OCD Work Unit No. 2542A
USNRDL-TR-67-125
10 August 1967

IGNITION HARDENING OF CELLULOSIC MATERIALS

by

N. J. Alvares
T. H. Anderson*

U.S. NAVAL RADIOLOGICAL DEFENSE LABORATORY

SAN FRANCISCO · CALIFORNIA · 94135

34

THERMAL RADIATION BRANCH
R. S. Alger, Head

RADIATION PHYSICS DIVISION
C. S. Cook, Head

ADMINISTRATIVE INFORMATION

This report covers a portion of the work authorized by the Office of Civil Defense under OCD Work Order DAHC20-67-C-0149, Work Unit 2542A.

*Present address: Ames Research Center, Moffett Field, California.

DDC AVAILABILITY NOTICE

This document has been approved for public release and sale; its distribution is unlimited

OCD REVIEW NOTICE

This report has been reviewed in the Office of Civil Defense and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Office of Civil Defense.

Eugene P. Cooper

Eugene P. Cooper
Technical Director

D. C. Campbell, CAPT USN
Commanding Officer and Director

SUMMARY OF REPORT

IGNITION HARDENING OF CELLULOSIC MATERIALS

USNRDL-TR-67-125, dated 10 August 1967

by N. J. Alvares and T. H. Anderson

The Problem

The objectives of this work are the following: (1) To determine the most effective fire retardant for fabrics in terms of ignition protection against high energy-fluxes; (2) To determine the concentration of such a retarder required to prevent a material from being ignited by a thermal pulse from a given nuclear weapon burst; (3) To investigate the retardation mechanisms of various types of retarder treatment from the point of view of predicting even more effective but as yet untried candidates. The first phase of the work will measure the ignition energy of alpha-cellulose as a function of retarder concentration for retarders selected from the list of fire retardant treatments recommended by the National Fire Protection Association. A more limited set of tests will be made on cotton and other household fabrics. The second phase of the work will examine different classes of treatments that might have potential value in thermal hardening. The third phase will involve the development of techniques necessary to study the retardation processes in detail.

The Findings

The significant results are: (1) Good flame and glow retardants make good flaming- or glowing-ignition inhibitors. (2) Retardant-treated cellulosics will ignite with only a transient flaming ignition when exposed to high-intensity thermal radiation. (3) Addition of phosphorus-containing compounds to cellulosics supplies protection from glowing ignition. (4) Cellulosics treated with intense gamma radiation do not ignite as readily as unirradiated cellulosics. (5) Cellulosics exposed to a large flux of neutrons show no change in ignition response from unexposed specimens. (6) Retardant-treated cellulose ignites faster in oxygen atmospheres than do untreated cellulosics.

ABSTRACT

The ignition response of blackened alpha-cellulose and cotton cloth, containing fire retardant additives, was compared to the ignition response of these materials without additives. This information was obtained by exposing the samples to various irradiance levels from a calibrated thermal radiation source. 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. These comparisons yielded further insight into the mechanism of thermal degradation. Similar ignition response measurements were made with specimens exposed to ionizing radiation.

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}. Above this value, transient ignition would occur but flaming would last only until the ignitible gases were exhausted from the samples. Cotton cloth containing a polymeric retardant with the designation THPC + MM was found to be ignition resistant below an irradiance of 7.0 cal cm^{-2} sec^{-1}. Comparison of the pyrolysis rates of the retardant treated alpha-cellulose and cotton showed that the retardant mechanism is qualitatively the same. It was also found that gamma radiation results in ignition retardance of cellulose, while irradiation by neutrons, does not.

SUMMARY

Problem

The objectives of this work are the following: (1) To determine the most effective fire retardant for fabrics in terms of ignition protection against high energy-fluxes; (2) To determine the concentration of such a retarder required to prevent a material from being ignited by a thermal pulse from a given nuclear weapon burst; (3) To investigate the retardation mechanisms of various types of retarder treatment from the point of view of predicting even more effective but as yet untried candidates. The first phase of the work will measure the ignition energy of alpha-cellulose as a function of retarder concentration for retarders selected from the list of fire retardant treatments recommended by the National Fire Protection Association. A more limited set of tests will be made on cotton and other household fabrics. The second phase of the work will examine different classes of treatments that might have potential value in thermal hardening. The third phase will involve the development of techniques necessary to study the retardation processes in detail.

Findings

The significant results are: (1) Good flame and glow retardants make good flaming- or glowing-ignition inhibitors. (2) Retardant-treated cellulosics will ignite with only a transient flaming ignition when exposed to high-intensity thermal radiation. (3) Addition of phosphorus-containing compounds to cellulosics supplies protection from glowing ignition. (4) Cellulosics treated with intense gamma radiation do not ignite as readily as unirradiated cellulosics. (5) Cellulosics exposed to a large flux of neutrons show no change in ignition response from unexposed specimens. (6) Retardant-treated cellulose ignites faster in oxygen atmospheres than do untreated cellulosics.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES

I. INTRODUCTION

The scope of work as given in the Task Order No. 66-200(77) is as follows:

> The objectives of this work are the following: (1) To determine the most effective fire retardant for fabrics in terms of ignition protection against high energy-fluxes. (2) To determine the concentration of such a retarder required to prevent a material from being ignited by a thermal pulse from a given nuclear weapon burst. (3) To investigate the retardation mechanisms of various types of retarder treatment from the point of view of predicting even more effective but as yet untried candidates. The first phase of the work will measure the ignition energy of alpha-cellulose as a function of retarder concentration for retarders selected from the list of fire retardant treatments recommended by the National Fire Protection Association. A more limited set of tests will be made on cotton and other household fabrics. The second phase of the work will examine different classes of treatments that might have potential value in thermal hardening. The third phase will involve the development of techniques necessary to study the retardation processes in detail. This will include development of a highly sensitive means of determining the time history of the pyrolysis products.
>
> The first and second phases of the work will be done as the first year of work. The third phase will be done in the second year.

Thermal hardening procedures are, by definition, "Passive countermeasures employed to reduce the fire losses of property and lives which could result from nuclear-weapons explosions."[1] Ignition of cellulosic materials by the thermal radiation would be one of the primary sources of fires, thus, ignition counter-measures are the first 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.[2,3,4] 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. It is possible that these chemicals will inhibit ignition in a similar manner.

The goal of this experimental program is to: (1) Test the effectiveness of "well known" fire retardants as ignition inhibitors; (2) Ascertain what class of chemical inhibitor is most effective in this respect; (3) Determine "HOW" the most effective retardant differs from the other retardants; (4) Attempt to find out "WHY" the most effective retardant works, and (5) Modify the molecular structure of the experimental cellulosic material by non-chemical methods, and observe the effect of this treatment on the ignition response.

II. EXPERIMENTAL PROCEDURE

The retardants chosen for study were: (1) A mixture of borax and boric acid (B.B.A.); (2) Potassium carbonate ($KHCO_3$); (3) Ammonium di-hydrogen phosphate $(NH_4)H_2PO_4$, and (4) Hydrated aluminum chloride ($A\ell C\ell_3 + 6H_2O$). All the above chemicals have been used as fire retardants, and they have been the subject of other research programs which are concerned with the mechanism of combustion inhibition.[5]

The cellulosic material used for most of the measurements was black alpha-cellulose, 20 mils thick and roughly 2 x 3 inches in size. The cellulose was blackened by 2.5% carbon black during its manufacture so that it would have 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 the controls had returned to their original weight, the treated specimens were ready for exposure to an ignition source. Table I 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 the NRDL Tungsten-Iodine source.[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 square-wave pulse of radiant energy, then determine the time to sample ignition. As the distance from the source increases, the irradiance decreases; thus, both the flaming- and glowing-ignition thresholds at various irradiance levels can be easily and accurately measured.[7] Figure 1 shows the experimental setup, and Figure 2 is the irradiance calibration of the source.

Determination of "HOW" the retardancy of one additive differed from another was examined by finding 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°C ± 5° for a pre-determined period of time, then measuring the relative weight loss with a sensitive torsion balance. This procedure is repeated for increasing periods of time, until the samples will consistently be consumed by glowing combustion, or no further weight loss is observed. Figure 3 shows the temperature response of an untreated, cellulose sample placed in the furnace. Note the time necessary for the sample to reach the furnace temperature was 60 seconds. This time to uniform temperature was found to be consistent for several determinations. Therefore, the weight-loss measurements were only valid after the initial heat-up time of 60 seconds.

