate of 0.09 milligram per minute (< 1 percent of the maximum weight loss rate). Table 3 shows the effect of amount of $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ on the threshold temperature for pyrolysis and combustion. The slight difference (8° C.) in the threshold temperatures for untreated cellulose in nitrogen and air is probably due to the difference in procedures for obtaining the environmental temperature in nitrogen and air. The lowering of threshold temperatures for treated fuels in air and nitrogen is also accompanied by a lowering of the temperature at which the maximum weight loss or reaction rate is observed. The temperature of the maximum weight loss was equally useful in comparing the effect of the different chemical concentrations.

Although the trends in TGA curves appear very similar for both chemicals, the DTG curves (pages 18, 19, 20, 21) which were run simultaneously with TGA, were much more sensitive to small differences in weight loss rates. These DTG curves, as well as the TGA curves, were very reproducible. In both air and nitrogen, the DTG curves show $(NH_4)_2SO_4$ treatment causes a rate of weight loss peak at about 250° C. In nitrogen, treatments as low as 0.500 percent cause this peak; in air, 1.00-percent treatments have the same effect. The curves for $(NH_4)_2HPO_4$ show a much more gradual shift of the peak to lower temperatures, with a peak at 250° C. developing only with high (greater than 10.0 percent) concentrations of chemical. Tables 4, 5, 6, and 7 give data for the rate of weight loss for peaks in the DTG curves and the temperature at which those peaks occur. Although numerical data are useful for comparison purposes, viewing the entire DTG thermograms (pages 18-21) provides a better picture of reaction differences.

The rate was normalized to correct for decreasing initial cellulose weights with increasing chemical treatment. The normalized rate was determined by:

$$\text{Normalized peak rate (mg. per minute)} = \frac{\text{Actual peak rate (mg. per minute)}}{\text{Fraction of cellulose in sample}}$$

Figure 2.--Effect of $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ on cellulose residue at 450° C. following pyrolysis.

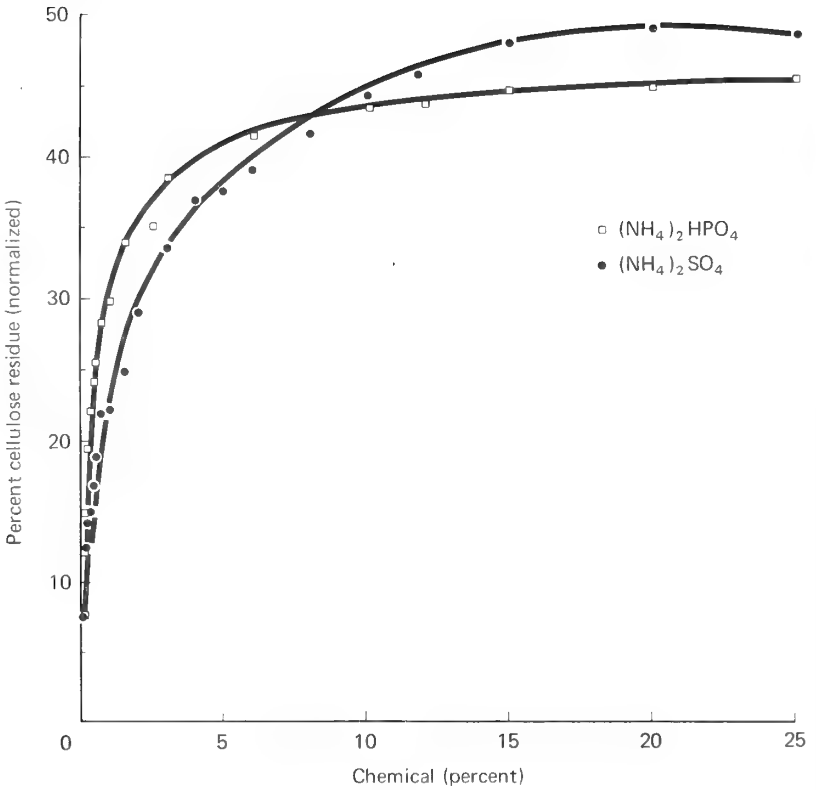
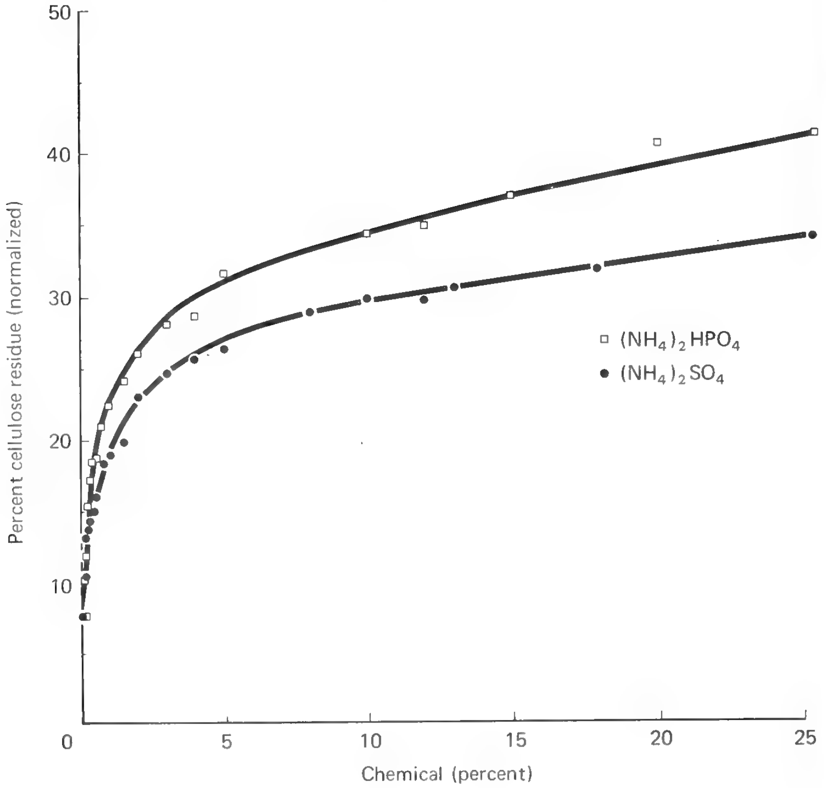


Figure 3.--Effect of $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ on cellulose residue at 450° C. following combustion.



An increase in the percent by weight chemical usually was accompanied by a decrease in the peak rate of weight loss. However, cellulose treated with 0.050 percent $(NH_4)_2HPO_4$ caused an increase over untreated in the ~~maximum~~ peak rate of weight loss during pyrolysis (page 18). The only other peak rates which exceeded untreated occurred at the low temperature peak (250° C.) with higher levels of $(NH_4)_2SO_4$ treated cellulose during pyrolysis. The maximum rate of weight loss for the low temperature peak increased with percent by weight chemical until a 10-percent treatment was reached. The rate decreased at treatment levels above 10 percent (page 19). The DTG curves for each particular chemical are quite similar for nitrogen and air except that rates of weight loss are somewhat higher in air.

Tables 4 through 7 also give data taken from TGA curves showing the effect of $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ on residue at 450° C. in both nitrogen and air. Cellulose residue can be estimated if the amount of inorganic chemical remaining at 450° C. is known. The TGA curves, shown on page 11, for the two chemicals indicate a 100-percent weight loss for $(NH_4)_2SO_4$ and 37-percent weight loss for $(NH_4)_2HPO_4$. Assuming the inorganic chemicals decompose the same whether cellulose is present or not, the normalized cellulose residue can be determined:

$$\text{Normalized cellulose residue at } 450^\circ \text{ C. (percent)} = \frac{\text{Percent residue} - (\text{percent chemical residue} \times \text{fraction chemical treatment})}{\text{Fraction cellulose in sample}}$$

The effect of $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ on cellulose residue after pyrolysis and combustion is shown in figures 2 and 3. As the chemical is increased (percent by weight), both chemicals increase residue at 450° C. In air and at the lower concentrations in nitrogen, $(NH_4)_2HPO_4$ causes a greater increase in residue than $(NH_4)_2SO_4$. The rate of volatilization of residue at 450° C. is less for $(NH_4)_2HPO_4$ treatments and the temperature required for its complete volatilization is higher (compare pages 16 and 17).

COMPARISON OF METHODS AND RESULTS

Comparison of DTA, TGA, and DTG curves for cellulose pyrolysis and combustion and cellulose treated with various concentrations of $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ shows reasonable agreement for each method. Small endothermic and exothermic reactions made determination of maximum rate temperatures impossible in TGA. The use of DTG provided information not otherwise obtainable and its sensitivity greatly added to ease of interpretation.

