

Effect of Flame-Retardant Treatment on the Thermal Behavior of Some Tropical Timbers

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Synopsis

Potassium aluminium sulfate, hereafter referred to as alum, was used as a flame retardant for some Nigerian timbers. It was observed that flame spread rate and after-glow time were drastically reduced. Thermogravimetric analysis shows that alum functions as a flame retardant (FR) by a complex process that entails the dehydration, condensed phase, and the vapor phase mechanisms.

INTRODUCTION

Flame retardant treatment of materials has been of long-standing importance to man, extending in history to the times of alchemy and the Roman Empire.¹ The first recorded attempt at applying flame retardants to cellulosic fabrics was probably in 1735 when a patent was granted to Johnnathon Wyld² for a flame retardant mixture consisting of alum, ferrous sulfate, and borax. However, it was not until 1821 that a systematic study on the uses and the mechanisms of flame retardants was published by Gay Lussac.³ Since then, chemists have tried all kinds of formulations on woods, papers, plastics, etc. In a recent review, Horrocks has documented the major FR finishes for cotton cellulosic fabrics, when used alone or in blends.⁴

Wood is mainly cellulose. It is impossible to make cellulosic materials completely flame-proof while still retaining their advantageous properties; the best that can be attained is a compromise between acceptable level of fire resistance and functional performance. Fortunately, the cellulose macromolecule has a functional group that makes it particularly amenable to treatments which render it resistant to both flaming and glowing combustions.

In this article are presented the results of the effects of impregnating some common Nigerian timbers with alum solution, on their thermal behavior. Four timbers, viz., *Chorophora excelsa*, *Nuclea diderichii*, *Ceibapentandra*, and *Terminalia superba*, subsequently to be called by their trade names of iroko, opepe, ceiba, and afara, respectively, were selected. Their flame propagation rate, after-glow time, and thermal decomposition patterns were investigated.

EXPERIMENTAL

Materials

The four timbers were procured from the local timber market and have the characteristics shown in Table I. The alum was obtained from Federal

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TABLE I

Timber	Iroko	Opepe	Afara	Ceiba
Specific gravity	0.56	0.23	0.45	0.18
Moisture content (%)	27.80	33.70	35.70	37.30
Porosity index (% water imbibition)	36.60	49.0	29.40	68.80

Superphosphate Fertilizer Plant at Kaduna, Nigeria, and assays as: Al_2O_3 (25.5%), Fe (0–0025%), insoluble matter (0.084%), and moisture content (18.47%).

Method

(i) Flame Retardant Treatment. Standard solutions of the alum were made in water. Weighed oven-dry wood splints were immersed completely in them. Residence time was 24 h. On removal from the dope, each sample was dried at 38.5°C and finally cured for 5 min in an air oven at 103°C. The sample was then conditioned at the same 38.5°C and RH of 59.8%, for 2 days, before being weighed again. Add-on (%) was calculated using the expression

$$\text{Add-on} = \frac{\text{wt after treatment} - \text{wt before treatment} \times 100}{\text{wt before treatment}}$$

(ii) Flame Propagation Rate. The sample was clamped vertically and then ignited in a draft-free room. The distance traveled at a stipulated time interval by the charfront was measured. The rate of flame propagation was calculated as the vertical distance traversed per second.

(iii) After-Glow Time. This was estimated by noting the time (s) between flame-out and the last visually perceptible glow.

(iv) Thermogravimetry. This was performed in air atmosphere by means of the METLER TA 300/TG 50 system. The sample was ground into powder and subjected to a heating program, using the specifications included in Figure 8. By means of a computer incorporated into the system, weight losses and peak temperatures at each decomposition step were obtained. The quantity of char left at the end of the thermal program was also measured.

RESULTS AND DISCUSSION

The results shown in Figure 1 indicate that the add-on is dependent not only upon the concentration of the alum solution, but more so on the specific gravity (SG) and the porosity index of the timbers. This observation is hardly surprising as more of the dope is expected to be imbibed by a more porous material.