Measurements were made of the ignition response and pyrolysis rate of untreated cotton cloth, and cotton cloth treated with polymeric fire retardants developed by the Department of Agriculture at New Orleans.[4] The treated cloth was generously supplied by the Southern Regional Laboratory of the U.S.D.A. to NRDL for inclusion in this program. The untreated cloth was the same thickness and weight as the treated cloth. However, it had been previously purchased in San Francisco 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.

Table II lists three retardant treatments which were subject not only to ignition measurements, but also to air-pyrolysis measurement. The solution of 3.5% borax, 1.5% boric acid, and 5% $(NH_4)H_2PO_4$ (B.B.P.) was made since we thought 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 $A\ell C\ell_3 + 6H_2O$ at 180°C for several hours, so that the conversion of $A\ell C\ell_3 + 6H_2O$ to insoluble $A\ell_2O_3$ + $HC\ell$ gas could occur. This procedure was suggested by Parker,[1] who stated that fire retardancy 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 $HC\ell$ by the above treatment could reduce the increase in the pyrolysis rate and yet still impart fire retardance.

The last retardant listed in Table II, THPC + MM, was selected from a variety of retardant-treated cotton cloths sent to NRDL by the 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 retardant-treated cotton samples were quite flame resistant; however, the THPC + MM-treated cotton with highest retardant loading had the greatest ignition resistance. This material also is a phosphorus-containing polymer, which is of interest because of its glow-retarding properties.

III. RESULTS

The ignition response of the retardant-treated samples, compared to the ignition response of the control are shown in Figures 4, 5, and 6. Figure 4 contains the data from samples treated with 0.2%, 2.0%, and 10.0% solutions of B.B.A. The data from samples treated with 2.0% and 10.0% solutions of $KHCO_3$ are shown in Figure 5. The effects of 2.0% solutions of $A\ell C\ell_3 + 6H_2O$ and $(NH_4)H_2PO_4$ are illustrated in Figure 6.

We can see from Figures 4 and 5, that the addition of similar amounts of both B.B.A. and $KHCO_3$ to cellulose results in similar ignition characteristics. Both additives significantly decrease the cellulose's susceptibility to flaming ignition, and they both enhance the chance of destruction by glowing ignition. In comparison, it appears that the B.B.A. is slightly more efficient as a flaming-ignition inhibitor, and is less susceptible to glowing ignition.

From Figure 6, it is obvious that the 2% solution of $A\ell C\ell_3 + 6H_2O$ imparts no retardancy to cellulose at relatively high irradiances, since it causes ignition to occur before untreated cellulose can ignite. Also the glowing-ignition threshold decreases at low irradiances. Cellulose treated with the 2.0% solution of $(NH_4)H_2PO_4$ is not as good a flaming-ignition retardant as the cellulose treated with 2.0% solutions of either B.B.A. or $KHCO_3$. But, most significantly, the $(NH_4)H_2PO_4$ treated cellulose would <u>not</u> glow.

It appeared that the pyrolysis rate was increased in all the treated specimens, since the evolution of gas occurred early in the exposure relative to untreated cellulose. In most cases, a large quantity of gas and vapor came out with a sudden puff, after which the visible evolution of gas was either non-existent or minimal. Only cellulose treated with 2.0% $(NH_4)H_2PO_4$ survived the exposure intact in the form of a carbonaceous, brittle char, vaguely resembling the original specimens. The other samples, if they were ignited, were completely consumed by glowing combustion.

The ignition response of specimens treated with the 10% solution of B.B.P., and the heat-treated $A\ell C\ell_3$-containing samples, compared to untreated cellulose, are shown in Figure 7. Combining the attributes of additives which are good flame and good glow retardants proves to be quite effective as an ignition inhibition technique. At irradiances less than 4.2 cal cm^{-2} sec^{-1}, cellulose treated with B.B.P. will not ignite. Above 4.2 cal cm^{-2} sec^{-1}, transient flaming ignition will occur until the ignitible gases are exhausted.

Pyrolysis was complete in a very short time at all irradiance levels, and the remaining residue is a brittle char which still retains its shape and some strength.

Holding the 2.0% $A\ell C\ell_3 + 6H_2O$-treated sample at 180°C and afterwards leaching out the residual $HC\ell$ obviously did not increase the retardancy of the cellulose. Indeed, the result of this treatment was to increase its susceptibility to both flaming and glowing ignition. No test was made which would indicate whether or not these procedures did result in the formation of $A\ell_2O_3$ other than the observation that the wash water was slightly acidic. It is entirely possible that the heating and leaching procedure was too vigorous, since it resulted in an average sample weight loss of 9.1%.

Figure 8 shows how the addition of retardants to cellulose modifies its pyrolysis rate. Addition of an inert blackening agent, such as carbon black, has no effect upon the rate of thermal degradation. This is obvious from a perusal of the top curve. Measurements on both black and white untreated cellulose are impossible after five minutes, since all of the samples glow beyond this point. The change in shape past four minutes indicates a region of faster pyrolysis which just precedes the onset of glowing combustion.

Samples treated with the B.B.P. solution pyrolize so fast that, by the time the specimens have attained isothermal conditions, most of the pyrolysis has occurred. The consistency of the residual weight, after two minutes, is an indication of the inertness of the residual char. Both the heat-treated and non-heat-treated samples containing $A\ell C\ell_3 + 6H_2O$ exhibit a similar pyrolysis rate. This evidence indicates that perhaps the heat treatments did not produce the anticipated conversion of $A\ell C\ell_3 + 6H_2O$ to $A\ell_2O_3 + HC\ell$. An indication of the pyrolysis rate of gamma irradiated cellulose is also shown in this figure. We note that the rate is faster than the rate of untreated cellulose, thus pointing to a very interesting effect to be studied in future research.

Figures 9 and 10 show, respectively: the ignition response of cotton cloth treated with THPC + MM compared to untreated cotton cloth; and the effect of the addition of THPC + MM to cotton cloth on the pyrolysis rate, as compared to the pyrolysis rate of untreated cotton cloth.

In Figure 9 we see only one ignition point for the treated cloth, at an irradiance of 7.0 cal cm^{-2} sec^{-1}, indicating the efficiency of this retardant process. We also note that there are no glowing-ignition points. This is undoubtedly due to the presence of a phosphorus compound in the retardant. The pyrolysis rates of the untreated and treated cloth exhibit no startling characteristics. The treated material has a faster pyrolysis rate than does the untreated material. Thus, the retardant mechanism is probably similar to the mechanism of the chemical additives in the alpha-cellulose. It is interesting to note that the pyrolysis rate of the cotton cloth containing no retardants is almost identical to the pyrolysis rate of untreated alpha-cellulose.

Several unusual techniques were employed to modify the cellulose molecule in such a way as to affect the ignition characteristics of the samples. For example, some of the cellulose samples were exposed to large fluxes of both neutrons and gamma rays. The total dose received by the neutron-exposed cellulose was 2.2×10^7 neutrons. This treatment caused no observable effect in either the ignition response or the general physical characteristics of the cellulose. A dose of 6×10^7 roentgens of gamma rays, however, resulted in a noticeable embrittlement of the cellulose. Furthermore, at an irradiance of 2.0 cal cm^{-2} sec^{-1} the time to ignition of the gamma-ray-treated specimens was on the average 12% longer than for the untreated specimens. The observed ignition delay could be due to cross-linking of the cellulose molecules, which could possibly interfere with the break-up of the molecules during pyrolysis. A similar embrittlement was caused by heating the cellulose samples at 180°C for a duration of one hour. But there was no noticeable effect upon the ignition response.

The ignition response of retardant-treated and -untreated cellulose in 1/3 and 1.0 atmospheres of pure oxygen were made with the result that the treated specimens always ignited first, relative to untreated specimens. These measurements were made with the apparatus shown in Figure 11. The ignition response of cellulose treated with 10% B.B.P. was closest to the ignition response of untreated cellulose. The difference in time to ignition was only 12% of 1.0 atmosphere and 6% at 1/3 atmosphere of pure oxygen. The other retardants caused ignition time as much as 50% faster than untreated cellulose.

Another interesting phenomenon resulting from retardant treatment of cellulosic materials was that the gases emanating from the irradiated surface were flammable. We observed that the initial puff of gas, caused by the accelerated pyrolysis rate was readily ignited when a hot wire pilot source was placed in the flow of gas.

In pure oxygen, it appears that increases in the pyrolysis rate result in decreases in the time to ignition. The exact opposite is true for samples pyrolyzing in air. Apparently the combustible gases and vapors are produced quite early during the pyrolysis of treated cellulose. In pure oxygen, where the critical irradiance of cellulosic materials is significantly lowered, the environmental conditions are probably favorable for ignition of the initial puff of gases. However, in air, most of the combustible gases have been dispersed before the surface temperature is hot enough to initiate ignition.