When cellulose is treated with $(NH_4)_2HPO_4$ and this retardant is increased between 0 and 25 percent, the following temperatures are lowered: the threshold temperatures for pyrolysis and combustion (table 3); the temperature of maximum rate of weight loss (tables 4 and 6); the temperature of the major pyrolysis endotherm (table 1); the temperature of the combustion exotherm (table 1). This increase in retardant exponentially increases the amount of cellulose residue (tables 4 and 6). Similar trends are observable in $(NH_4)_2SO_4$ treatments; furthermore, the effects of this retardant are usually more pronounced for lower treatment levels than for $(NH_4)_2HPO_4$ treatments. For example, a treatment of 0.0500 percent $(NH_4)_2SO_4$ lowers the threshold temperature for pyrolysis 33° C. while the same treatment of $(NH_4)_2HPO_4$ lowers it only 4° C. Though similar comparisons can be made for other treatments of less than 1.00 percent, treatments from 1.50 to 25 percent result in nearly the same threshold temperature for both $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ (table 3).

The differences in chemicals and similarities in analysis methods are graphically depicted in figure 4.

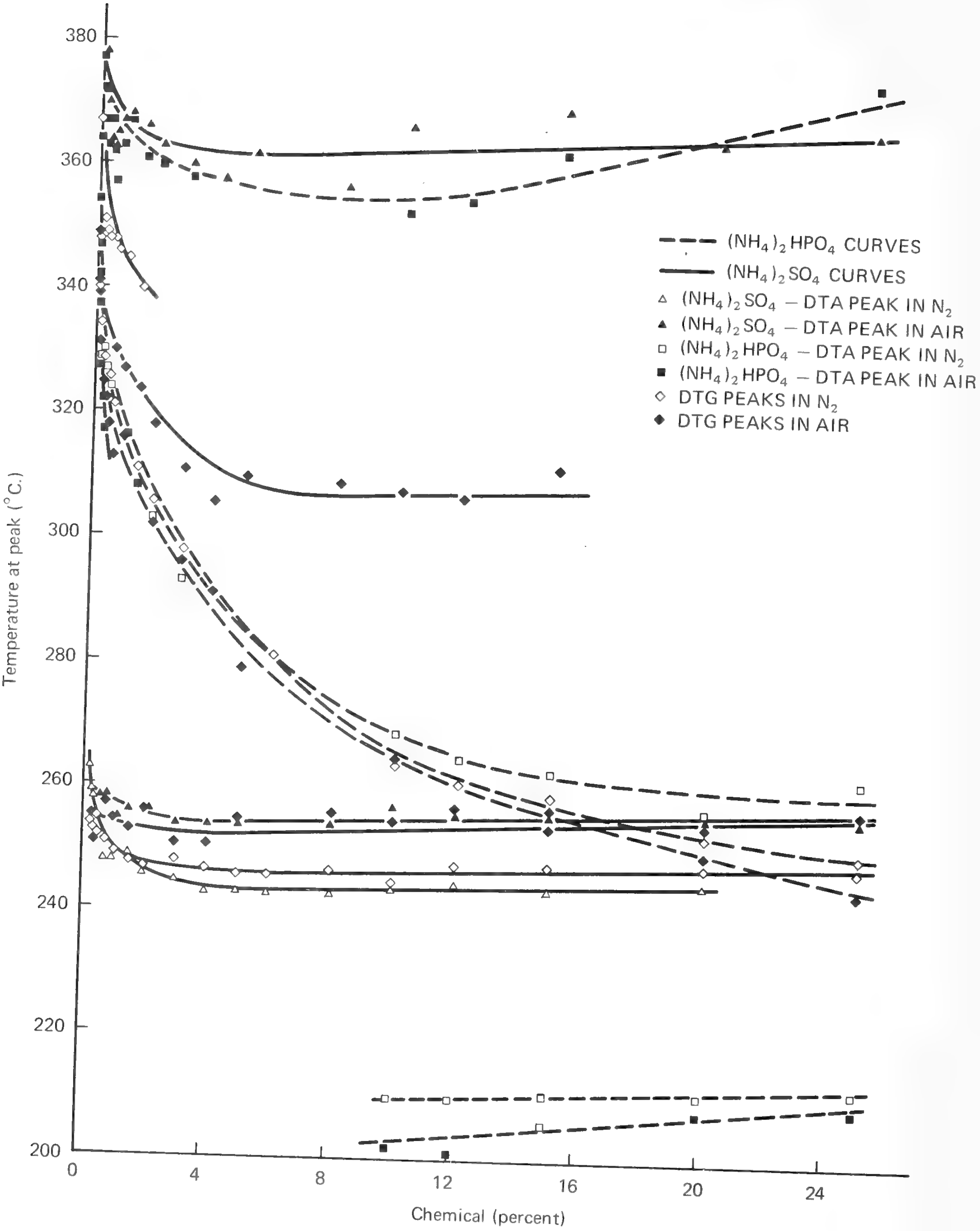


Figure 4.--Comparison of the peak temperatures for chemicals and thermal analysis method.

Discussion

Differential thermal (DTA), thermogravimetric (TGA), and derivative thermogravimetric (DTG) methods of analyses show significant differences in the effects ammonium sulfate and ammonium phosphate have on the degradation of cellulose in either nitrogen or air atmosphere. Some of the general effects and the differences can be summarized:

1. Both ammonium sulfate and ammonium phosphate lower the threshold temperature and activation energy required to initiate cellulose decomposition in nitrogen and air.

2. Increasing the amount of either retardant chemical decreases the maximum weight loss rate occurring during decomposition until the temperature of the peak nears 250° C. An increase in the amount of either retardant beyond the concentration required to obtain a maximum rate at 250° C. causes an increase in the peak rate without shifting its temperature. Any additional increase further reduces the maximum weight loss rate.

3. Increasing retardant chemical causes an increase in the residue or char production.

4. Ammonium phosphate is more effective in increasing char production in an air atmosphere than is ammonium sulfate.

5. While a 2-percent treatment of ammonium sulfate causes a shift to near 250° C. in the maximum decomposition rate, five times this quantity of ammonium phosphate (on a molar fraction basis) is required to produce the same effect, indicating a sizable difference in the action of the two chemicals on cellulose.

It is theorized that the differences ammonium sulfate and phosphate have on cellulose pyrolysis and combustion are either due to the availability of the inorganic fraction involved in the reaction or to a different mechanism by which these chemicals alter pyrolysis and combustion.

1. Such theorizing is based on the fact that ammonium sulfate decomposes at a lower temperature than ammonium phosphate and may not be available in similar concentrations or at the necessary time. For instance, ammonium sulfate is completely decomposed by 420° C., a temperature which may preclude glowing combustion reactions. This is borne out by the fact that ammonium sulfate treated cellulose produces less residue at 450° C. than does ammonium phosphate.

2. Major shifts in cellulose decomposition occurred prior to losses of significant amounts of the sulfate or phosphate portion of the compound. Because the molecular weight is the same for both compounds (132.05 and 132.14 for $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$, respectively), the treatments can be considered as being on a molar basis. Thus, provided the difference in NH_3 production rates is not responsible for the difference (equal total amounts of NH_3 are produced by both compounds) it is likely there is a difference in the mechanism by which these compounds alter both pyrolysis and combustion. It is unlikely that NH_3 is important in the process since $(NH_4)_2HPO_4$ and $NH_4H_2PO_4$ have the same effect on pyrolysis and combustion when the comparison is made on an equivalent PO_4 basis. This is also supported by the fact empirical fire tests have shown H_3PO_4 as well as $(NH_4)_2HPO_4$ and $NH_4H_2PO_4$ to be equally effective when compared on an equivalent PO_4 basis.

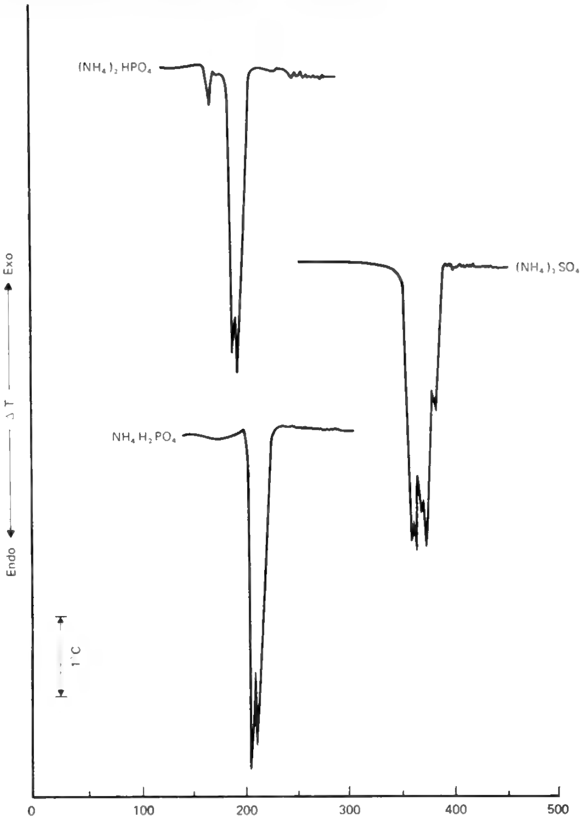
It is possible that the differences in the effects of $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ can be attributed to both theorized causes previously mentioned. A different mechanism by which pyrolysis and combustion are altered may exist at lower temperatures for the compounds while the difference in high temperature availability of a portion of the compound may affect glowing combustion, and thus residue, differently.

