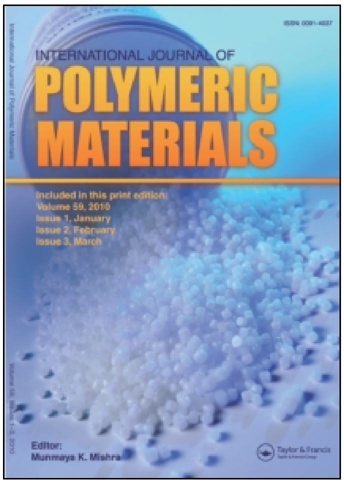

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Mechanistic Study of Sodium Tetraborate Decahydrate as Flame Suppressant for Wood Cellulose

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Some selected tropical woods were impregnated with solutions of sodium tetraborate decahydrate, hereafter to be referred to as borax. Our results revealed that the borax functioned effectively as flame suppressant (FS) in flaming, vapor and condensed phase mechanisms. It was also observed that on heating, borax decomposes producing molecules that interfere with the chemistry of pyrolysis of the wood cellulose. The thermal behaviour of the cellulosic materials were drastically altered. Thus, flame propagation rate, after-glow time and calorific value were reduced significantly as a result of this treatment. On the other hand, Oxygen Index and char formation increased with increasing borax concentration.

Keywords: Flame suppresants; wood cellulose; sodium tetraborate

INTRODUCTION

Boron compounds function as flame suppressants in both the flaming and condensed phase mechanisms. Flame phase-active boron compounds are generated from combustion of borates and halogenated organic compounds [1].

In order to determine the role of halogens (such as boron) as flame suppressant [2] it is necessary to examine the heat balance that occurs

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at the surface of the polymer. Heat received by the polymer surface may arise either as heat flux from the flame ($\dot{Q}_T$) or as an externally applied heat flux ($\dot{Q}_E$) derived from another source. Heat is lost either as the heat required for gasification ($\dot{Q}_G$) of the polymer or as heat lost ($\dot{Q}_L$) through radiation, conduction, convection, dripping, etc. $\dot{Q}_T$ and $\dot{Q}_G$ are agent dependent whereas $\dot{Q}_E$ is obviously agent independent, except in char-forming system. $\dot{Q}_L$ may be agent dependent if the agent acts by increasing the drip rate of the burning polymer. Halogenated agents affect the heat balance through $\dot{Q}_T$, $\dot{Q}_G$ and $\dot{Q}_L$. Although phosphorous may act in the gas phase, it appears to be the most important element affecting $\dot{Q}_G$ and $\dot{Q}_E$ through char formation [2].

In essence, the burning process involves heating of the substance to a temperature high enough to drive off flammable vapours. When the rate of vapour evolution becomes high enough to generate a flammable mixture, the mixture ignites. If the rate of vapours or gas evolution becomes sufficiently high, the heat produced by the combustion process may return enough heat to the substrate so that the evolution of fuel becomes self-sustaining.

When a flame suppressant that acts in the vapour phase is added to the system, part of the vapour that distils from the polymer does not contribute to the heat of combustion but results only in a reduction in the mass fraction of the oxygen and fuel in the combustion zone. Hence, there is an increase in the total mass of material that must be vaporized per unit time in order to keep the fire burning. A corresponding increase in the amount of energy must be added to the system from an external heat source, $\dot{Q}_E$ in order to vaporize the extra material.

Both dripping and char formation interfere with the energy feedback cycle ($\dot{Q}_T$ and $\dot{Q}_E$) and consequently cause an increase in the intensity of the external heat flux required to balance the energy-fuel cycle (see Fig. 1).

When the flame is actively spreading over the surface of a material, the elemental composition of the vapour being evolved ahead of the moving flame is not necessarily the same as the elemental composition of the polymer. The composition of the vapours may vary considerably between the temperature at which the material first begins to evolve vapours and the temperature at which the rate of evolution supports the flame.