The relative response of retardant treated cellulose in pure oxygen environments appears to be directly related to the glow-retardant efficiency of the additive. We observe, in Figures 4 and 5, that the more B.B.A. or $KHCO_3$ we add to our specimens, the more susceptible they are to glowing ignition. From Figures 6 and 7, we see that compounds containing phosphorus salts show no glowing ignition response. Figure 8 shows that the weight-loss-rate of cellulose treated with both B.B.P. and $A\ell C\ell_3$ has been significantly increased over the rate for untreated cellulose. Further, the B.B.P.-treated samples lose weight faster than any of the other samples. Increasing the pyrolysis rates should result in corresponding decreases in the time to ignition in pure oxygen. Since the B.B.P. treated cellulose violates this observation, we can only attribute its relatively longer ignition time to the glow retardance properties of the phosphorus-salt compounds.

Measurements made of the ignition response of retardant-treated and -untreated cotton cloth contained in pure oxygen show similar results to that of the alpha-cellulose.

IV. DISCUSSION

The class of fire retardants tested during this research promoted an accelerated pyrolysis rate in the cellulosic fuel so treated. The increased rate is presumed to be due to the breakup of the cellulosic molecule by the action of acidic or basic components of the retardant salt, which are formed during pyrolysis. This breakup results in a decrease in the formation of flammable fuels, and an increase in char.[9]

Apparently, the inhibition of flaming ignition observed during these measurements is due simply to the fact that pyrolysis is complete before the surface temperature becomes high enough to cause ignition.

We do not understand why glowing ignition is promoted when $KHCO_3$ or B.B.A. is used as the retardant. We also do not know why compounds containing phosphorus completely protect the cellulose from glowing. There is some evidence that glow retardants act as catalysts which favor the production of carbon monoxide in the reaction between carbon and oxygen, while the other retardants allow the carbon and oxygen to react directly and form carbon dioxide, which is a far more energetic process. However, our measurements show that the 10% B.B.P. mixture is very effective in erasing the hazard of both flaming- and glowing-ignition by thermal radiation below an irradiance level of 4.2 cal cm^{-2} sec^{-1}. This combination also reduces the ignition hazard above 4.2 cal cm^{-2} sec^{-1}. Similar mixtures have been previously employed as combustion retardants with a large measure of success.[3]

Cotton cloth, treated with the polymeric retardants, are quite ignition resistant, as we see from Figure 9, which shows that THPC + MM-treated cloth will not ignite at irradiances below 7.0 cal cm^{-2} sec^{-1}. The retardant mechanism probably is similar to the retardant mechanism of the treated alpha-cellulose, since the pyrolysis rates are in qualitative agreement. The retardance afforded by this process is obviously superior to the method of adding retardants by simply soaking materials in chemical solutions. However, this treatment is also more complicated and expensive.

The critical irradiance (Hc, with units of cal cm^{-2} sec^{-1}) of an ignitible solid fuel is defined as the lowest irradiance at which the fuel will ignite. Hc for black alpha-cellulose is about 0.4.[7] Thus, black alpha-cellulose would never ignite if exposed to a thermal-radiation flux where $H < 0.4$. This does not mean that the cellulose will not slowly pyrolize, and change structure, but it will not ignite. Addition of retardants to cellulosic fuels serves to increase Hc. For example, Hc for alpha-cellulose treated with a 10% solution of B.B.P. will not ignite where $H < 4.2$; therefore the Hc for B.B.P. treated alpha-cellulose is 4.2. Similarly, cotton cloth treated with THPC + MM will not ignite below $H = 7.0$. Therefore, Hc for this material is 7.0.

For the purpose of ignition protection from the thermal pulse of a nuclear weapon, we can be assured that cellulosic fuels containing the same additives will not ignite so long as the peak irradiance (Hp) never exceeds the Hc of the treated materials. Even if Hp is larger than Hc, ignition may not occur if the time that the thermal pulse exceeds Hc is small. If Hp is significantly larger than Hc, then transient flaming ignition will occur. However, the flame will extinguish, as soon as the ignitible fraction of the THPC + MM- or B.B.P.-treated cellulosic has been exhausted, even if the material is still exposed to thermal radiation. As stated before, these materials still retain some strength after pyrolysis and if they are not disturbed, they can still afford thermal shielding to protect other combustible items from ignition by thermal radiation.

Use of these materials will abolish the hazard of fire spread by radiation from established fires, since the intensity of thermal radiation emitted from fires seldom attains the magnitude of the Hc for B.B.P. treated cellulose. Further, fire spread by embers and brands is minimized due to the known flame inhibition qualities of the retardant-treated cellulosics.

We made no attempt to assess the deleterious side effects incurred by adding the retardant compound to our cellulose samples, other than noting that they were a bit more brittle and heavier than the untreated samples. The treated cotton cloth samples were slightly stiffer than similar untreated cloth. More detailed accounts of the detrimental effects of retardant treatments are found in the other references.[1,3]

V. CONCLUSIONS AND RECOMMENDATIONS

We can sum up our conclusions as follows:

1. As a general rule, good combustion retardants are good ignition inhibitors.

2. A mixture of 10% B.B.P. makes an excellent temporary additive for ignition inhibition.

3. The additives developed by the Department of Agriculture for cotton cloth are excellent, permanent retardants for ignition by thermal radiation.

4. At irradiances intense enough to ignite cellulosics treated with the B.B.P. or the THPC + MM retardants described herein, 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.

5. Materials containing the additives discussed in this report are extreme fire hazards in oxygen-rich environments.

6. The gases initially expelled from pyrolyzing retardant-treated cellulose are ignitible.

7. Retardant compounds containing phosphorus appear to be more successful in preventing glow than those that do not contain phosphorus.

8. There is evidence which shows that ionizing radiation does afford ignition protection to cellulosic materials by some process which has not, as yet, been defined.

This paper provides evidence which indicates that established fire-retardant techniques can be used to produce very effective ignition inhibition in cellulosic materials. It is our contention that the use of these additives in drapery and upholstery materials would reduce the hazard of fire initiation and spread by a large degree. Indeed, because of the nature of the pyrolysis mechanism of retardant-treated cellulosics, there may be no danger of fire spread from these materials.

Both the THPC + MM and the B.B.P. retardant treatments have proven to be effective ignition inhibitors. Unfortunately, both treatments produce destructive side effects in cellulosic materials. Further research as to the kinetics and mechanisms of cellulose pyrolysis, and as to the effect that retardant compounds have upon the pyrolysis mechanism may lead to techniques of combustion and ignition retardance which are more effective, less expensive, and can be applied to more materials than those that exist now. We may also discover techniques which have less detrimental side effects on the other properties of the protected materials.

REFERENCES

1. Parker, W. J., "Thermal Hardening Considerations Pertaining to Residential Areas," USNRDL-TR-984, 24 Feb 1966..

2. Trylon, G. H., "Fire Protection Hand Book," 12th Edition, National Fire Protection Association, 60 Batterymarch Street, Boston 10, Mass., 1962.

3. Little, R. W., "Flame Proofing, Textile Fabrics," American Chemistry Society Monograph No. 104, Reinhold Publishing Corporation, New York, 1947.

4. Perkins, R. M., Drake, Jr., G. L., and Reeves, W. A., "DTA and TGA Studies of Flame-Resistant Fabrics," Journal of Applied Polymer Science, Vol. 10, 1966.

5. Tang, W. K. and Neill, W. K., "Effect of Flame Retardants on the Pyrolysis and Combustion of Cellulose," Journal of Polymer Science, Vol. 6, 1964.

6. Jenkins, R. J., "Calorimeters and Radiometers for the Measurement of Large Thermal Irradiances," USNRDL-TR-839, 6 Apr 1965.

7. Martin, S. B. and Alvares, N. J., "Ignition Thresholds for Large-Yield Nuclear Weapons," USNRDL-TR-1007, 11 Apr 1966.

8. Lipska, Anne E., "Isothermal Degradation of Untreated and Fire Retardant Treated Cellulose at 350°C," Paper No. 67-19, 1967 Spring Meeting, Western States Section, The Combustion Institute, La Jolla, California.

9. Browne, F. L., "Theories of the Combustion of Wood and Its Control," Forest Products Laboratory Report #2136, Dec 1958.