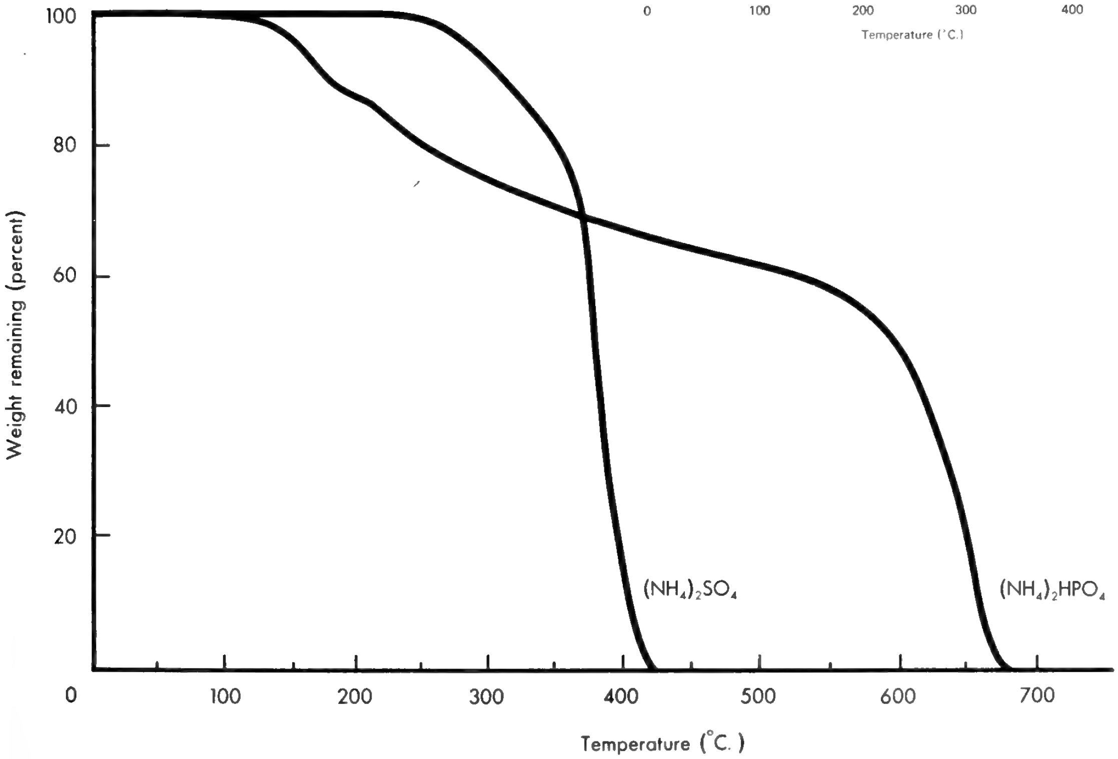
An important conclusion demonstrated by this study is related to the effect of treatment level on pyrolysis and combustion. A direct comparison or classification of inorganic chemicals on the basis of the effects these chemicals have on pyrolysis and combustion at one treatment level may often be misleading and lead to erroneous conclusions concerning other levels of treatment.

Correlation of the results of this study with actual fire test data will be required to fully characterize the relationships. Further studies including quantification of volatile products as a function of chemical quantity will help to indicate the reactions involved.

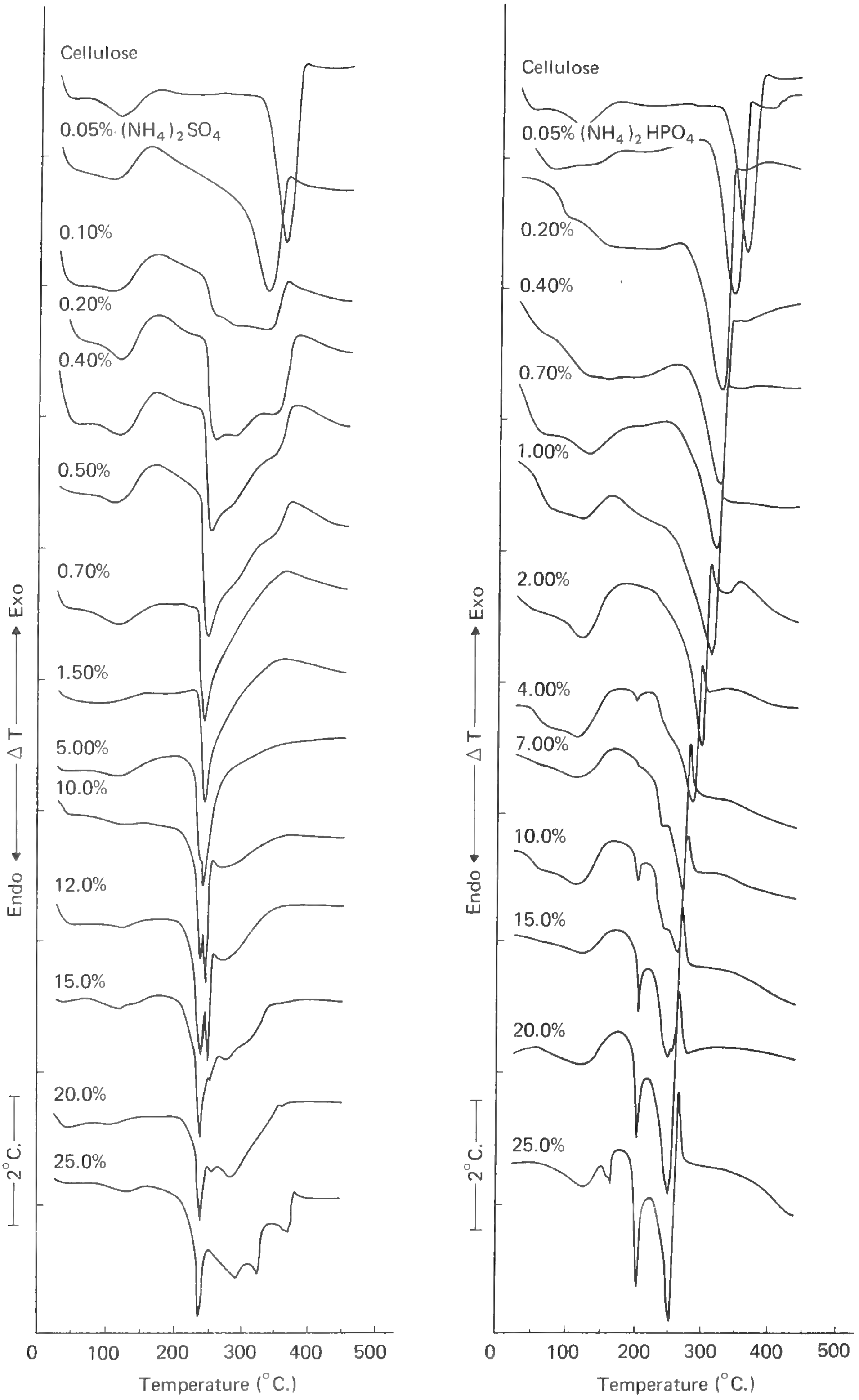
THERMOGRAMS

A--DTA thermograms of $(NH_4)_2HPO_4$, $NH_4H_2PO_4$, and $(NH_4)_2SO_4$ when heated at 25° C. per minute in a flow of 1 liter per minute air.