For untreated samples, the rate of flame spread increases with porosity and varies inversely with SG. Specific gravity is a measure of the material in a body. This means that at any time a greater quantity of the sample has to be burned/decomposed as the flame traverses the surface of a more dense timber

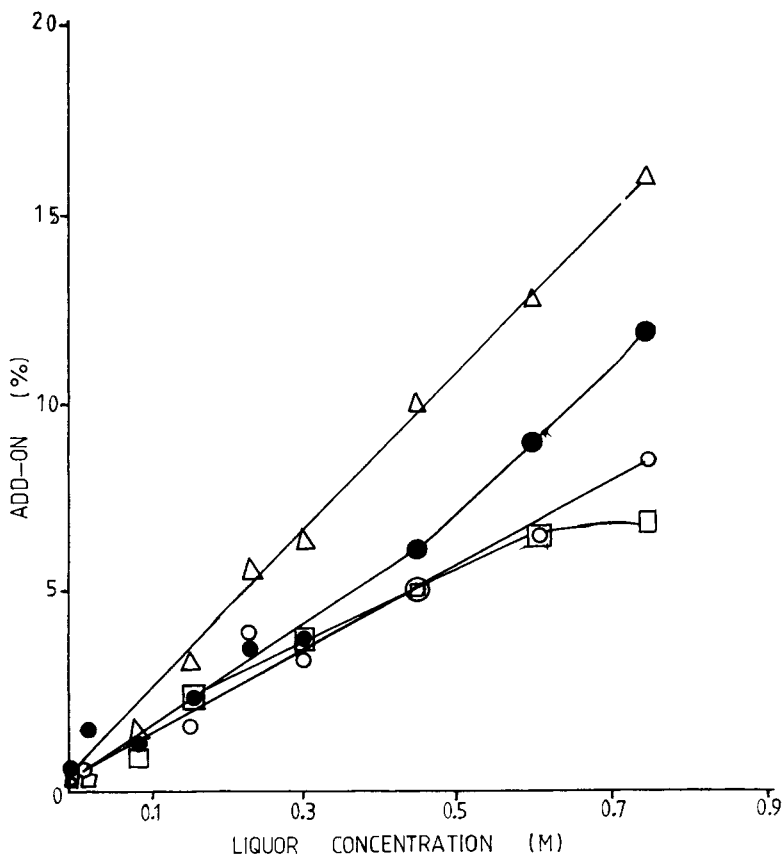
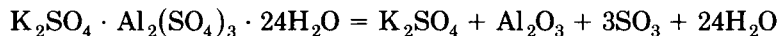


Fig. 1.

than a less dense one. Thus the flame spreads less readily in the former than in the latter, as shown in Figure 2.

The drastic reduction in the flame propagation rate with the FR treatment is explained as follows: At high temperatures, alum decomposes according to the equation



The flame inhibiting property of alum is interpreted in terms of the vapor phase and condensed phase mechanisms. The gaseous products, SO_3 and H_2O , dilute the combustible volatile pyrolysates of cellulose, thereby reducing their concentration in the flame zone. In addition, the evolution of water absorbs heat. Furthermore, K_2SO_4 , but more importantly, alumina (Al_2O_3), are excellent heat conductors that deflect heat away from the pyrolyzing/burning surface. As the concentration of alum in the sample increases, therefore, the heat budget of the system decreases. Thus flame propagation rate is expected to diminish. This expectation is borne out by the result shown in Figure 2.