NRDL-417-67

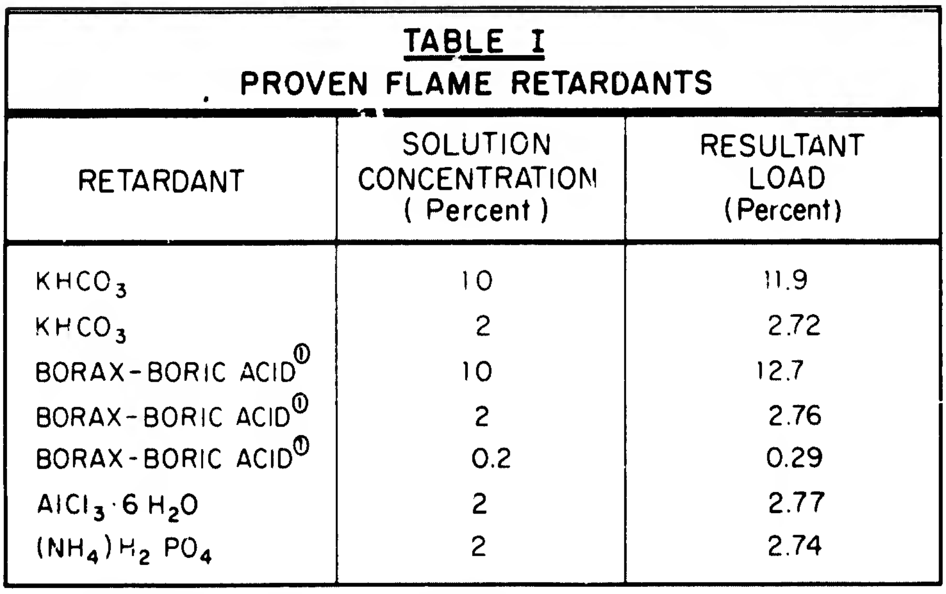


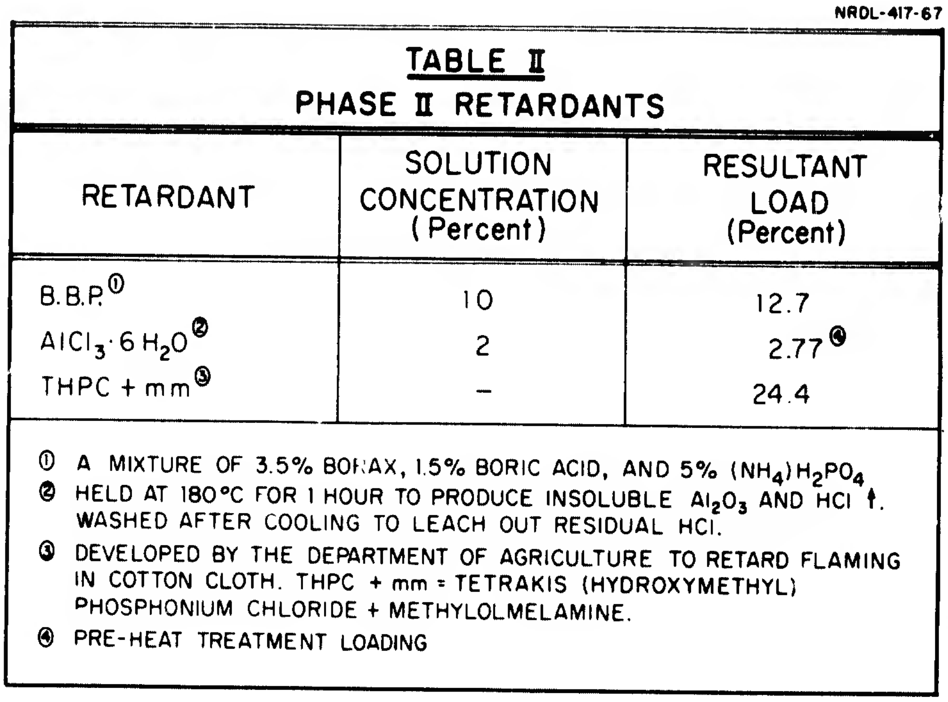
TABLE I

PROVEN FLAME RETARDANTS

RETARDANT	SOLUTION CONCENTRATION (Percent)	RESULTANT LOAD (Percent)
$KHCO_3$	10	11.9
$KHCO_3$	2	2.72
BORAX-BORIC ACID①	10	12.7
BORAX-BORIC ACID①	2	2.76
BORAX-BORIC ACID①	0.2	0.29
$AlCl_3 \cdot 6H_2O$	2	2.77
$(NH_4)H_2PO_4$	2	2.74

① A MIXTURE OF 7% BORAX AND 3% BORIC ACID (N.F.P.A. HANDBOOK, RETARDANT FORMULA NUMBER 2)

Table I Standard Chemical Flame Retardants, Solution Concentrations and Sample Weight Add-On.



NRDL-417-67

TABLE II
PHASE II RETARDANTS

RETARDANT	SOLUTION CONCENTRATION (Percent)	RESULTANT LOAD (Percent)
B.B.P.①	10	12.7
$AlCl_3 \cdot 6H_2O$②	2	2.77④
THPC + mm③	–	24.4

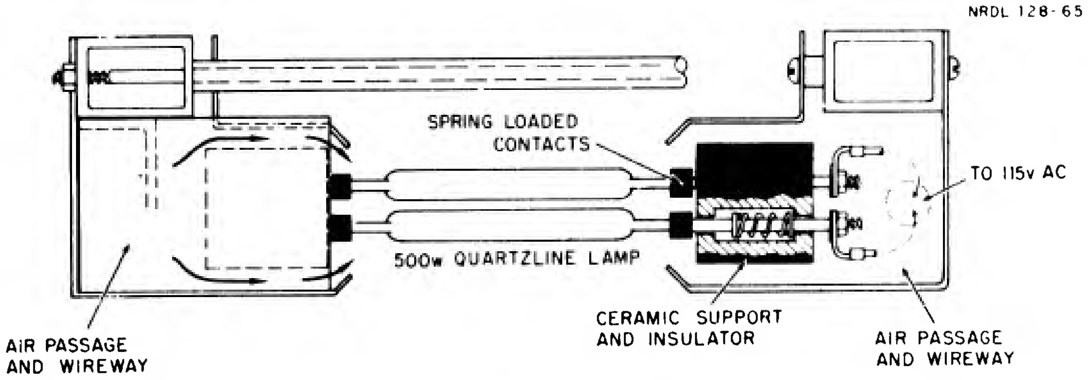
① A MIXTURE OF 3.5% BORAX, 1.5% BORIC ACID, AND 5% $(NH_4)H_2PO_4$

② HELD AT 180°C FOR 1 HOUR TO PRODUCE INSOLUBLE Al_2O_3 AND HCl ↑. WASHED AFTER COOLING TO LEACH OUT RESIDUAL HCl.

③ DEVELOPED BY THE DEPARTMENT OF AGRICULTURE TO RETARD FLAMING IN COTTON CLOTH. THPC + mm = TETRAKIS (HYDROXYMETHYL) PHOSPHONIUM CHLORIDE + METHYLOLMELAMINE.

④ PRE-HEAT TREATMENT LOADING

Table II Unusual Chemical Additives for Use in Ignition Inhibition.