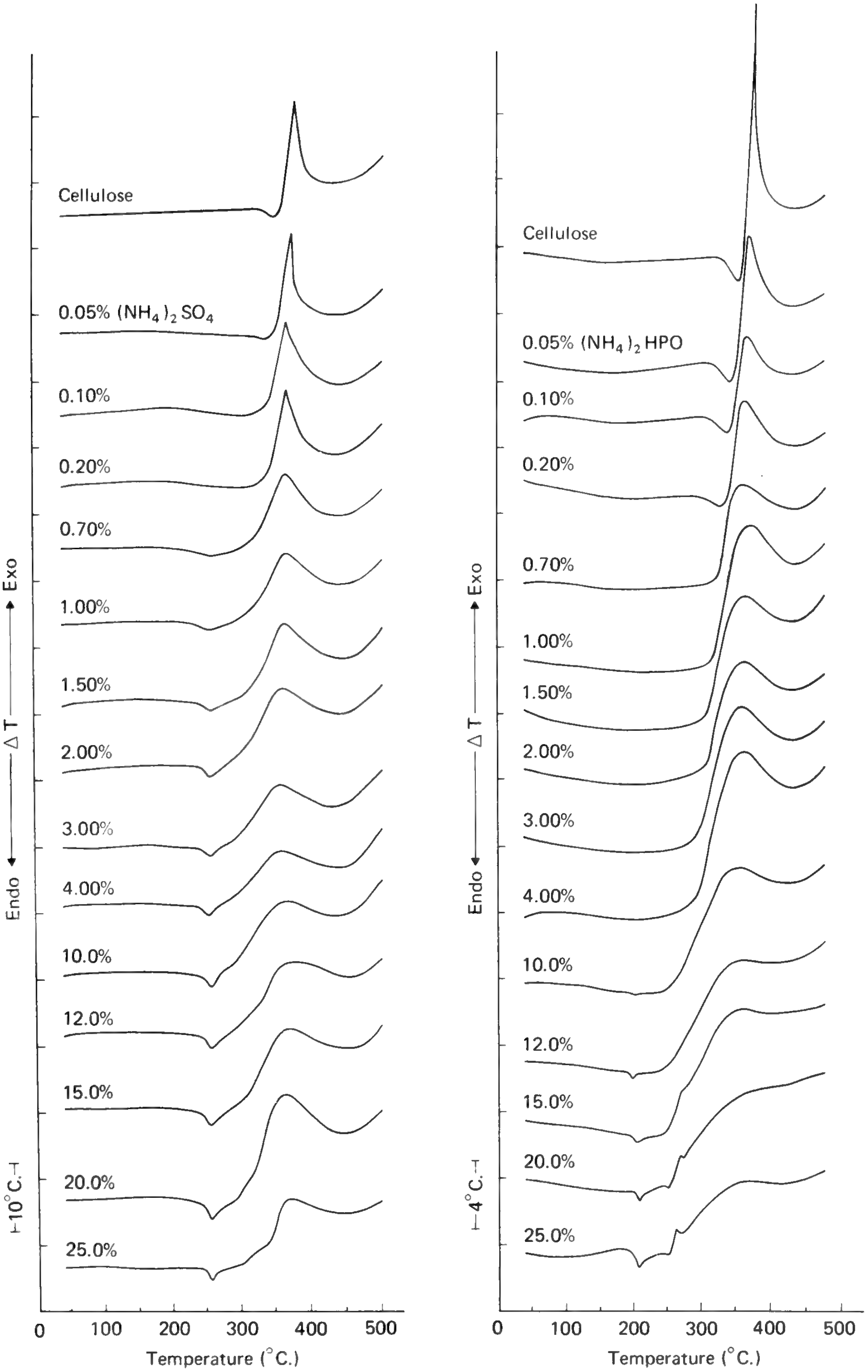




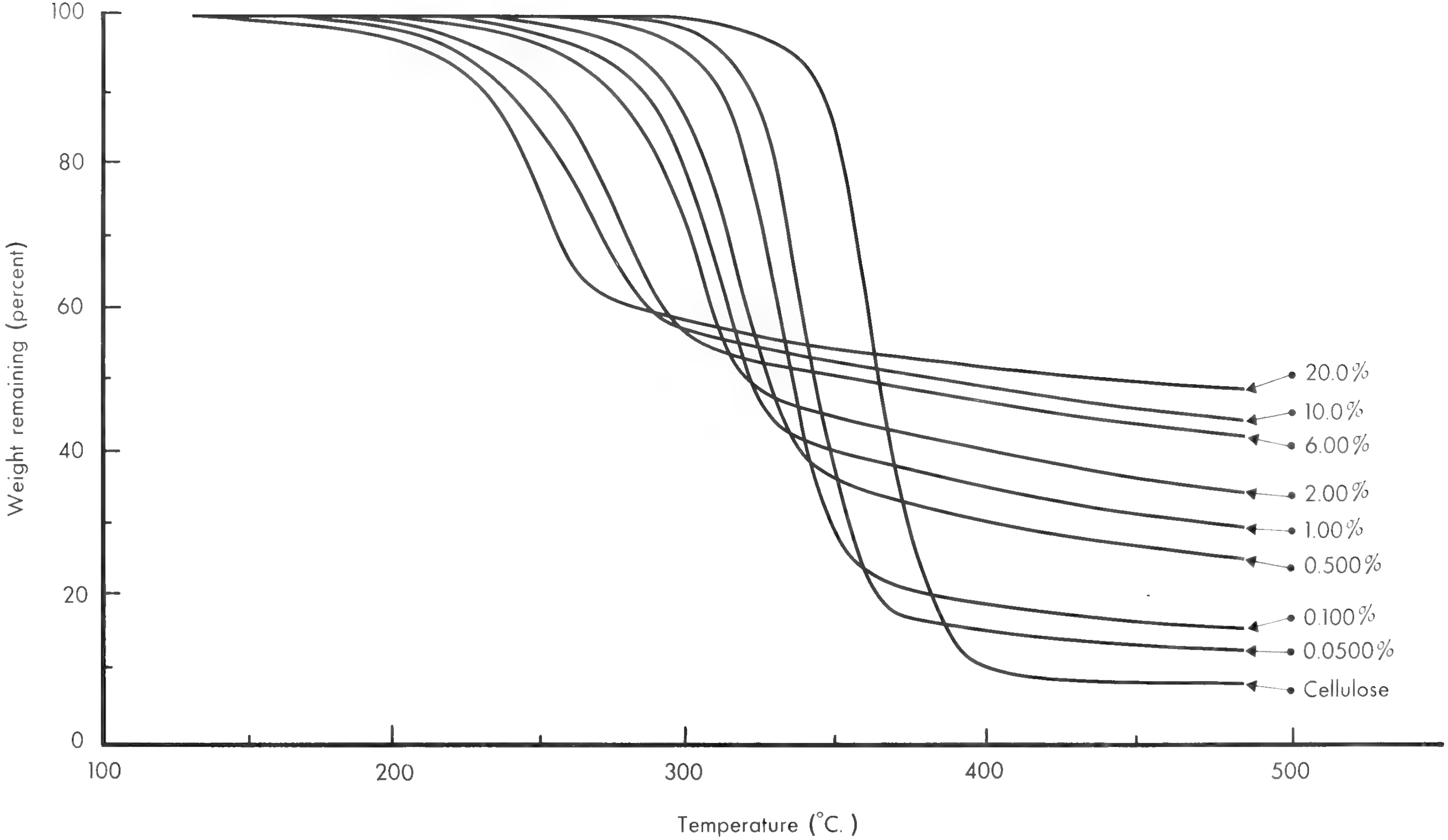
B--TGA thermograms for $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ heated at 25° C. per minute in a flow of 1 liter per minute air.



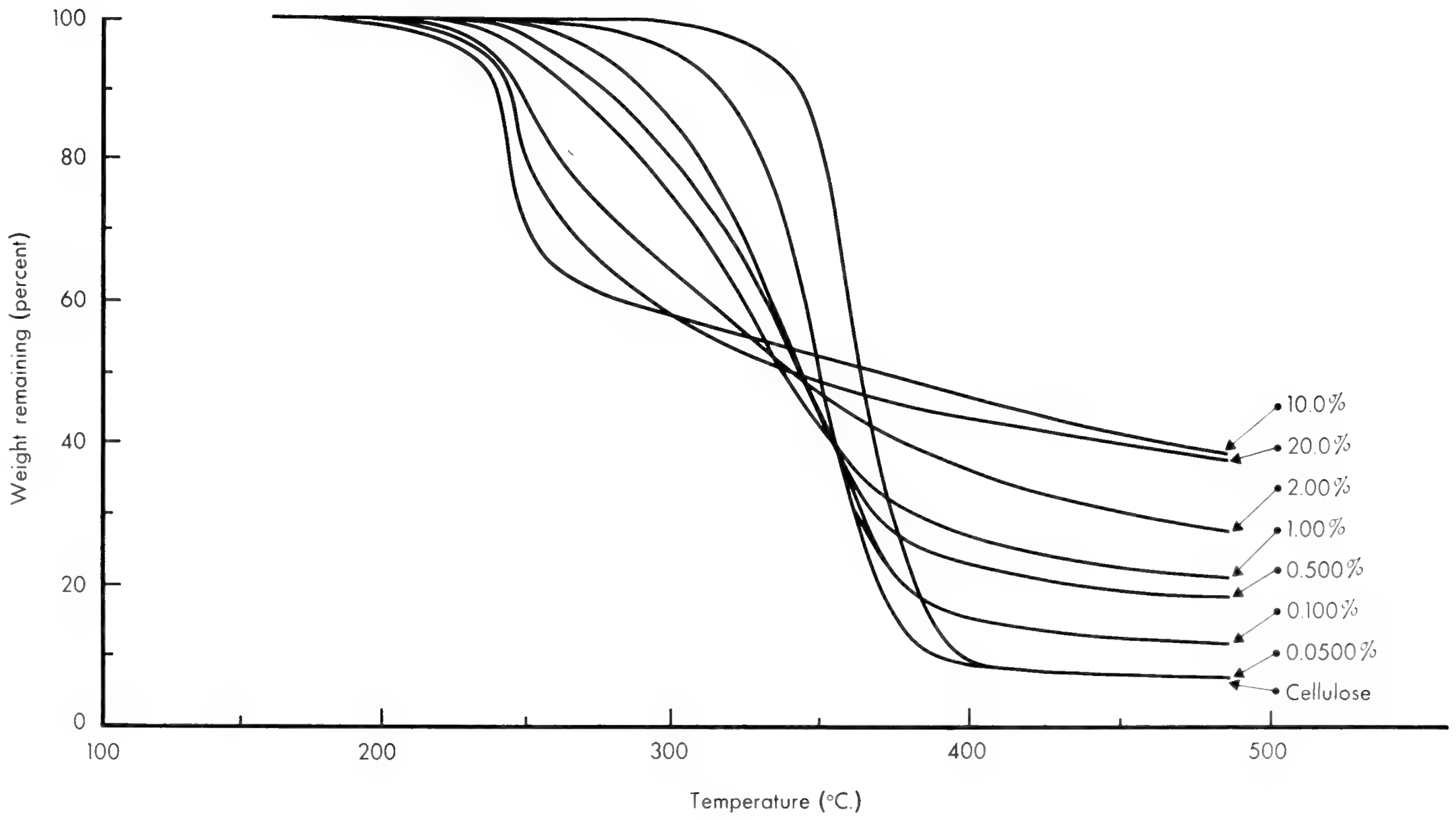
DTA thermograms of cellulose and treated cellulose heated at 25° C. per minute in a flow of 1 liter per minute nitrogen.