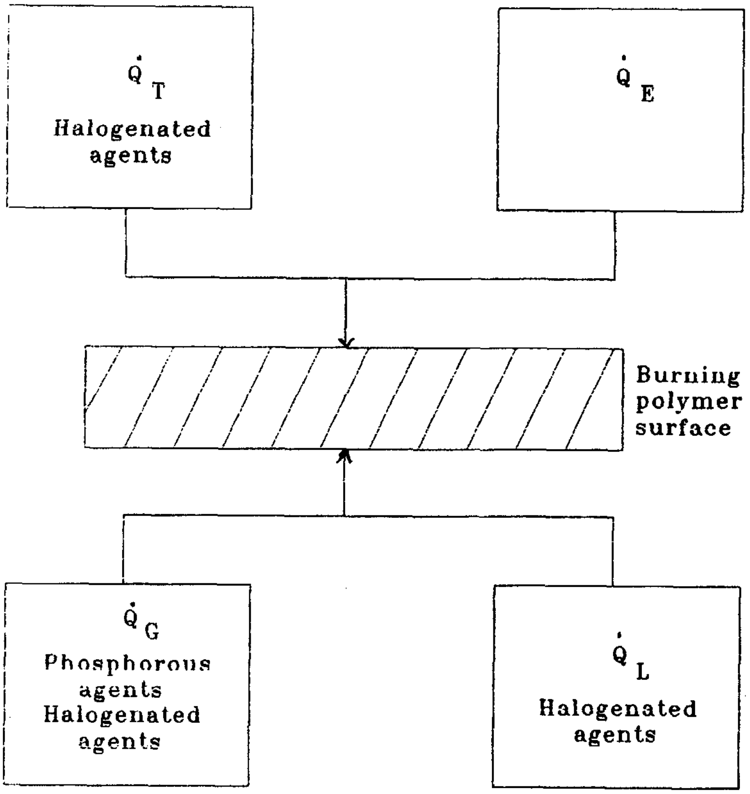

FIGURE 1 Heat balance at the surface of a burning polymer. $\dot{Q}_T$ = the total heat flux from the flame; $\dot{Q}_E$ = the heat flux from any external heat source; $\dot{Q}_G$ = the heat flux required for gasification of the polymer; $\dot{Q}_L$ = total heat flux lost owing to convection, radiation, dripping etc. Active halogen participation occurs in $\dot{Q}_T$, $\dot{Q}_G$ and $\dot{Q}_L$.

There are five fundamental methods used to fire-retard both natural and synthetic polymer systems [3]. They are

(i) *Increase the decomposition temperature of the polymer.* This is generally accomplished by increasing the cross-linking density of the polymer, as with ladder polymers (increase $\dot{Q}_G$).

(ii) *Reduce the fuel content of the system.* This approach generally involves halogenizing the polymer backbone, adding halogenated additives, inert fillers, or by resorting to inorganic systems (increase $\dot{Q}_G$, decrease $\dot{Q}_T$).

(iii) *Induce polymer flow by selective chain scission.* This approach is generally applicable to thermo-plastic polymer systems where interrupting the polymer backbone results in reduction of the viscosity of the polymer and promotes dripping (increase $\dot{Q}_L$).

(iv) *Induce selective decomposition pathways.* This method is most applicable to cellulosics where the introduction of phosphorous compounds degenerates phosphorous acids which catalyze the loss of water and retention of the carbon as char (increase $\dot{Q}_G$, decrease $\dot{Q}_T$).

(v) *Apply mechanical means.* These include (1) bonding a non-flammable skin on the polymer, (2) covering the polymer with an intumescent coating, (3) design of the system, and (4) the use of sprinklers (decrease $\dot{Q}_E$).

Bromine and chlorine compounds are the only halogens commercially significant as flame suppressant chemicals. Fluorine compounds are expensive and, except in special cases ineffective. Iodine compounds, although effective, are expensive and too unstable to be used.

Bromine compounds have a number of inherent properties that make them excellent flame suppressants. For example, bromine compounds generally are twice as effective as chlorine compounds having the same halogen content on a weight basis and are 1.7 times as dense as chlorine compounds.

Bromine-containing compounds such as borax generally decompose in the range of 200–300 °C because of the relatively low carbon-bromine bond energy. Thus, borax can effectively function as flame suppressant by both vapour and condensed phase mechanisms [4].