Glow is a heterogeneous oxidative surface reaction and depends on the amount of "burnt" material and oxygen available. Therefore, the trend in the after-glow time of the pure samples: iroko > agara > opepe > ceiba (Fig. 3) is

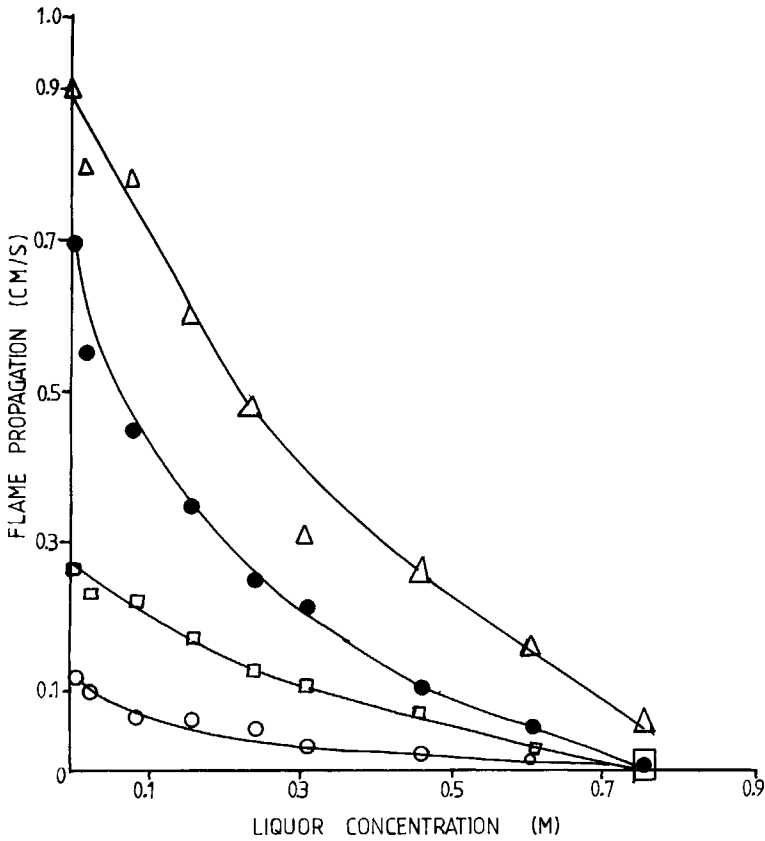


Fig. 2.

in agreement with expectation, as this is the order of their SGs in the figure; it is also seen that FR treatment reduces after-glow time. This is hard to explain as our TG experiments indicate an enhancement in char formation with increases in FR concentration (Fig. 6). Perhaps a plausible explanation is as follows: The peak temperature of pyrolysis is reduced by FR treatment [Fig. 4(a)]. In other words, the timber pyrolyzes more readily, leaving less material. So, after-glow should decrease as well.

It is clear in Figures 4(a) and 4(b), as well as in Figure 8, that cellulose exhibits a two-step decomposition pattern, which is not altered by FR treatment. It can be inferred from this that there is hardly any new compound(s) formed between alum and cellulose. An interesting observation is that whereas the decomposition temperature decreases with the quantity of FR in step I, in step II, the opposite is the case. Obviously two distinct mechanisms must be operating. As stated earlier, the first step involves a simultaneous decomposition of cellulose and alum. The decomposition temperature of this "mixture" is likely to be lower than that of pure cellulose—the plasticization phenomenon. This perhaps explains why, at the first step, peak temperature decreases with the quantity of FR. The Al_2O_3 from step I forms a seal around the cellulose macromolecule, reducing the amount of heat reaching the underly-