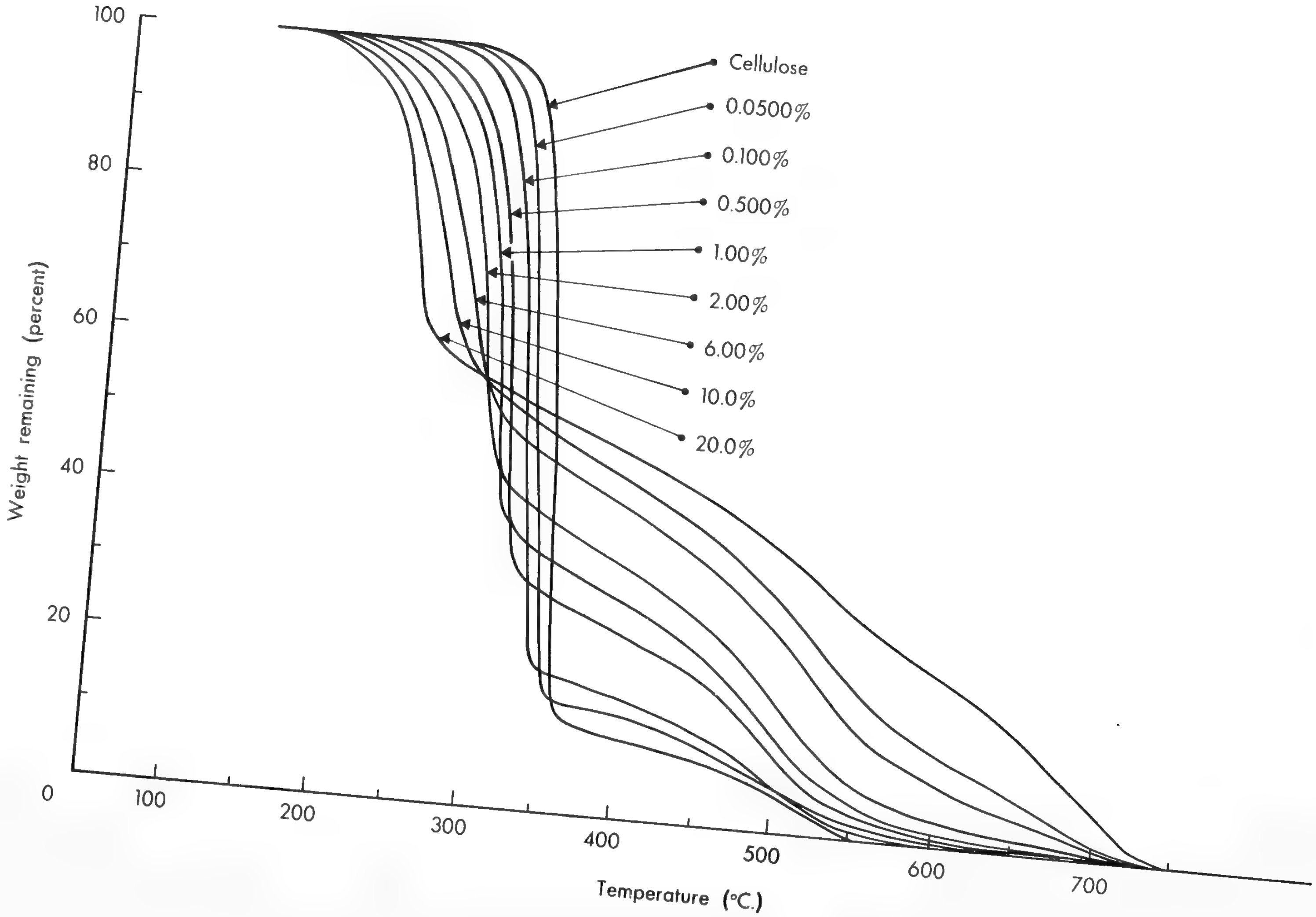
DTA thermograms of cellulose and treated cellulose heated at 25° C. per minute when fluidized with 100 cc. per minute air.



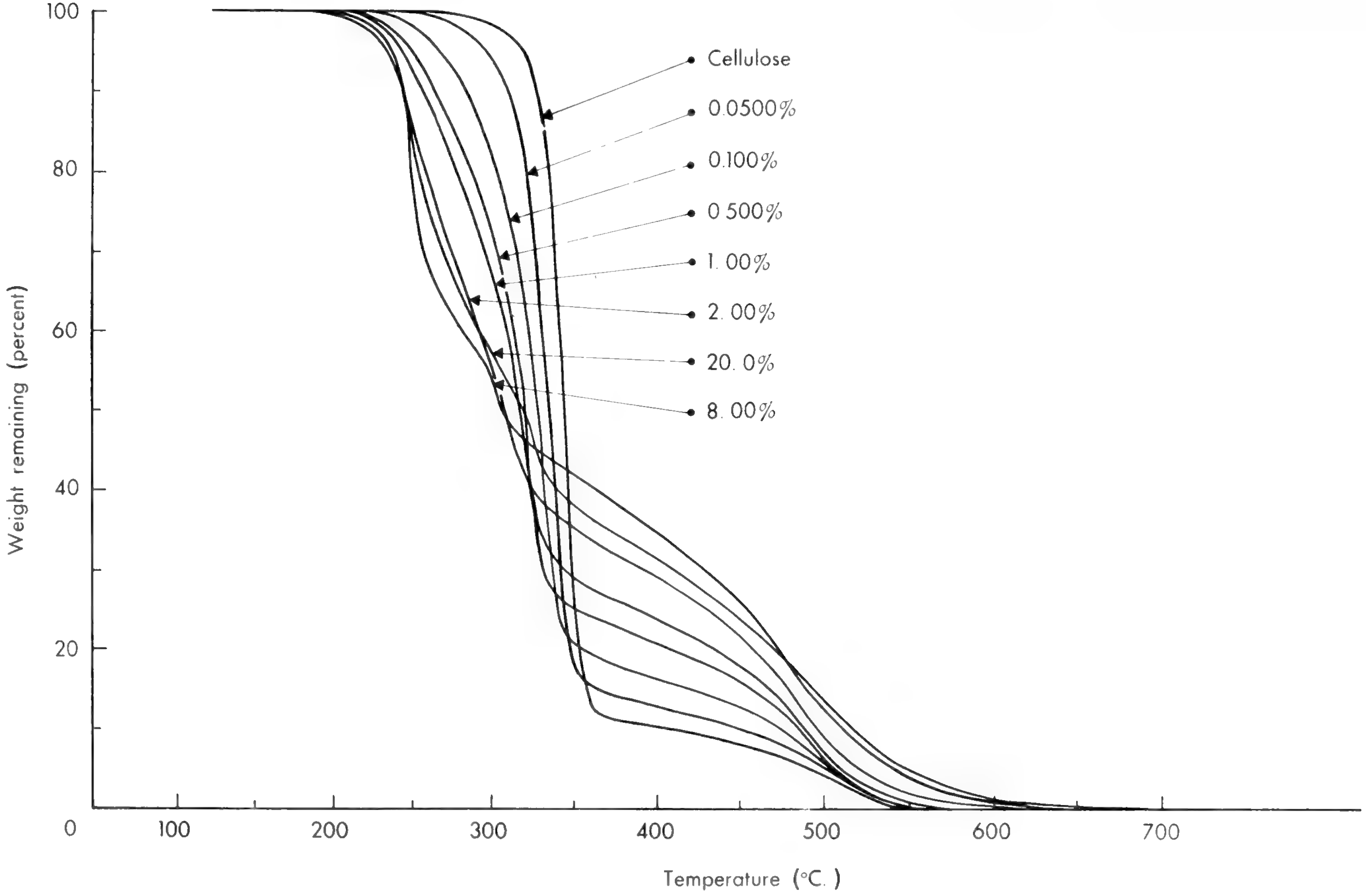
TGA thermograms of cellulose and $(NH_4)_2HPO_4$ *treated cellulose heated at 25° C. per minute in a flow of 100 cc. per minute nitrogen.*