EXPERIMENTAL

Materials

The flame suppressant (FS) material used, sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$), known as borax was obtained from British Drug House, Poole, England. The three wood species studied were procured from a local market. They are commonly known as Mahogany, Obeche and Obuba. They are scientifically known as

Khaya gradifoliola, *Manosonia altissma* and *Isobelina doka* respectively. Their specific gravity are 0.65, 0.35 and 0.49 respectively.

Methods

i) Sample Treatment

Standard borax concentrations (g/dm^3) were made and weighed wood splints were immersed completely in them. Residence time was 24 hrs. On removal, each sample was dried at room temperature and finally cured in an oven at 103 °C for 15 minutes. The samples were then conditioned at the same room temperature (26.38 °C) for 24 hrs and reweighed [5–9].

ii) Add-on (%)

Add-on was calculated using the expression

$$\text{Add-on} = \frac{W_a - W_b}{W_b} \times 100$$

where
W_a weight after treatment,
W_b weight before treatment.

iii) After-Glow Time

This was simply determined by noting the time between flame-out and the last visually perceptible glow.

iv) Flame Propagation Rate

The sample was held vertically in position at room temperature and ignited. The distance travelled at a stipulated time interval by the char front was recorded. The rate of flame propagation was calculated as the vertical distance traversed per second.

v) Calorific Value

The calorific value [5]: The heat liberated when a unit quantity of fuel is completely burnt was determined for both treated and untreated samples using fuel/food calorimeter Model L04–340.

vi) Oxygen Index, OI

In the analysis, an American Standard Test Method No. ASTMD 2863–76, Oxygen Index Test was adopted [5]. In this test, wood sample (6 × 3 × 80 mm) was placed vertically in a chimney with a controlled atmosphere, and the upper end was ignited with a gas flame. By varying the oxygen: nitrogen ratio, the ratio that just supports a flame was determined. The Oxygen Index was calculated as follows;

$$\mathrm{OI}(\%) = \frac{O_2}{O_2 + N_2} \times 100$$

where
O_2 = volumetric flow of oxygen (cm^3/min),
N_2 = volumetric flow of nitrogen (cm^3/min).

vii) Char Formation

Few grammes of the sample were taken in a crucible and heated in a muffle furnace at 700°C until a constant weight was obtained [9, 10].

Discussion of Results

One of the most common approaches used to modify the burning properties of polymers at present time is by incorporation of halogens into the polymer matrix, either directly or through the use of the halogenated additives. The usual rationale for the use of the halogens as flame retardants is based on the theory that they function in the gas phase as radical traps [1, 2]. It is generally agreed that the combustion of gaseous fuels is a high temperature process which proceeds via a free radical mechanism. The overall reaction, i.e.,

$$\text{fuel} + O_2 \rightarrow CO_2 + CO + H_2O + \text{heat} + \text{light} \qquad (1)$$

involves a great variety of discrete reactions depending on the nature of the fuel. However, a relatively small number of propagation and chain-branching reactions are common to most fuels and are critical for maintaining the combustion process. These reactions are of the type

$$\cdot OH + CO \rightarrow CO_2 + H\cdot \qquad (2)$$

$$\cdot OH + RCH_3 \rightarrow RCH\cdot_2 + H_2O \qquad (3)$$

$$RCH\cdot_2 + O_2 \rightarrow RCHO + \cdot OH \qquad (4)$$

$$H\cdot + O_2 \rightarrow \cdot OH + \cdot O\cdot \text{(chain branching)} \qquad (5)$$

Halogenated compounds have been shown to enter into flame chemistry via a series of reactions

$$HBr + \cdot OH \rightarrow H_2O + Br\cdot \qquad (6)$$

$$HBr + \cdot O\cdot \rightarrow \cdot OH + Br^{\cdot} \qquad (7)$$

$$HBr + H\cdot \rightleftharpoons H_2 + Br\cdot \qquad (8)$$

$$HBr + RCH_2 \rightleftharpoons RCH_3 + Br\cdot \qquad (9)$$

$$RBr \rightleftharpoons R\cdot + Br\cdot \qquad (10)$$

In the radical-trap theory of flame inhibition it is through that equations 6–10 effectively compete with equations 2–5 for those radical species that are critical for flame propagation, i.e., ·OH and ·O·, thereby showing the rate of energy production and resulting in the extinction of the flame [3]. The radical-trap theory of flame inhibition, although attractive in that it can be adapted to any situation, tends to lead to the belief that the simple inclusion of small amounts of halogen into a polymer system will render the system flame retardant [4].