DETAIL OF QUARTZLINE LAMP

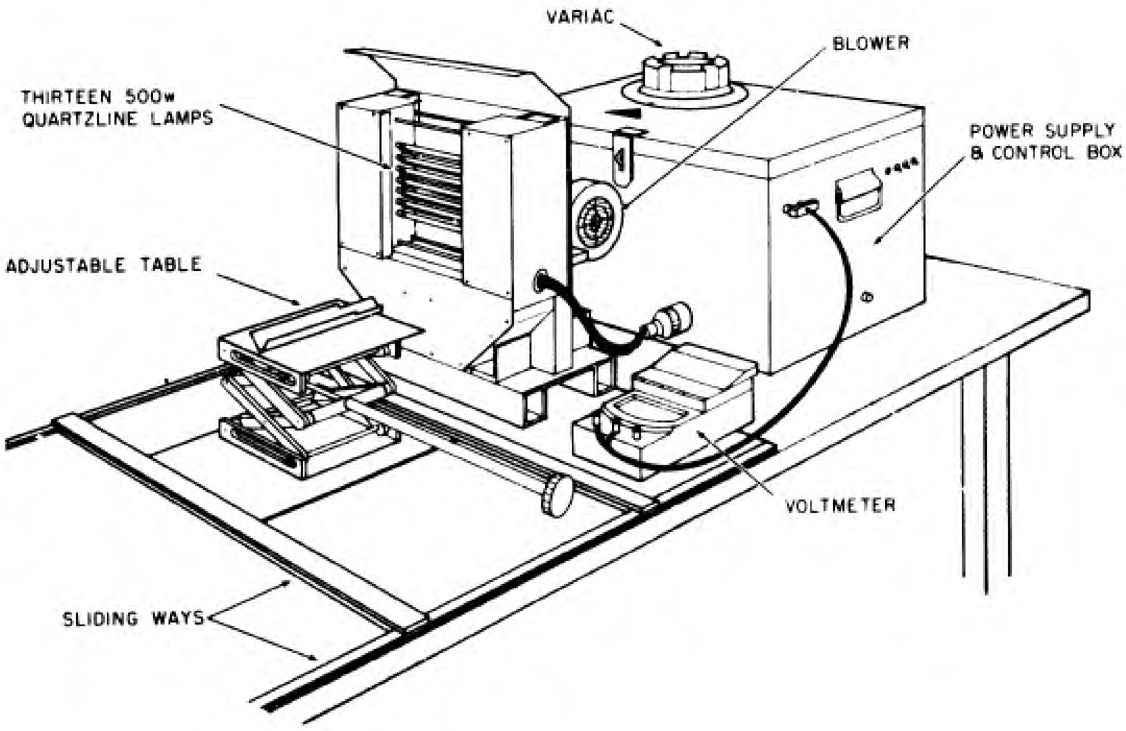


Fig. 1 Calibrated Tungsten Iodine Thermal Radiation Source

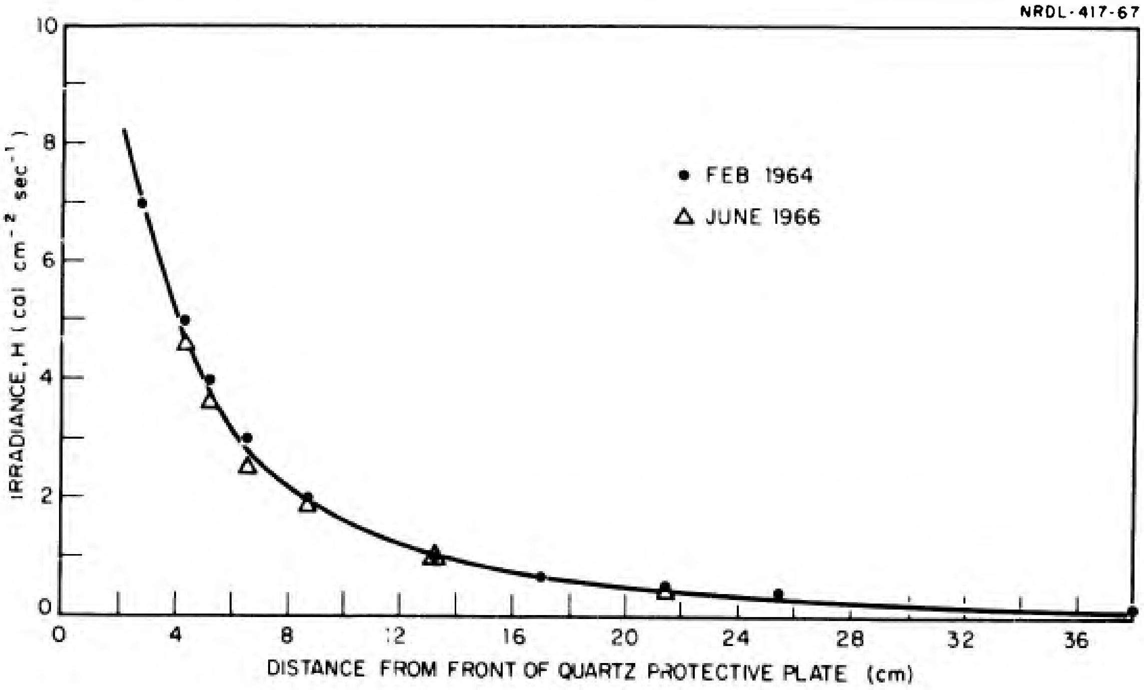


Fig. 2 Calibration of Tungsten-Iodine Source in cal cm^{-2} sec^{-1} versus distance from source bank.

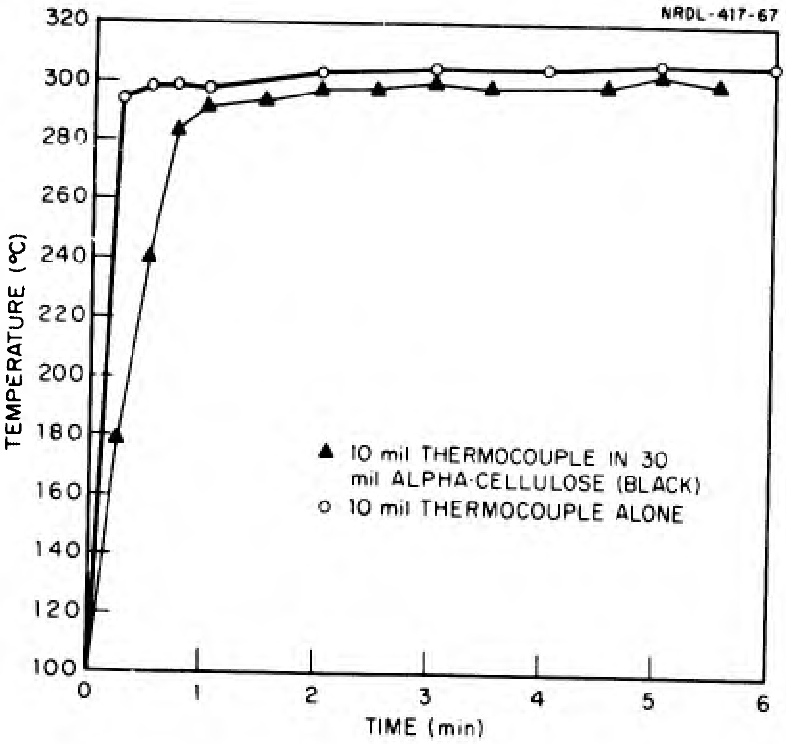


Fig. 3 Temperature Response of Cellulosic Sample in Pyrolysis Furnace.

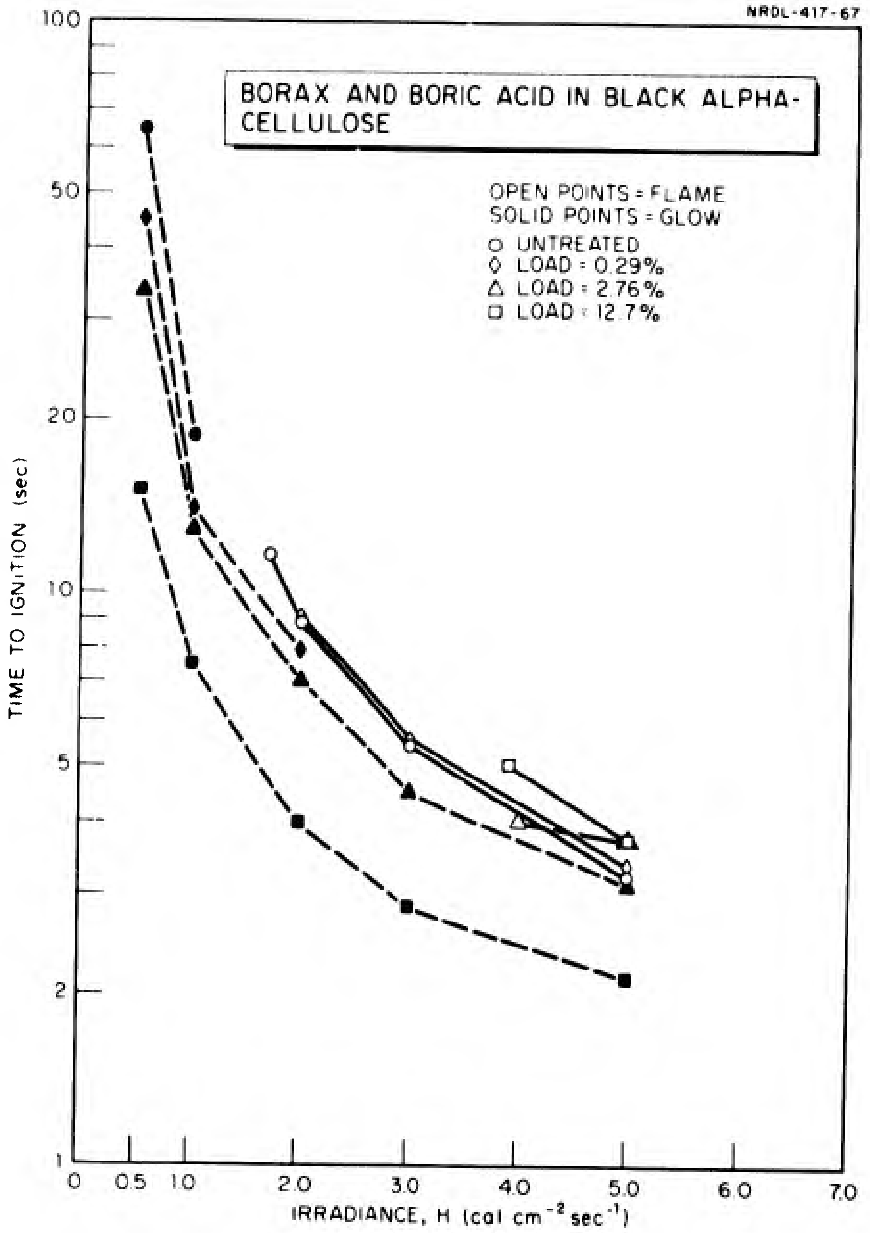


Fig. 4 Ignition Response of Black Alpha Cellulose and Black Alpha Cellulose Treated with Various Concentrations of B.B.A.