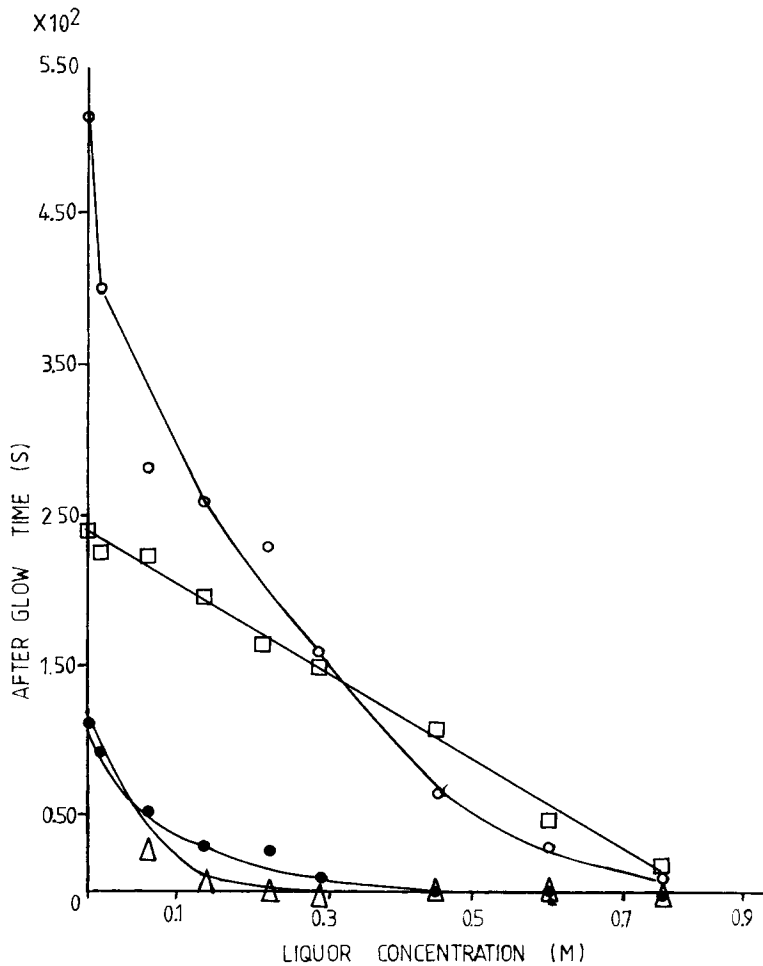


Fig. 3.

ing layer. More heat, hence higher temperature, is therefore required to pyrolyze this underlay than if Al_2O_3 were not there. This influence of Al_2O_3 would of course, rise as FR concentration increases [Fig. 4 (b)].

The above argument also explains the observations depicted in Figures 5(a) and 5(b). Alum decomposes more readily than cellulose. The Al_2O_3 forms a seal around the polymer, preventing potentially flammable gases from entering the flame. Thus weight loss decreases as alum concentration increases [Fig. 5(a)]. The pattern is reversed at the second step [Fig. 5(b)]. Apparently this means that at higher temperatures, the barrier is no more stable—hence greater weight losses.

Cellulose pyrolysis occurs by either of two known routes.⁵ In one, laevoglucosan is first formed which then disintegrates to oxidizable volatiles, e.g., CO, alcohols, ketones, aldehydes, etc. The second route, catalyzed by acids, is by evolution of water and difficultly combustible char. Our result, Figure 6, shows

