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IGNITION INHIBITORS FOR CELLULOSIC MATERIALS

Norman J. Alvares

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IGNITION INHIBITORS FOR CELLULOSIC MATERIALS*

Norman J. Alvares
Lawrence Livermore Laboratory, University of California
Livermore, California 94550

SUMMARY

By exposing samples to various irradiance levels from a calibrated thermal radiation source, the ignition responses of blackened alpha-cellulose and cotton cloth with and without fire-retardant additives were compared. Samples treated with retardant compounds which showed the most promise were then isothermally pyrolyzed in air so that comparisons between the pyrolysis rates of the samples could be obtained. This was done to gain further insight into the mechanisms of ignition and degradation in attempts to arrive at a better understanding of flammability.

Alpha-cellulose samples containing a mixture of boric acid, borax and ammonium di-hydrogen phosphate could not be ignited by irradiances up to 4.0 cal cm^{-2} sec^{-1} (16.7 W/cm^2). At higher irradiances the specimens ignited, but flaming lasted only until the flammable gases were depleted. Cotton cloth containing a polymeric retardant with the designation THPC + MM was found to be ignition-resistant to all irradiances below 7.0 cal cm^{-2} sec^{-1} (29.3 W/cm^2). Comparison of the pyrolysis rates of the retardant-treated alpha-cellulose and the retardant-treated cotton showed that the retardant mechanism is qualitatively the same.

Similar ignition-response measurements were also made with specimens exposed to ionizing radiation. We observed that gamma radiation results in ignition retardance of cellulose, while irradiation by neutrons does not.

INTRODUCTION

Thermal hardening procedures are, by definition, "passive counter-measures" employed to reduce the fire losses of property and lives.[1] Ignition of cellulosic materials by thermal radiation from fires is one of the primary mechanisms for fire spread. Thus, ignition counter-measures should be a primary consideration for thermal-hardening research.

The most desirable ignition-inhibiting technique is to treat the cellulosic material by some as yet unknown method to render it permanently non-flammable, while, at the same time, not appreciably changing its normal physical characteristics. Chemical fire-retardants have been developed which have the ability to effectively prevent fire spread in cellulosic materials.[2-4] The fire retardancy is accomplished by modification of the molecular structure during pyrolysis to produce a reduction in the fraction of flammable gases and tars.[5] It is probable that these chemicals will inhibit ignition in a similar manner.

The goals of these experimentals were to:

- Test the effectiveness of "well known" fire retardants as ignition inhibitors;
- Ascertain what class of chemical inhibitor is most effective in this respect;

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- Modify the molecular structure of the experimental cellulosic material by non-chemical methods, and observe the effect of this treatment on the ignition response.

IGNITION EXPERIMENTS

The cellulosic material used for most of the measurements was black alpha-cellulose, 0.5 mm (0.020-in.) thick and roughly 50 × 75 mm (2 × 3 inches) in size. The cellulose was blackened by 2.5% carbon black during its manufacture so that it has a uniformly high absorptivity during exposure to thermal radiation pulses. A number of samples were soaked in the respective retardant solutions, then pressed between clean paper towels to remove excess liquid, and finally air-dried. The difference between the pre- and post-treatment weight of the samples was an effective measure of the retardant loading. Control samples were soaked in distilled water and dried along with the treated specimens. When controls had returned to their original weight, the treated specimens were ready for exposure to an ignition source. Table 1 lists the retardant salts, solution concentrations, and average dry-weight retardant loading in the cellulose samples.

The thermal radiation source used for these measurements was a 6- by 7.5-cm array of tungsten-halogen high-intensity lamps.[6] The technique of measurement was to place the sample on an adjustable table parallel to the source bank, expose the sample to a calibrated squarewave pulse of radiant energy, and then determine the time to sample ignition. As the distance from

Table 1. Retardants and their loads in the tested materials.