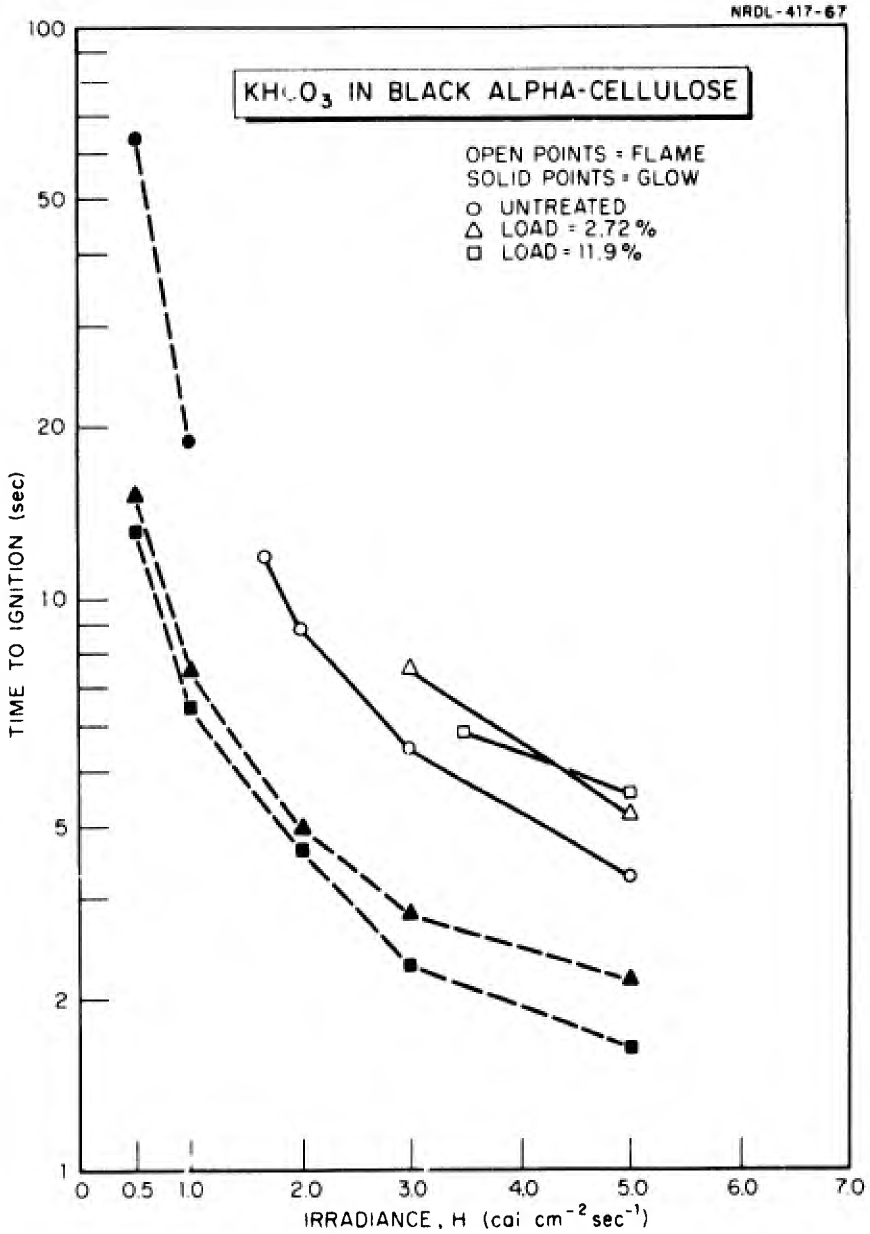


Fig. 5 Ignition Response of Black Alpha Cellulose and Black Alpha Cellulose Treated with Various Concentrations of $KHCO_3$.

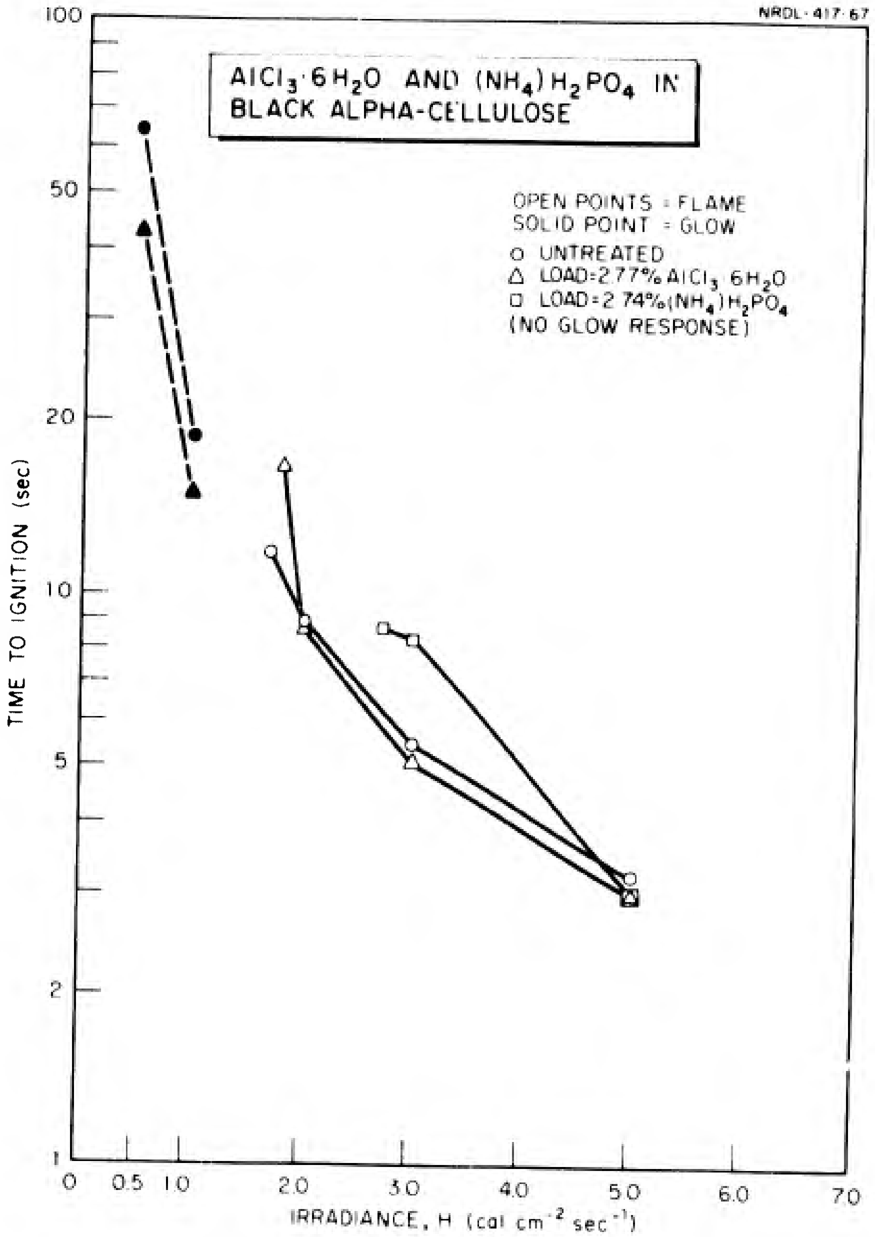


Fig. 6 Ignition Response of Black Alpha Cellulose and Black Alpha Cellulose Treated both with 2% Solutions of $AlCl_3 + 6H_2O$ and $(NH_4)H_2PO_4$.