A recent physical theory of flame suppression by the halogens, although conceding that the halogens enter into flame chemistry, suggest that this participation perse cannot be the primary mechanism by which the halogens functions. Rather, it is postulated that the halogens act by altering the physical properties. The physical theory is primarily based on the observations that boric acid and borax are effective condensed phase flame retardants in polyhydroxy compounds especially in cellulosic fibres. When these compounds are exposed to a flame they melt and form a glass like coating around the fibres. Prolonged exposure causes the coating to dehydrate, generating water which cools the flame and cause it to extinguish.

Figure 2 shows that all the wood samples considered readily absorb borax solution and that the tendency to do so, depends upon the dope concentration. This is hardly surprising, as the mechanism of chemisorption of small molecules by polymerics, including cellulosics, has been extensively discussed in the literature [7].

The thermal characteristics of borax treated grass is explained as follows: Cellulose, the major constituent of wood is known to pyrolysis via two possible routes

$$\begin{array}{ll} & \text{Laevoglucosan} \rightarrow \text{CO, alkanes, alkenes} \\ & \text{alcohols, aldehydes, ketones, and other} \\ & \text{combustible volatiles} \\ [C_6H_{10}O_5]_n & \nearrow \\ \text{cellulose} & {}_{\text{acid}}\searrow \\ & H_2O + C\,(\text{char}) \end{array} \tag{11}$$

In the first route, an intermediate, glucosan, is formed firstly which later decomposes into a cock-tail of volatile and combustible/oxidizable molecules. The alternative pathway, often mediated by flame suppressants, is the generation of difficulty combustible char. The flame inhibiting property of borax, as illustrated by the observations in Figures 3–7 arises from the fact that on heating, it decomposes

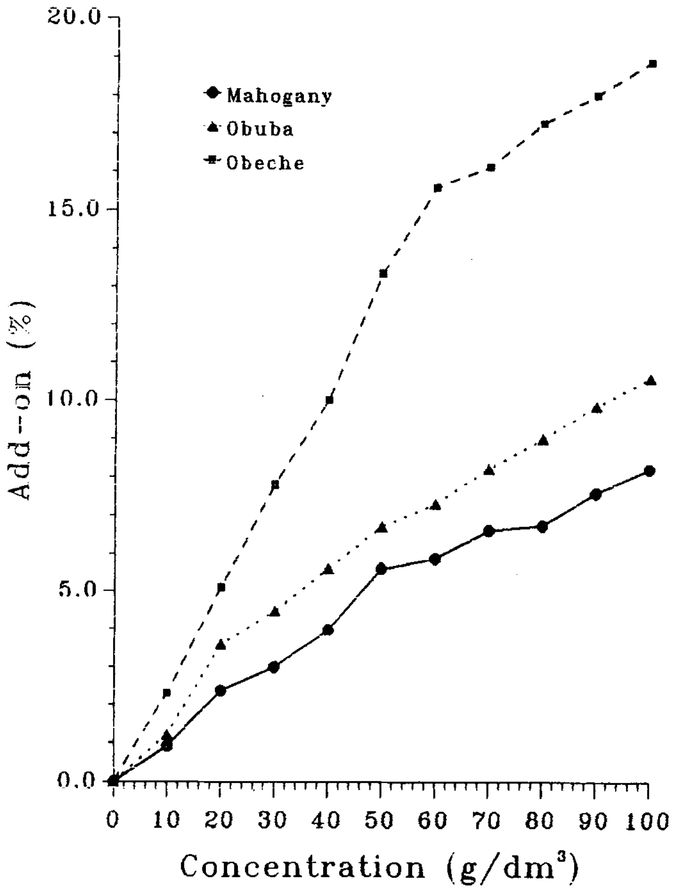

FIGURE 2 Plot of concentration vs Add-on.