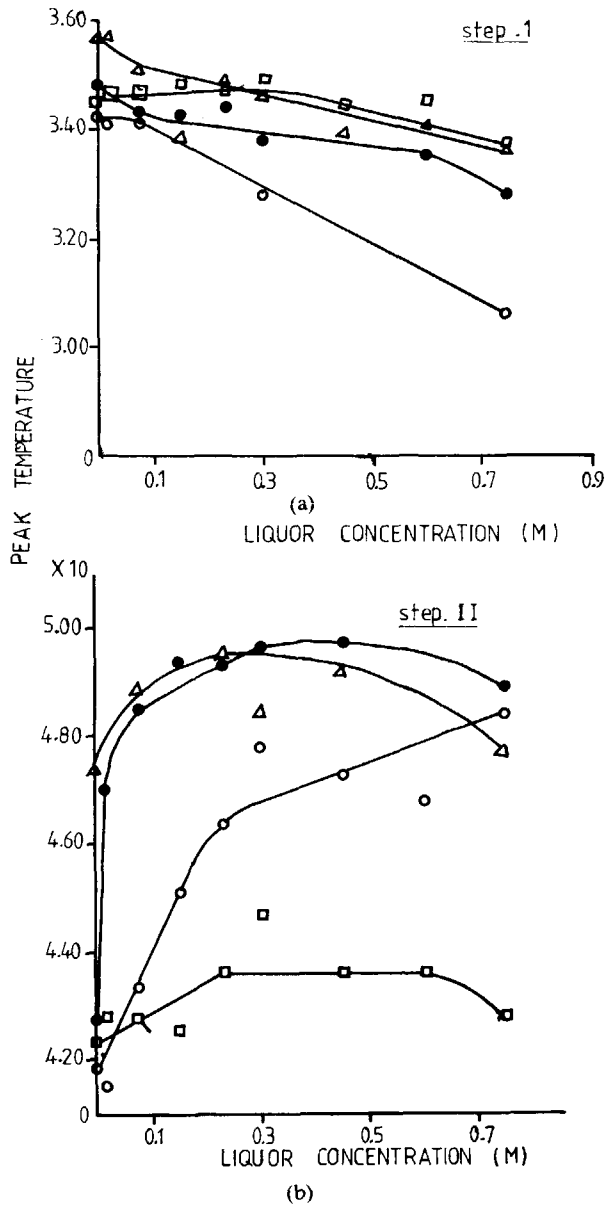


Fig. 4.

that, in all instances, FR treatment enhances char formation. Thus alum also functions as an FR by the so-called dehydration mechanism.

In Figure 7 it is evident that the overall activation energy of the pyrolysis/combustion reaction (first step only) decreases as the concentration of FR increases. This observation is in accord with those of Figure 4(a) and helps explain the FR mechanism of alum in this system. As a result of FR treatment, the material decomposes more readily at a lower temperature than would the unimpregnated sample. This forced low temperature pyrolysis