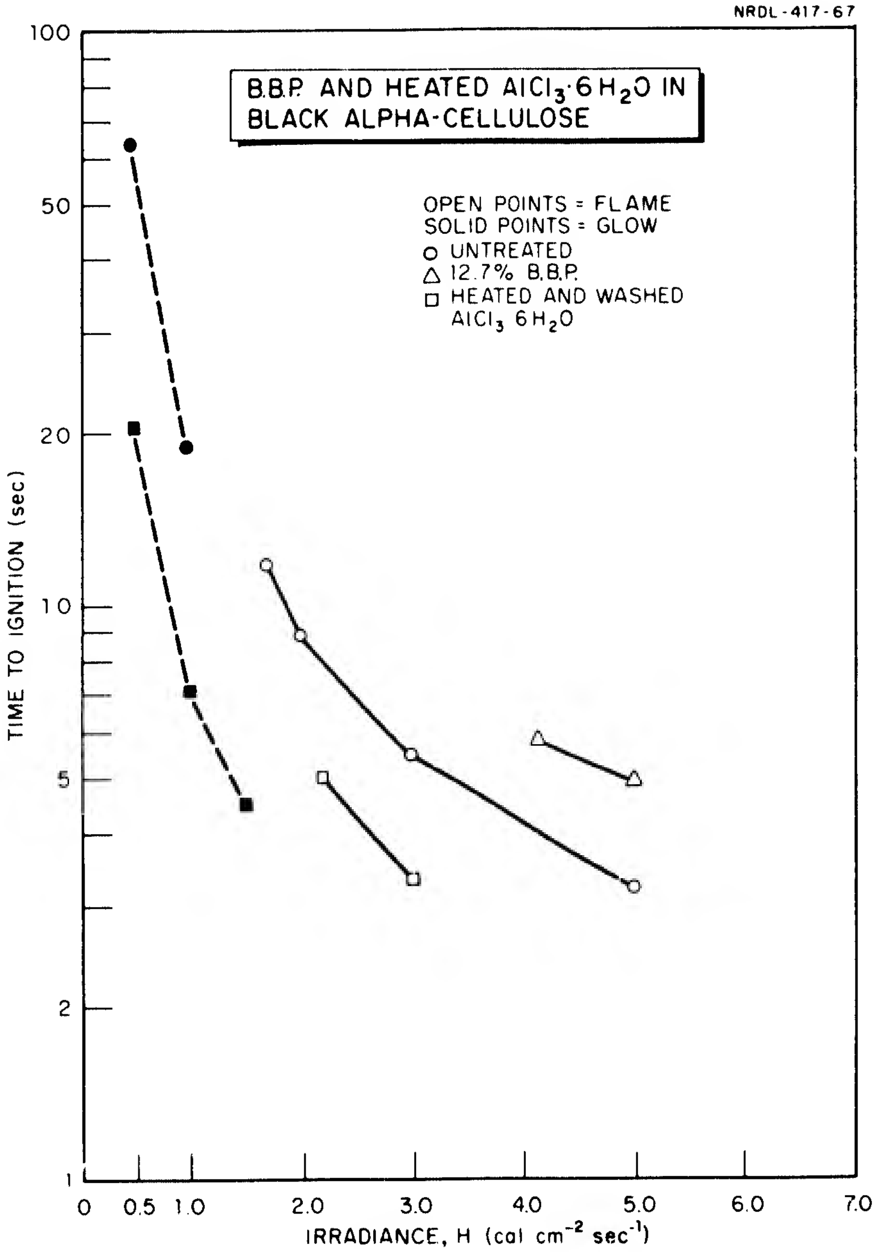


Fig. 7 Ignition Response of Black Alpha Cellulose and Black Alpha Cellulose Treated Both with B.B.P. and Heated $AlCl_3$.

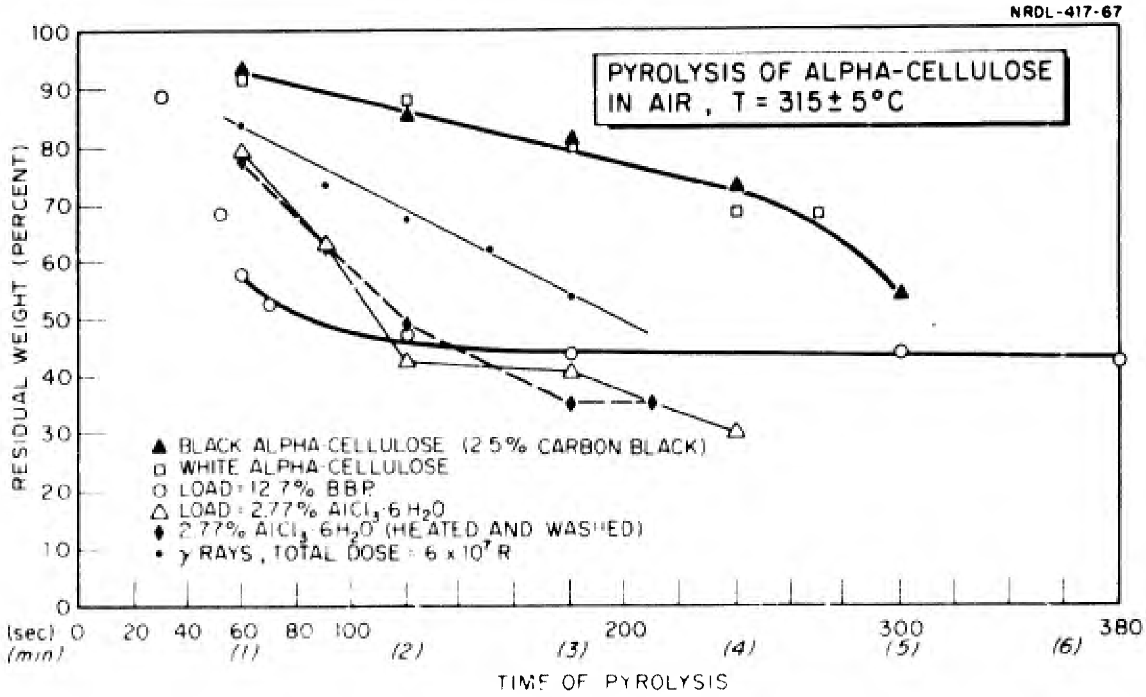


Fig. 8 Pyrolysis in Air of 1, Black Alpha Cellulose; 2, White Alpha Cellulose; 3, B.B.P. Treated Alpha Cellulose; 4, $AlCl_3 + 6H_2O$ Treated Alpha Cellulose; 5, Heated $AlCl_3 + 6H_2O$ Treated Alpha Cellulose; 6, Gamma Irradiated Alpha Cellulose.