	Retardant	Solution concentration (%)	Resultant load (%)
1.	$KHCO_3$	10	11.9
2.	$KHCO_3$	2	2.72
3.	Borax-boric acid*	10	12.7
4.	Borax-boric acid*	2	2.76
5.	Borax-boric acid*	0.2	0.29
6.	$AlCl_3 \cdot 6H_2O$	2	2.77
7.	$(NH_4)H_2PO_4$	2	2.74
8.	B.B.P.§	10	12.7
9.	$AlCl_3 \cdot 6H_2O$†	2	2.77††
10.	THPC + mm◆	—	24.4

*A mixture of 7% borax and 3% boric acid (N.F.P.A. Handbook, Retardant Formula Number 2).

§A mixture of 3.5% borax, 1.5% boric acid, and 5% $(NH_4)H_2PO_4$.

†Held at 180°C for 1 hr to produce insoluble Al_2O_3 and HCl ↑. Washed after cooling to leach out residual HCl.

◆Developed by the Department of Agriculture to retard flaming in cotton cloth. THPC + mm = tetrakis (hydroxymethyl) phosphonium chloride + methylolmelamine.

††Pre-heat treatment loading.

the source increases, the irradiance is reduced. Thus, both the flaming- and glowing-ignition thresholds at various irradiance levels can be easily and accurately measured.[7]

PYROLYSIS EXPERIMENTS

To determine the relative retardance between the additives, we examined the rate of pyrolysis of the specimens in air. These measurements were made by placing the specimens in a highly stabilized furnace set at 315° ± 5°C for a predetermined period of time, and then measuring the relative weight loss with a sensitive torsion balance. This procedure was repeated for increasing periods of time until the samples ignited to a glowing combustion, or no further weight loss was observed.

Measurements were made of the ignition response and pyrolysis rate of untreated cotton cloth, and cotton cloth treated with polymeric fire retardant developed by the Department of Agriculture at New Orleans.[4] The untreated cloth was the same thickness and weight as the treated cloth. However, it had been previously purchased for other ignition work. The main difference between these specimens was the color and the retardant treatment. The treated cloth was dark green, while the untreated cloth was black.

EXPERIMENTAL PROCEDURE

The retardants chosen for ignition studies are shown in Table 1. These are: (1) a mixture of borax and boric acid (B.B.A.); (2) potassium bicarbonate ($KHCO_3$); (3) ammonium di-hydrogen phosphate $(NH_4)\ H_2PO_4$, and (4) hydrated aluminum chloride ($AlCl_3 + 6H_2O$).

Table 1 also lists three synthesized retardant treatments which were subjected not only to ignition measurements, but also to air-pyrolysis measurements. The solution of 3.5% boric acid and 5% $(NH_4)H_2PO_4$ (B.B.P.) was made with the hopes that the combination of good flaming and glowing ignition inhibitors may produce a good "all around" inhibitor. Another process was to hold samples treated with the 2.0% solution of $AlCl{\cdot}6H_2O$ at 180°C for several hours so that the conversion of $AlCl_3{\cdot}6H_2O$ to insoluble Al_2O_3 + HCl gas could occur. This procedure was suggested by Parker[1] who stated that fire retardance in treated cellulose may be a result of a catalytic action by the oxygen-bearing retardants, causing greater conversion of pyrolysis products to char. Further, the acidic or basic characteristics of the retardant salts serve simply to increase the rate of molecular scissions, thus increasing the pyrolysis rate. Removal of HCl by the above treatment could reduce the [increase in] the pyrolysis rate and yet impart fire retardance.

The last retardant listed in Table 1, THPC + MM, was selected from a variety of retardant-treated cotton cloths supplied by the Department of Agriculture Southern Regional Laboratory. The basis of selection was governed by determining which of the retardant-treated material took the longest to ignite when exposed to a constant thermal flux. All of the treated cotton samples were found to be quite flame resistant; however, the THPC + MM-treated cotton with highest retardant loading had the greatest resistance to ignition. This material also is a phosphorus-containing polymer which is of interest because of its glow-retarding properties.

RESULTS

The ignition response of the retardant-treated samples, compared to the ignition response of the control, are shown in Fig. 1 in conjunction with the identification code of Table 1. The pyrolysis data are presented in Fig. 2.