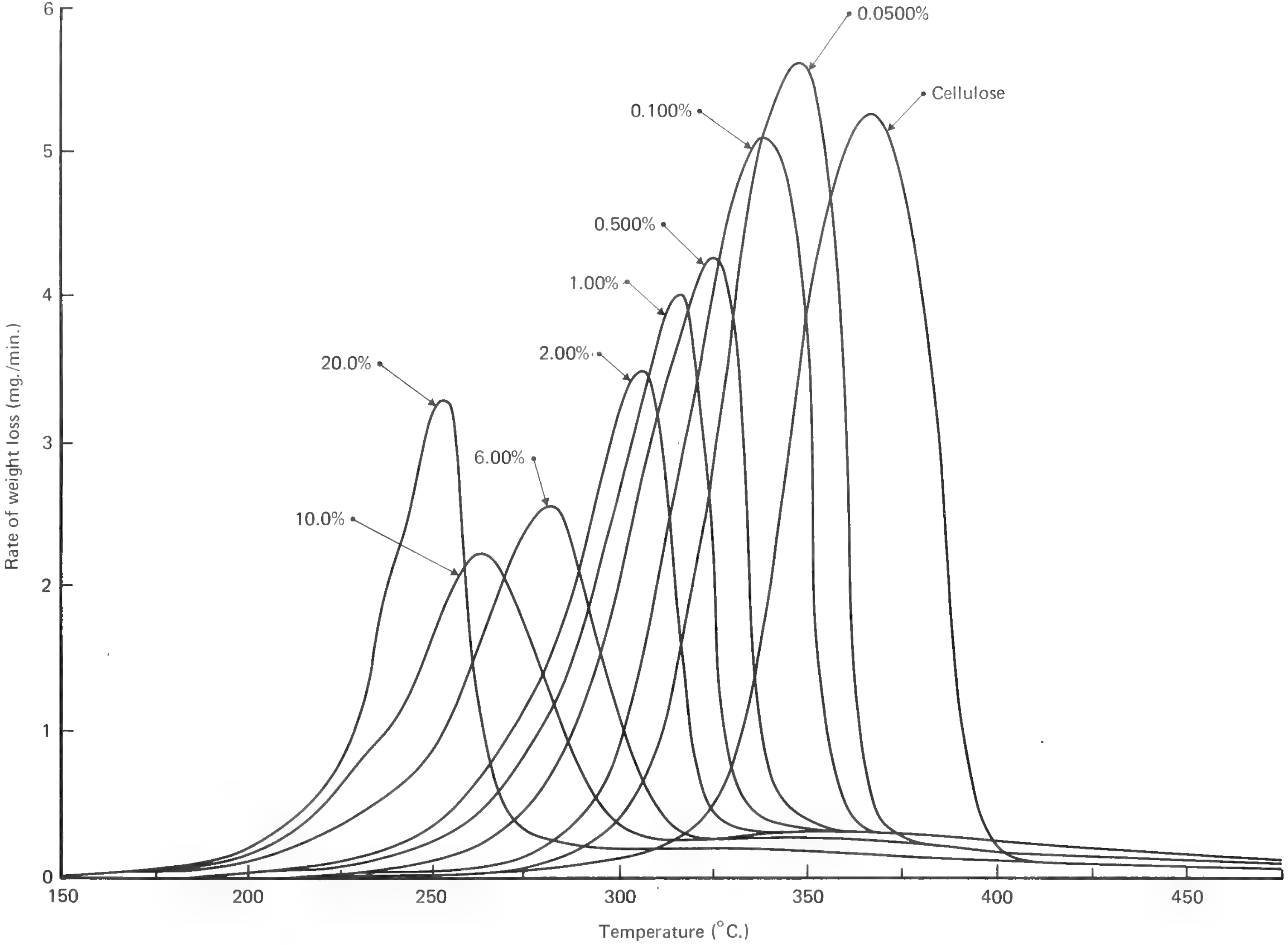
TGA thermograms of cellulose and $(NH_4)_2SO_4$ treated cellulose heated at 25° C. per minute in a flow of 100 cc. per minute nitrogen.



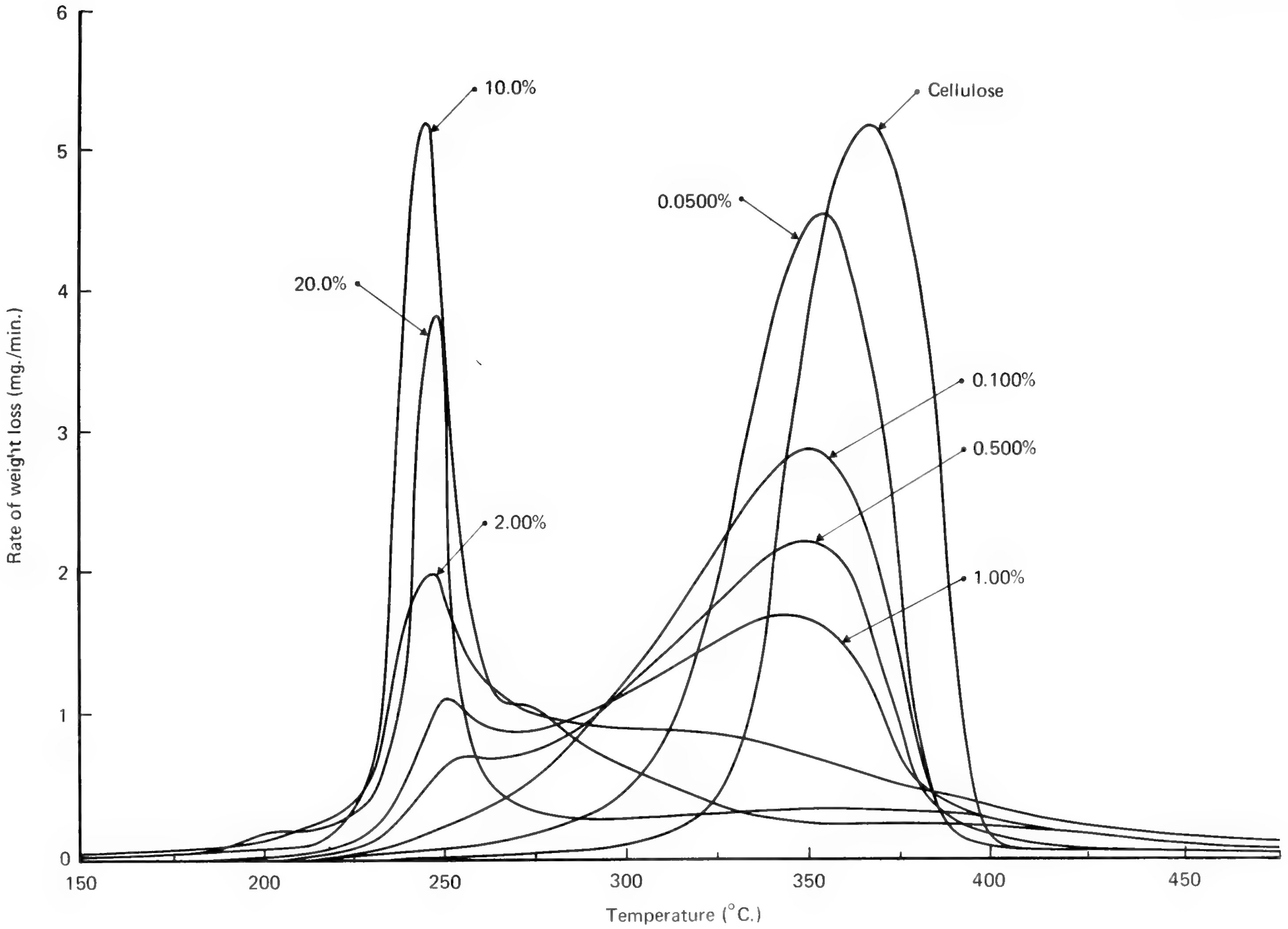
TGA thermograms of cellulose and $(NH_4)_2HPO_4$ treated cellulose heated at 25° C. per minute in a flow of 100 cc. per min