according to the equation

$$Na_2O{\cdot}2B_2O_3{\cdot}10H_2O \xrightarrow[heat]{} Na_2O{\cdot}2B_2O_3{\cdot}5H_2O$$

$$\xrightarrow[heat]{} Na_2O{\cdot}2B_2O_3{\cdot}4H_2O \longrightarrow Na_2O{\cdot}2B_2O_3 \qquad (12)$$

thereby releasing the water of crystallization and the spongy $Na_2O{\cdot}2B_2O_3$. The gaseous water dilutes the effective concentration of the volatile combustible pyrolysates in the flame zone, thereby inhibiting

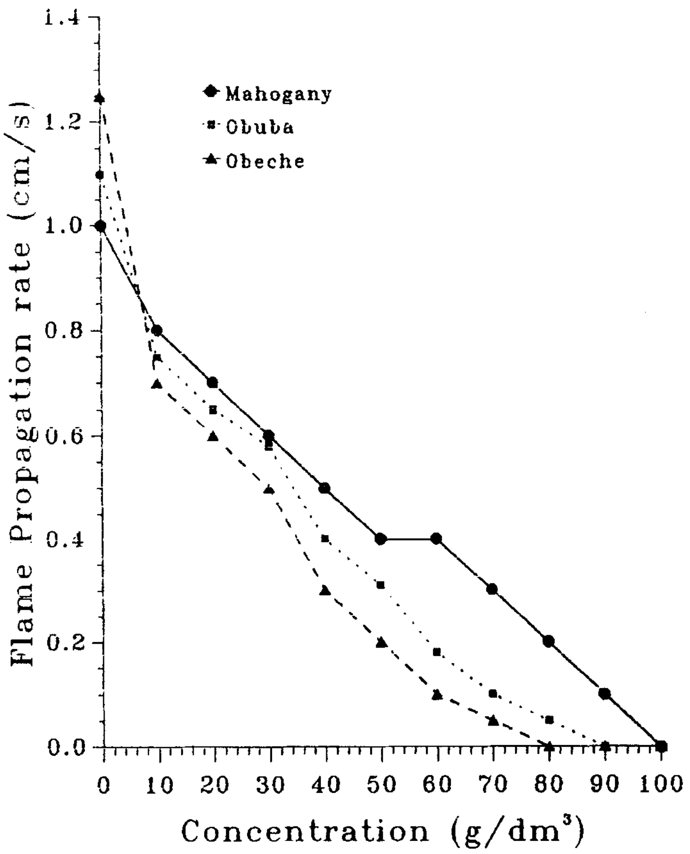

FIGURE 3 Plot of Flame propagation rate vs FS concentration.

the attainment of the optimum pyrolysate-oxygen concentration necessary for ignition and the sustenance of burning. On the other hand, the spongy dehydrated borax product form an impervious layer on the pyrolysing wood cellulose, hence preventing the escape of the small molecules that feed the flame region. Furthermore, the borax residue chemically combines with hydroxyl groups of cellulose to generate additional water and form inorganic char that is difficult to ignite (see Fig. 7). The char is an insulator that slows down the rate of polymer degradation and fuel formation, that is why Figures 3, 4, and 5 shows decrease in flame propagation rate after-glow time and calorific value respectively.