Figure 1 shows that most of the additives reduce the susceptibility of the tested cellulosic materials to flaming ignition, depending on the amount

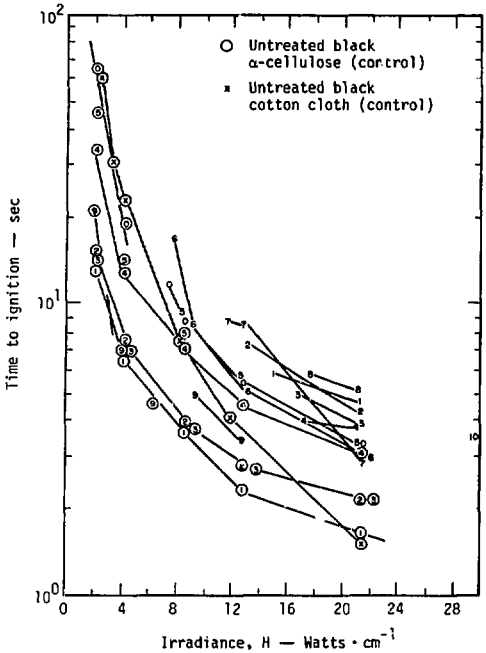

Fig. 1. Ignition in air. Numbers refer to identification of retardants listed in Table 1. Uncircled numbers refer to flaming points; circled numbers refer to glowing points.

of additive absorbed in the material. Many of these retardants increased the susceptibility of the materials to glowing ignition.

Figure 2 shows that the pyrolysis rate increases in all the treated specimens. In most cases, a large quantity of vapor is initially evolved after which the visible evolution of gas is either non-existent or minimal. The gases of this evolution are readily ignitable with a hot wire pilot source placed in the flow. Only cellulose treated with 2.0% $(NH_4)H_2PO_4$ survives the exposure intact in the form of a brittle char, which vaguely resembles the original specimens. The other samples, if they were ignited, are completely consumed by glowing combustion.

Note that the addition of an inert blackening agent, such as carbon black, has no effect upon the rate of thermal degradation. Also interesting is the fact that the pyrolyses of untreated alpha-cellulose and cotton cloth are quite similar. It is impossible to measure weight loss of both black and

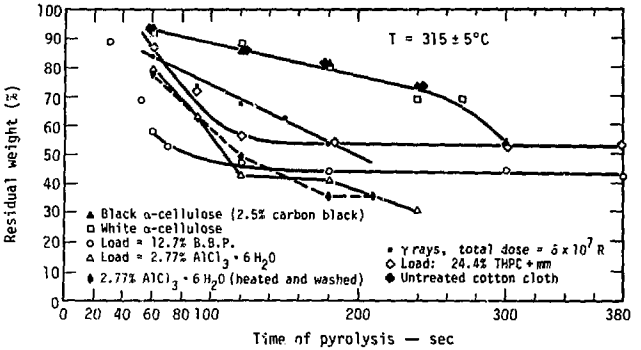

Fig. 2. Pyrolysis of α-cellulose.

white untreated cellulose after 5 min. at the testing temperature since all of the samples glow beyond this point. The abrupt change in the shape of the weight regression curve past 4 min. indicates a region of faster pyrolysis which just precedes the onset of glowing combustion.

CONCLUSIONS

The following conclusions summarize the work reported here:

- As a general rule, good combustion retardants are also good ignition inhibitors.
- A mixture of 10% B.B.P. makes an excellent temporary additive for inhibiting ignition.
- The additives developed by the Department of Agriculture for cotton cloth are excellent, semi-permanent retardants for ignition by thermal radiation.
- At irradiances intense enough to ignite cellulosics treated with the B.B.P. or the THPC + MM retardants described here, only transient flaming ignition will occur. Furthermore, flaming will last only until pyrolysis is complete, leaving an inert residual char. Since the duration of flaming combustion is short, the opportunity for the spread of fire is greatly reduced.
- The gases initially expelled from pyrolyzing retardant-treated cellulose are ignitable.
- Retardant compounds containing phosphorus appear to be more successful in preventing afterglow than those that do not contain phosphorus.
- There is evidence which shows that ionizing radiation does afford ignition protection to cellulosic materials by some process which has not been defined.

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