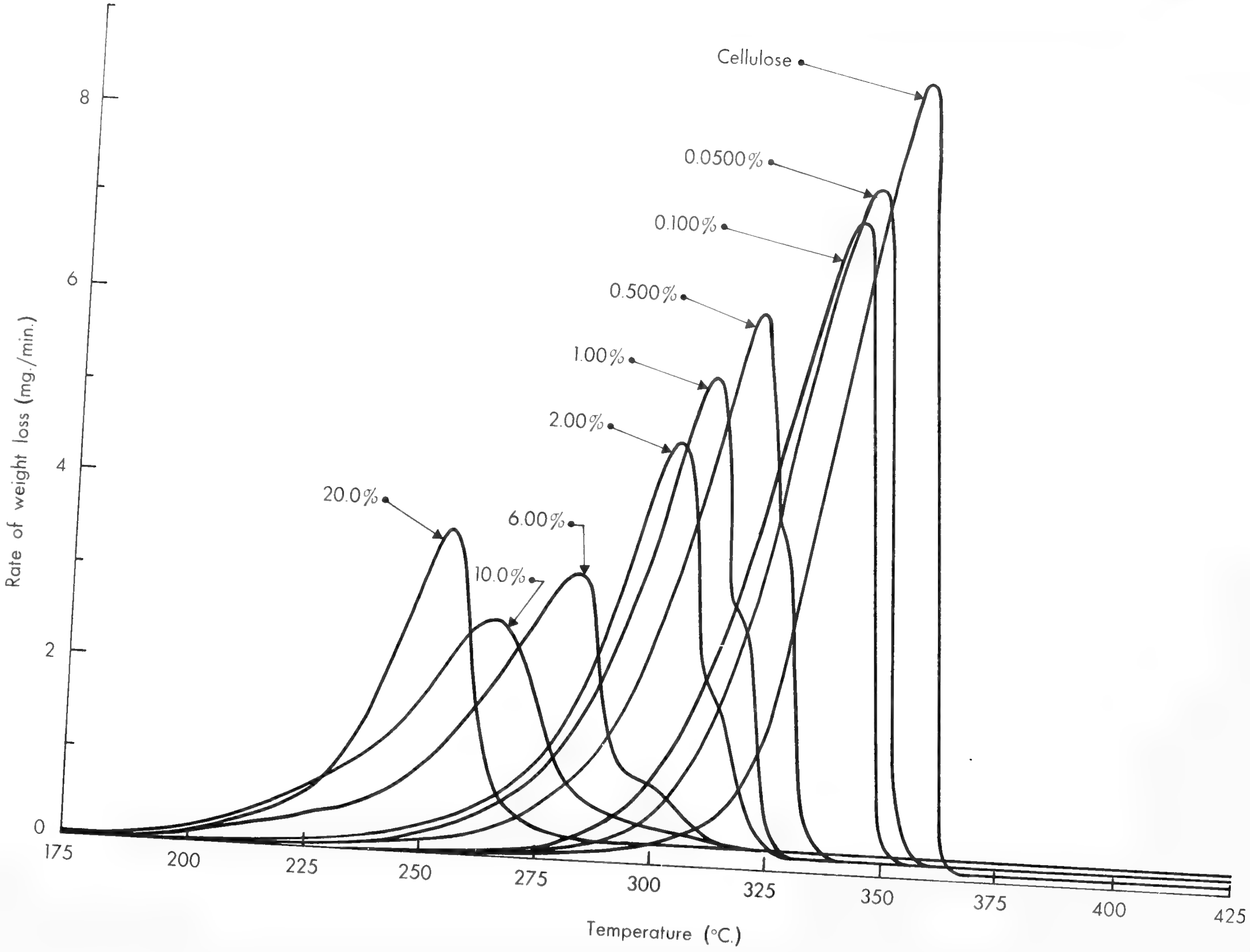
TGA thermograms of cellulose and $(NH_4)_2SO_4$ treated cellulose heated at 25° C. per minute in a flow of 100 cc. per minute air.



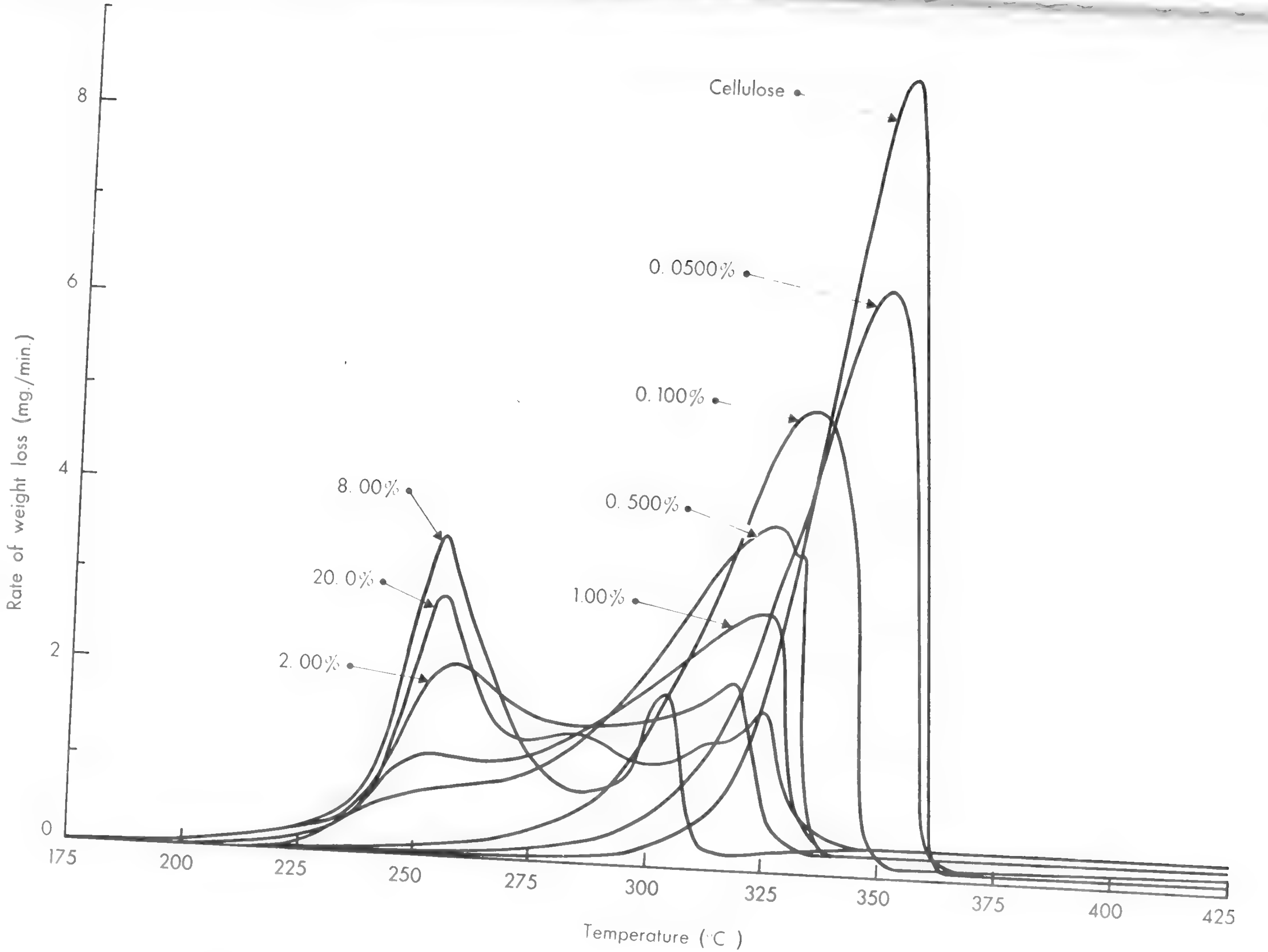
DTG thermograms of cellulose and $(NH_4)_2HPO_4$ treated cellulose heated at 25° C. per minute in a flow of 100 cc. per minute nitrogen.



DTG thermograms of cellulose and $(NH_4)_2SO_4$ treated cellulose heated at 25° C. per minute in a flow of 100 cc. per minute nitrogen.



DTG thermograms of cellulose and $(NH_4)_2HPO_4$ treated cellulose heated at 25° C. per minute in a flow of 100 cc. per minute air.



DTG thermograms of cellulose and $(NH_4)_2SO_4$ treated cellulose heated at 25° C. per minute in a flow of 100 cc. per minute air.

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APPENDIX

Table 1.--*DTA thermal behavior of cellulose and* $(NH_4)_2HPO_4$ *treated cellulose*

Treatment	Nitrogen				Air			
	Thermal effect	Peak temperature °C.	Thermal effect	Peak temperature °C.	Thermal effect	Peak temperature °C.	Thermal effect	Peak temperature °C.
Untreated cellulose			endo	364	endo	354	exo	377
Treated cellulose[1]								
0.0500			endo	347	endo	342	exo	372
.100			endo	340	endo	337	exo	367
.200			endo	329	endo	327	exo	363
.300			endo	330	endo	322	exo	367
.400			endo	327	endo	317	exo	362
.500			endo	324			exo	357
.700			endo	321			exo	363
1.00			endo	316			exo	367
1.50			endo	308			exo	361
2.00			endo	303			exo	360
3.00			endo	293			exo	358
6.00			endo	275			exo	355
10.0	endo	210	endo	269	endo	202	exo	353
12.0	endo	210	endo	265	endo	201	exo	360
15.0	endo	211	endo	263	endo	206	exo	363
20.0	endo	211	endo	257	endo	208	exo	370
25.0	endo	212	endo	262	endo	209	exo	375

[1] Percent by weight chemical.

Table 2.--*DTA thermal behavior of cellulose and* $(NH_4)_2SO_4$ *treated cellulose*

Treatment	Nitrogen				Air			
	Thermal effect	Peak temperature °C.	Thermal effect	Peak temperature °C.	Thermal effect	Peak temperature °C.	Thermal effect	Peak temperature °C.
Untreated cellulose			endo	364	endo	354	exo	377
Treated cellulose[1]								
0.0500			endo	339	endo	339	exo	378
.100			endo	339			exo	372
.200	endo	263	endo	347			exo	370
.300	endo	259					exo	364
.400	endo	258					exo	363
.500	endo	255			endo	258	exo	365
.700	endo	248			endo	258	exo	367
1.00	endo	248			endo	255	exo	368
1.50	endo	249			endo	256	exo	366
2.00	endo	246			endo	256	exo	363
3.00	endo	245			endo	254	exo	360
4.00	endo	243			endo	254	exo	358
5.00	endo	243			endo	254	exo	362
6.00	endo	243			endo	254	exo	357
8.00	endo	243			endo	254	exo	357
10.0	endo	244			endo	257	exo	367
12.0	endo	245			endo	256	exo	378
15.0	endo	244			endo	256	exo	370
20.0	endo	245			endo	256	exo	365
25.0	endo	245			endo	256	exo	367

[1] Percent by weight chemical.