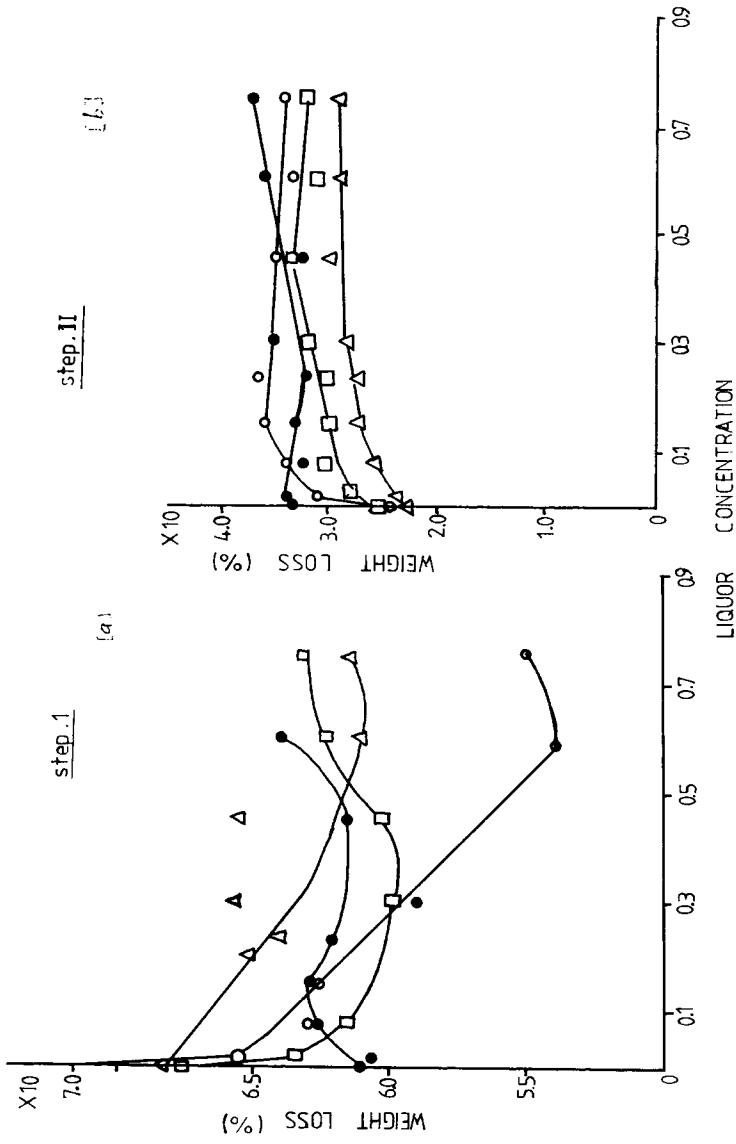


Fig. 5.

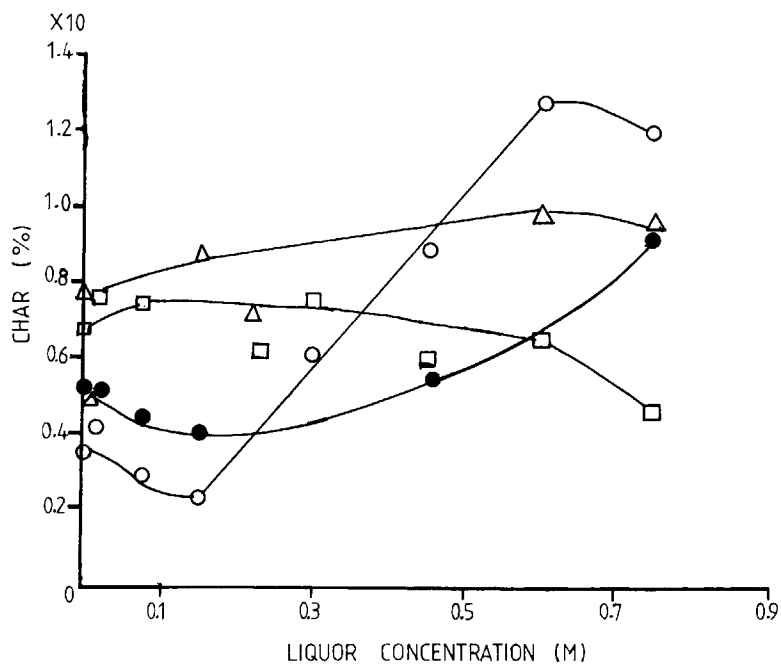


Fig. 6.

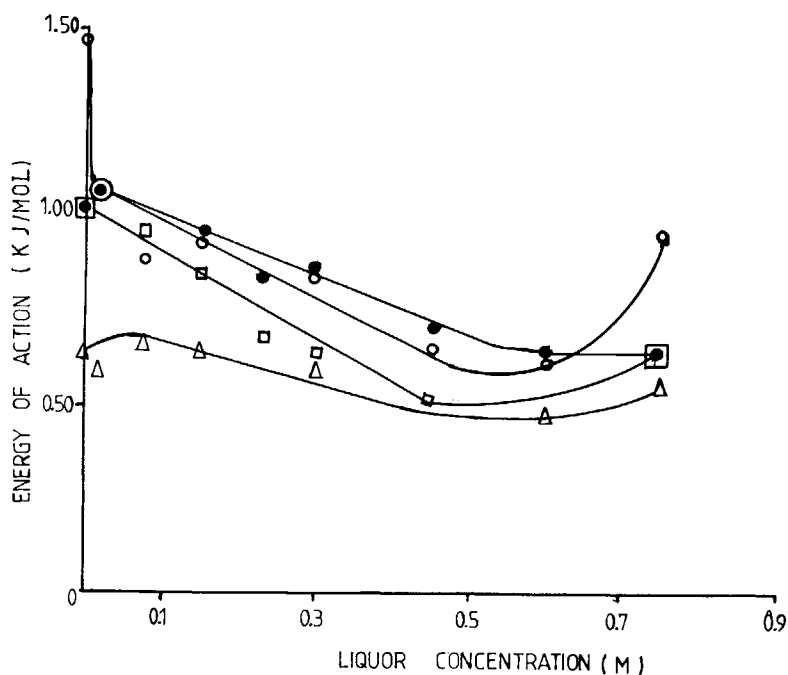


Fig. 7.