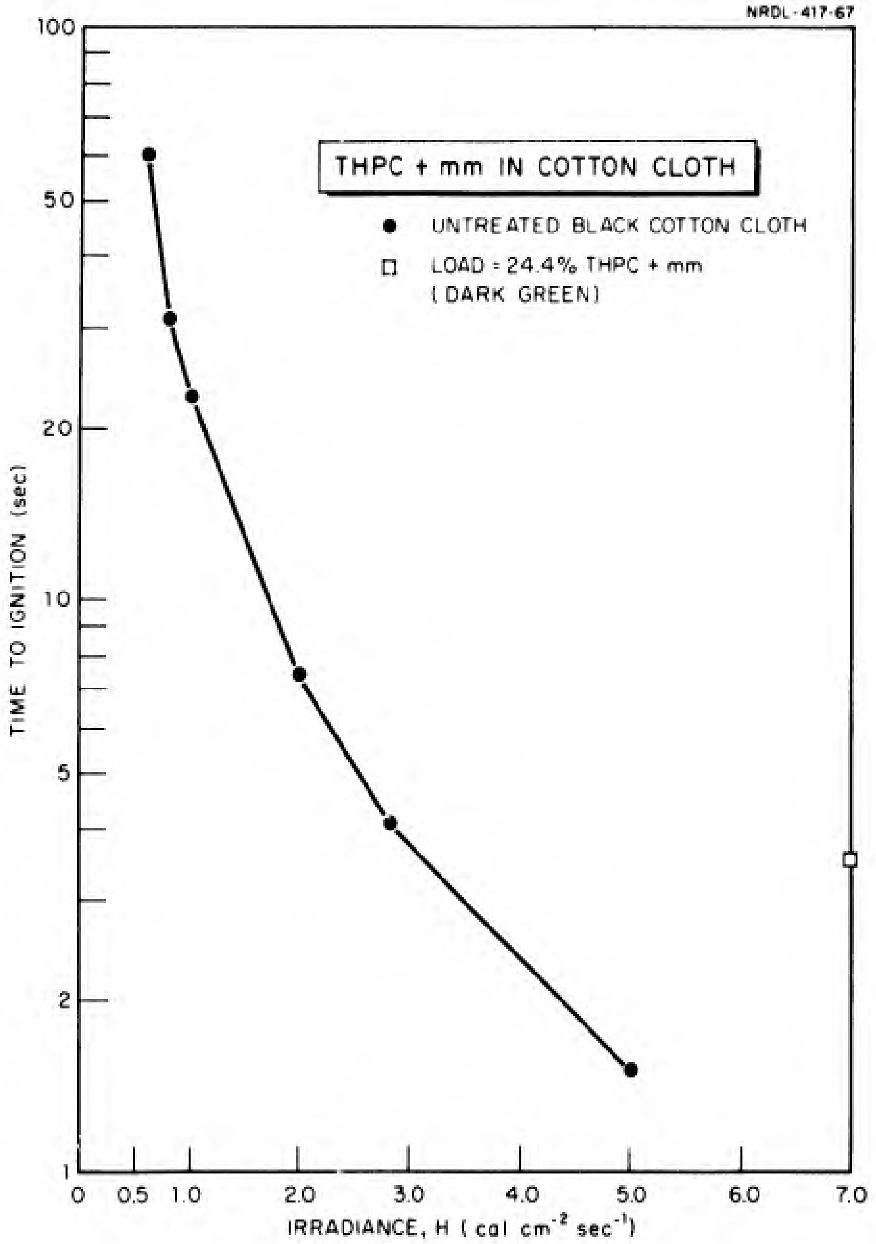


Fig. 9 Ignition Response of Cotton Cloth and Cotton Cloth Treated with THPC + MM.

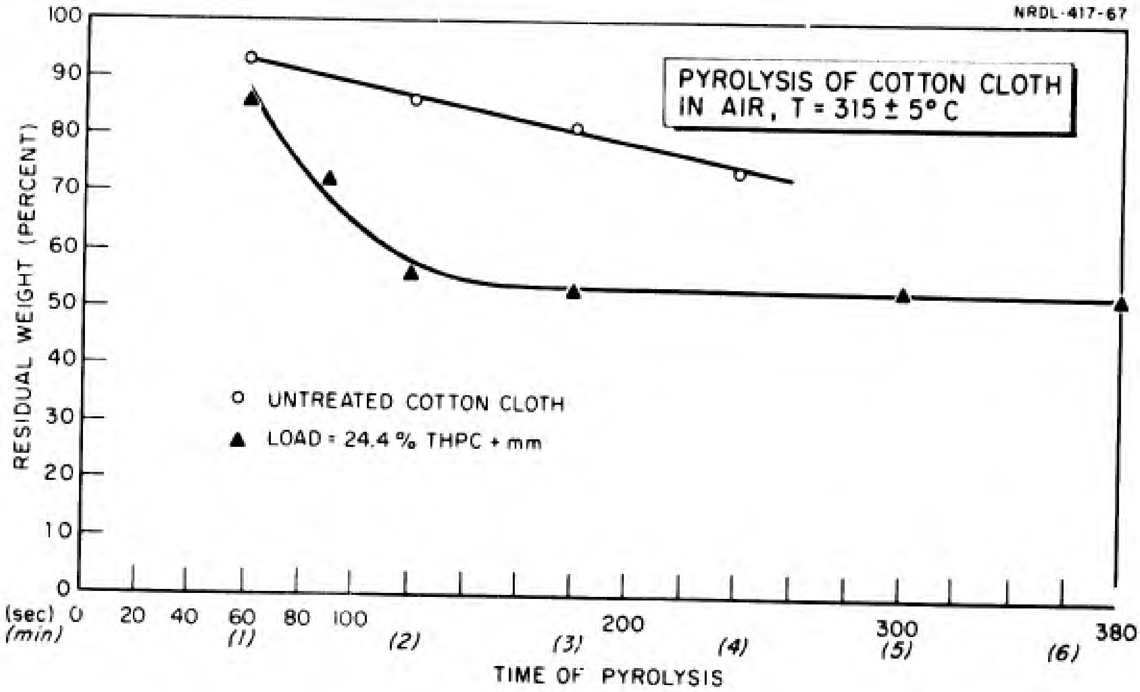


Fig. 10 Pyrolysis in Air of Cotton Cloth, and Cotton Cloth Treated with THPC + MM.

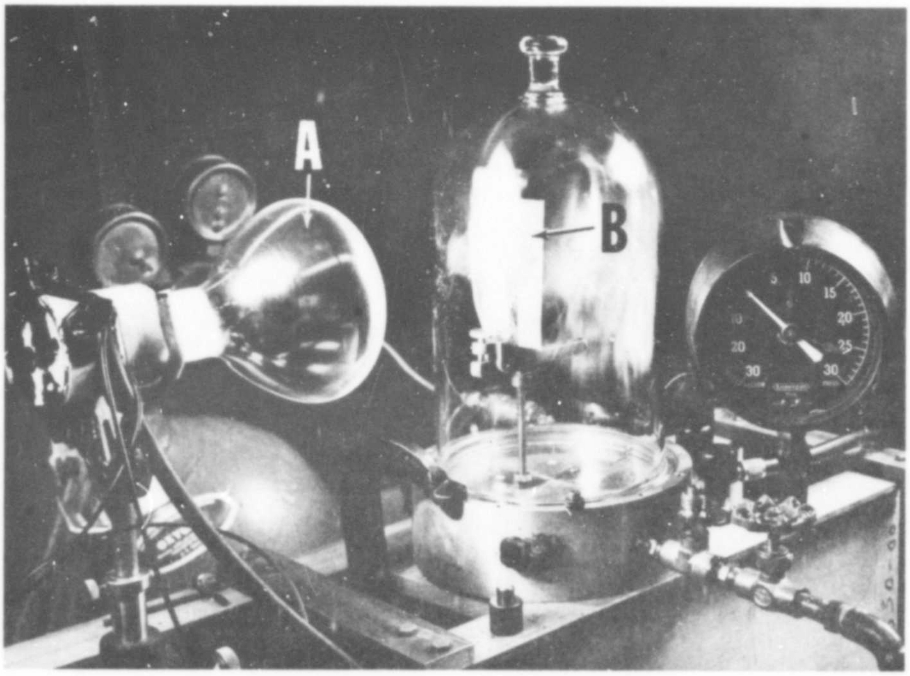


Fig. 11 Ignition Apparatus for Ignition Measurement in Pure Oxygen Atmospheres. A, is a focused Tungsten Iodine lamp, used as an ignition source and B, is the Black Alpha Cellulose sample, with the oxygen chamber, just after the occurrence of ignition.

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*

U. S. Naval Radiological Defense Laboratory
San Francisco, California 94135

2a. REPORT SECURITY CLASSIFICATION

UNCLASSIFIED

2b. GROUP

3. REPORT TITLE

IGNITION HARDENING OF CELLULOSIC MATERIALS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

5. AUTHOR(S) *(First name, middle initial, last name)*

Norman J. Alvares
Thomas H. Anderson

6. REPORT DATE

26 December 1967

7a. TOTAL NO. OF PAGES

40

7b. NO. OF REFS

9

8a. CONTRACT OR GRANT NO.

OCD Work Order DAHC20-67-C-0149, Work

b. PROJECT NO. Unit 2542A

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

USNRDL-TR-67-125

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

Office of Civil Defense
Washington, D. C. 20310

13. ABSTRACT

The ignition response of blackened alpha-cellulose and cotton cloth, containing fire retardant additives, was compared to the ignition response of these materials without additives. This information was obtained by exposing the samples to various irradiance levels from a calibrated thermal radiation source. 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. These comparisons yielded further insight into the mechanism of thermal degradation. Similar ignition response measurements were made with specimens exposed to ionizing radiation.

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}. Above this value, transient ignition would occur but flaming would last only until the ignitible gases were exhausted from the samples. Cotton cloth containing a polymeric retardant with the designation THPC + MM was found to be ignition resistant below an irradiance of 7.0 cal cm^{-2} sec^{-1}. Comparison of the pyrolysis rates of the retardant treated alpha-cellulose and cotton showed that the retardant mechanism is qualitatively the same. It was also found that gamma radiation results in ignition retardance of cellulose, while irradiation by neutrons, does not.

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Thermal hardening						
Ignition retardants						
Chemical fire inhibitors						
Cotton ignition retardants						
Cellulose ignition retardants						