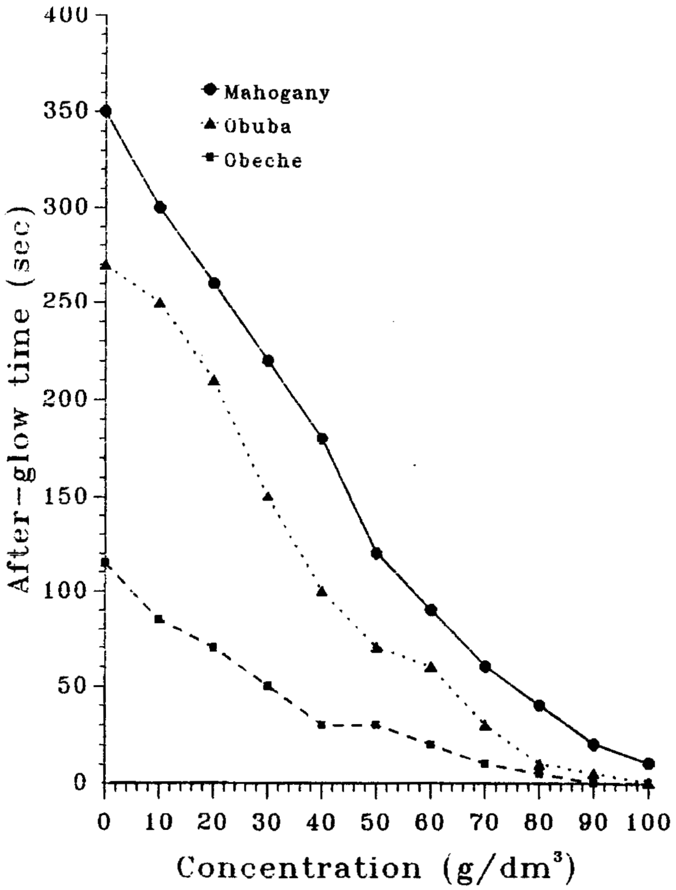

FIGURE 4 Plot of After-glow time vs FS concentration.

Figure 6 shows an increase in Oxygen Index with increasing borax concentration. The higher the index values, the more flame suppressant the polymer [3].

A functional relationship has been shown to exist between a polymer burning rate and the mass transfer number, B, where

$$\frac{\frac{M_0}{\tau} H_c - c_p(T_s - T_a)}{H_G} \tag{13}$$

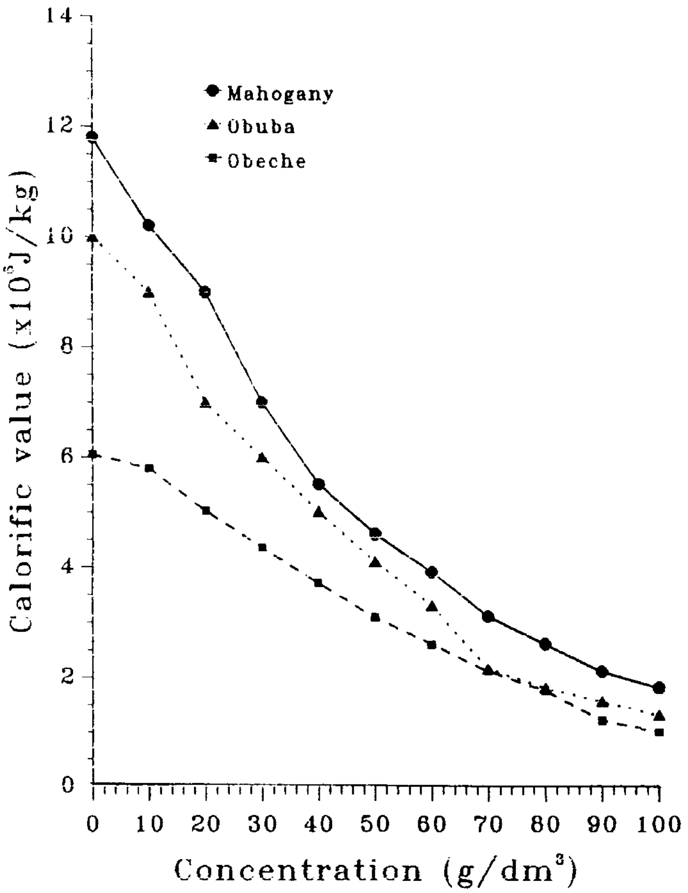

FIGURE 5 Plot of Calorific value vs FS concentration.

M_0 is the mass fraction of oxygen in the combustion zone; H_c is the net heat of combustion of the sample (J/g); r is the stoichiometric mass oxygen/fuel ration; c_p is the specific heat capacity of the gases in the combustion zone; T_s is the surface temperature of the sample (°C), T_a is the ambient temperature and H_G is the apparent heat of gasification (J/g). The B number contains the fundamental properties of the polymeric materials. Thus, the burning rate or burning intensity can be related to fundamental properties of the material.