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SCREEN
90-MAR-88      12:01

SCAN PARAMETERE
START TEMP. °C      40
RATE K/MIN.        20
END TEMP. °C        900
TIME ISO. MIN       0
PLOT CM            15
RANGE FS mG        20
OFFSET °/D         90
VALVE T/t 1/2      0
SCREEN
DYN/TSO 1/2        1
START              50
END                880
BASELINE TYPE      1
PLOT CM            10
PLOT MODE          2031

IDENT NO.          0-003
WEIGHT mG          16.237
    
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FIG. 5. A TYPICAL TG/LTG THIRMOHAM

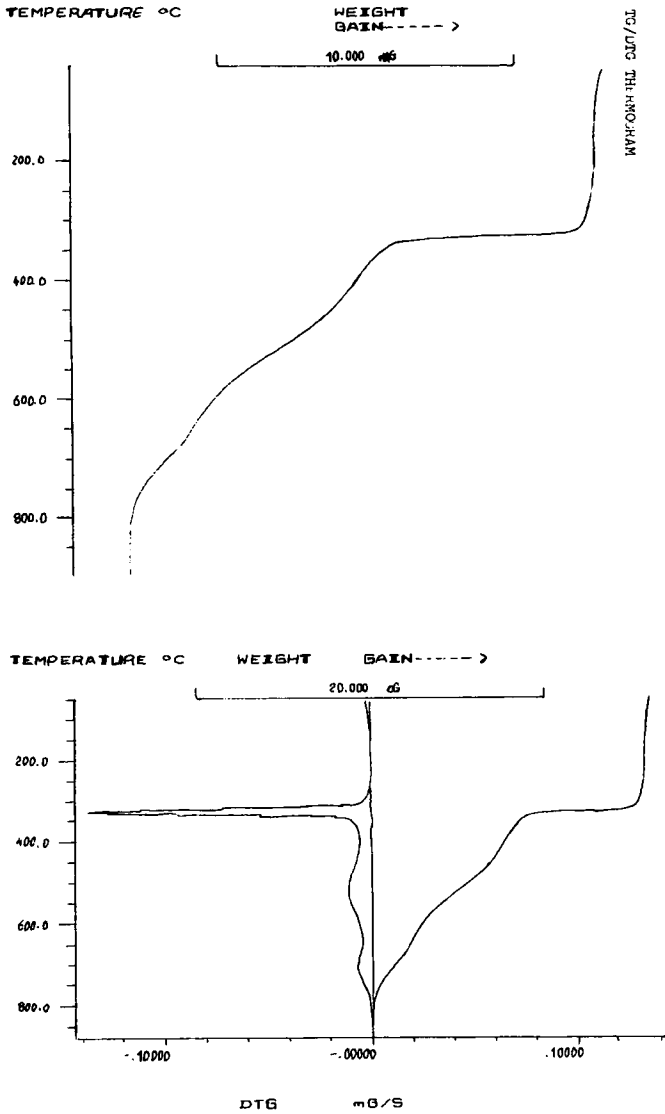


Fig. 8.

would come to such a point that not enough heat energy is available for sustained combustion—hence extinguishment of the flame.

CONCLUSION

The following conclusions can be made from this investigation: Alum functions as a flame retardant for the four timbers by complex processes that entail the vapor phase, the condensed phase, and the dehydration mechanism. Cellulose pyrolyzes/decomposes by the distinct steps. This pattern is not altered by FR treatment. Incorporation of alum into these timbers reduces the flame spread rate, the after-glow time, the peak temperature of decomposition, and the overall activation energy of the pyrolysis reaction (first step only).

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