Table 3.--*Effect of $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ on pyrolysis and combustion threshold temperature (°C.)*[1]

Treatment	$(NH_4)_2HPO_4$ treated cellulose		$(NH_4)_2SO_4$ treated cellulose	
	Pyrolysis (N_2)	Combustion (air)	Pyrolysis (N_2)	Combustion (air)
Untreated cellulose	290	298	290	298
Treated cellulose[2]				
0.0500	286	294	257	280
.100	274	285	239	250
.200	264	272	234	242
.300	255	266	230	239
.400	253	262	231	231
.500	250	254	229	229
.700	243	252	228	231
1.00	234	249	224	230
1.50	230	241	229	225
2.00	216	237	213	228
3.00	212	221	210	221
4.00	209	213	202	217
5.00	207	210	201	213
6.00	199	209	200	212
8.00	196	208	199	211
10.0	189	206	196	208
12.0	190	202	195	210
15.0	187	200	194	208
20.0	190	199	195	205
25.0	186	193	190	203

[1] The threshold temperature is arbitrarily denoted as the temperature required to produce a weight loss rate of 0.09 milligrams per minute (< 1 percent of the maximum weight loss rate).

[2] Percent by weight chemical.

Table 4.--*TGA-DTG thermal behavior of cellulose and $(NH_4)_2HPO_4$ treated cellulose in nitrogen*

Treatment	Residue at 450° C.	Normalized cellulose residue at 450° C.	Peak rate of weight loss	Normalized peak rate of weight loss	Peak temperature
	Percent	*Percent*	*Mg./min.*	*Mg./min.*	*°C.*
Untreated cellulose	7.6	7.6	5.13	5.13	367
Treated cellulose[1]					
0.0500	12.2	12.2	5.50	5.50	348
.100	15.0	14.9	5.00	5.00	340
.200	19.6	19.5	4.48	4.49	334
.300	22.2	22.1	4.38	4.39	329
.400	24.4	24.3	4.26	4.28	328
.500	25.8	25.6	4.20	4.22	326
.700	28.6	28.4	4.05	4.08	321
1.00	30.2	29.9	3.96	4.00	316
1.50	34.4	34.0	3.52	3.57	311
2.00	35.8	35.2	3.43	3.50	306
3.00	39.4	38.4	2.90	3.02	298
6.00	42.8	41.4	2.52	2.68	281
10.0	45.2	43.2	2.19	2.43	264
12.0	46.0	43.6	2.33	2.65	261
15.0	47.4	44.6	3.05	3.59	259
20.0	48.4	44.8	3.23	4.04	253
25.0	49.2	44.5	3.66	4.88	250

[1] Percent by weight chemical.

Table 5.--*TGA-DTG thermal behavior of cellulose and $(NH_4)_2SO_4$ treated cellulose in nitrogen*

Treatment	Residue at 450° C.	Normalized cellulose residue at 450° C.	Low temperature peak			High temperature peak		
			Rate of weight loss	Normalized rate of weight loss	Peak temperature	Rate of weight loss	Normalized rate of weight loss	Peak temperature
	Percent	*Percent*	*Mg./min.*	*Mg./min.*	*°C.*	*Mg./min.*	*Mg./min.*	*°C.*
Untreated cellulose	7.6	7.6	--	--	--	5.13	5.13	367
Treated cellulose[1]								
0.0500	7.6	7.6	--	--	--	4.49	4.49	354
.100	12.4	12.4	--	--	--	2.84	2.84	351
.200	14.2	14.2	--	--	--	2.64	2.65	349
.300	15.0	15.0	0.49	0.49	254	2.61	2.62	349
.400	16.8	16.9	.53	.53	253	2.45	2.46	348
.500	18.8	18.9	.71	.71	252	2.22	2.23	348
.700	21.8	22.0	1.01	1.02	251	1.77	1.78	346
1.00	22.1	22.3	1.11	1.12	249	1.70	1.72	345
1.50	24.6	25.0	1.39	1.41	248	1.44	1.46	340
2.00	28.5	29.1	2.12	2.16	247	--	--	--
3.00	32.8	33.7	2.53	2.61	248	--	--	--
4.00	35.4	36.9	2.95	3.07	247	--	--	--
5.00	35.8	37.6	3.20	3.37	246	--	--	--
6.00	36.8	39.0	3.38	3.60	246	--	--	--
8.00	38.6	41.7	3.97	4.32	247	--	--	--
10.0	40.0	44.2	5.19	5.77	245	--	--	--
12.0	40.4	45.7	4.90	5.57	248	--	--	--
15.0	40.8	47.6	4.17	4.91	248	--	--	--
20.0	39.2	48.5	3.83	4.79	248	--	--	--
25.0	36.4	47.9	3.55	4.73	248	--	--	--

[1] Percent by weight chemical.

Table 6.--*TGA and DTG thermal behavior of cellulose and $(NH_4)_2HPO_4$ treated cellulose in air*

Treatment	Residue at 450° C.	Cellulose residue at 450° C.	Peak rate of weight loss	Normalized peak rate of weight loss	Peak temperature
	Percent	*Percent*	*Mg./min.*	*Mg./min.*	*°C.*
Untreated cellulose	7.7	7.7	8.41	8.41	349
Treated cellulose[1]					
0.0500	10.2	10.2	7.43	7.43	341
.100	12.0	11.9	7.06	7.07	339
.200	15.5	15.4	6.34	6.35	331
.300	17.4	17.3	6.15	6.17	325
.400	18.8	18.6	5.82	5.84	322
.500	19.0	18.8	6.07	6.10	318
.700	21.4	21.1	5.60	5.64	313
1.00	22.9	22.5	5.35	5.40	316
1.50	24.8	24.2	4.90	4.97	308
2.00	26.8	26.1	4.63	4.72	302
3.00	29.2	28.1	4.04	4.16	296
4.00	30.1	28.7	3.91	4.07	291
5.00	33.3	31.7	4.50	4.73	279
10.0	37.2	34.3	2.69	2.99	265
12.0	38.3	34.9	2.65	3.01	257
15.0	40.7	36.8	3.61	4.25	254
20.0	43.2	38.3	3.56	4.45	250
25.0	46.3	40.7	4.08	5.44	244

[1] Percent by weight chemical.

Table 7.--*TGA-DTG thermal behavior of cellulose and $(NH_4)_2SO_4$ treated cellulose in air*

Treatment	Residue at 450° C.	Cellulose residue at 450° C.	Low temperature peak			High temperature peak		
			Rate of weight loss	Normalized rate of weight loss	Peak temperature	Rate of weight loss	Normalized rate of weight loss	Peak temperature
	Percent	*Percent*	*Mg./min.*	*Mg./min.*	*°C.*	*Mg./min.*	*Mg./min.*	*°C.*
Untreated cellulose	7.7	7.7	--	--	--	8.41	8.41	349
Treated cellulose[1]								
0.0500	10.4	10.4	--	--	--	6.29	6.29	344
.100	13.2	13.2	--	--	--	5.00	5.01	332
.200	13.8	13.8	--	--	--	4.56	4.57	332
.300	14.3	14.3	0.46	0.46	255	4.11	4.12	330
.400	15.0	15.1	.60	.60	251	4.01	4.03	326
.500	16.0	16.1	.71	.72	252	3.71	3.73	325
.700	18.3	18.4	1.02	1.03	257	2.93	2.95	330
1.00	18.8	19.0	1.12	1.13	255	2.90	2.93	327
1.50	19.6	19.9	1.43	1.45	253	2.72	2.76	324
2.00	22.6	23.1	2.13	2.17	256	1.75	1.78	318
3.00	24.1	24.7	2.69	2.77	251	1.37	1.41	311
4.00	24.8	25.7	3.22	3.35	251	1.90	1.98	306
5.00	25.2	26.4	3.38	3.56	255	1.66	1.75	310
8.00	26.9	29.0	3.45	3.75	256	1.75	1.90	309
10.0	27.0	29.8	4.13	4.57	255	.96	1.06	308
12.0	26.4	29.7	3.69	4.19	257	2.11	2.39	307
15.0	26.3	30.6	3.50	4.12	257	1.48	1.74	312
20.0	25.7	31.6	2.88	3.60	255	--	--	--
25.0	25.8	33.7	3.00	4.00	257	--	--	--

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[1] Percent by weight chemical.

Headquarters for the Intermountain Forest and Range Experiment Station are in Ogden, Utah. Field Research Work Units are maintained in:

- Boise, Idaho
- Bozeman, Montana (in cooperation with Montana State University)
- Logan, Utah (in cooperation with Utah State University)
- Missoula, Montana (in cooperation with University of Montana)
- Moscow, Idaho (in cooperation with the University of Idaho)
- Provo, Utah (in cooperation with Brigham Young University)