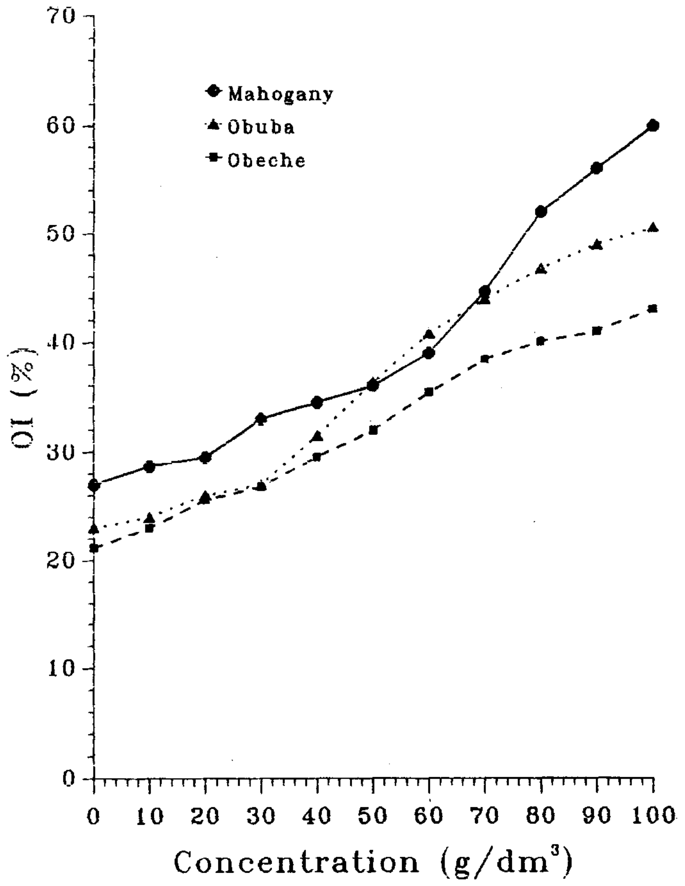

FIGURE 6 Plot of OI vs FS concentration.

CONCLUSION

The thermal properties of wood cellulose were modified by the control addition of borax as flame suppressant to achieve very high performance standards. Therefore, it is envisaged that the devastation caused by fire on wooden materials treated with borax could be reduced. From Figures 3 to 7, the results show that the effect of this treatment was more pronounced in resinous soft woods such as Obeche than hardwoods such as mahogany. However, in all respect, borax functions as flame suppressant.

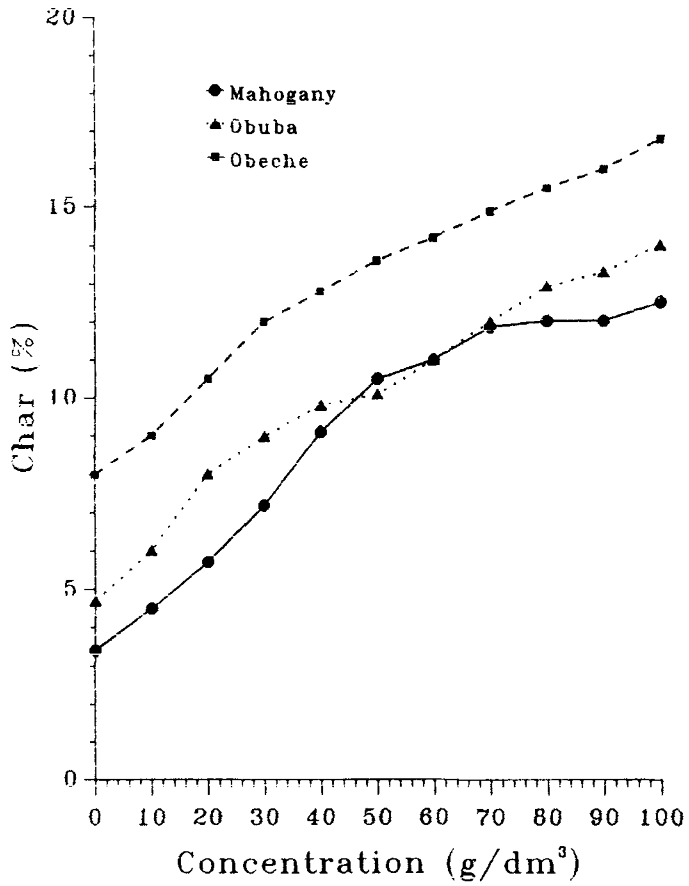

FIGURE 7 Plot of Char vs FS concentration.

Flame suppressant treatment is aimed at delaying the spontaneous spread of the fire when it does occur, such that reasonable lives and properties may be saved.

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