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Research Article

Investigation of Nigerian kaolinite clays as additives in fire retardant formulations

Adiat I. Arogundade^{1*}, Ibrahim D. Muhammad¹, Kafayat O. Adeyemi¹, Musa. T. Zarmai¹, Saratu Mamman²

¹Department of Mechanical Engineering, University of Abuja, Abuja, Nigeria ²Department of Chemistry, University of Abuja, Abuja, Nigeria

Abstract: In this work, kaolin clay from two deposits were characterized for material properties using X-ray diffraction analysis, X-ray florescence analysis, thermogravimetric analysis, scanning electron microscopy and fourier transform infra-red spectroscopy, in order to determine their suitability as additives in intumescing paints. Results indicated that compared to Kankara clay, Darazo clay has more crystalline kaolinite. Based on this, Darazo clay appeared more thermally stable, releasing less water of dehydroxylation. Kankara clay appeared less thermally stable producing consistent endothermic reaction that continuously drew heat away from the wood surface, creating a thermal plateau. The clays appeared to have no effect on the intumescent action. However, their high residual masses of over 90% reduced the total amount of fuel available at the flame front, thereby reducing flammability. At the end of the 10 minutes fire test, and using 11 wt% addition of both Kankara and Darazo clays, the reduction in backside temperature for Kankara is 13.6% while that of Darazo is 7.7%. The hybrid formulation gave the highest cooling effect at 20.56% temperature reduction compared to the control. All the coated boards recorded lower percent mass loss compared to the uncoated wood. Therefore, Nigerian kaolins have potential to serve as additives in fire retardant paints.

Keywords: Kaolinite Clay; Characterization; Dehydroxylation; Fire-retardant Coating; Fire-retardant Additive

1. INTRODUCTION

Fire hazards are common occurrences in homes, offices and commercial buildings. The losses of lives and properties to fire incidents every year is a perennial problem that has led to a wide field of research into fire ralated materials including fire-retardant materials, fire-stops, and a host of others. These serve to contain the fire and buy time for the occupants to make their escapes before the arrival of the fire-fighting team. The use of fire-retardant materials is not common-spread in Nigeria and other African countries. First, because of the relative novelty of the technology and second because most of the products are imported, therefore expensive. There is, therefore, a pressing need to explore the local contents as alternative raw materials in the production of locally-made fire retardant materials. The present work in response to this need

examines two locally sourced kaolin, one from Kankara in North-West geopolitical zone of Nigeria and the other from Darazo in North-East geopolitical zone of Nigeria.

Kaolin clay has a wide range of properties and uses depending on its location and age. This is due to the fact that the parent feldspars are a group of rockforming silicate minerals having potassium as in orthoclase (KAlSi3O8), sodium as in albite (NaAlSi3O8), calcium as in anorthite (CaAl2Si2O8) or a combination of any two of these primary forming elements as may be found in the plagioclase feldspar (oligoclase, andesine, labradorite and bytownite); the alkali feldspars (anorthoclase, sanidine and orthoclase-microcline) or the less common barium, rubidium, strontium or iron feldspars (Jongs, Jock,



Ekanem, & Jauro, 2018; Kumari & Mohan, 2021; Valentini & Mascarin, 2021). Kaolin may have other ancillary minerals including mica and quartz, and auxiliary minerals like illite, montmorillonite, ilmenite, anatase, haematite, bauxite, graphite and halloysite among others. This varied composition is responsible for a wide range of properties necessitating the careful characterization of each deposit for optimal utilization (Kumari & Mohan, 2021; Olafadehan, Okolie, & Kehinde, 2018)..

Kaolin clay, when not colored by impurities such as iron oxides and hydroxides has a white to whitepinkish coloration and find popular use in the paper and paint industries as a pigment and filler, its softness adding to the smoothness and gloss of high quality paper sheets (Raji & Bouhfid, 2020; Sanz, Tomasa, Sidki-Rius, & Sidki-Rius, 2022; Tamar-Agha, Mustafa, & Ibrahim, 2020). Kaolin clay, due to its good refractory properties was for centuries the traditional material for the production of high-quality porcelain and fired clays. Though kaolinite is not absorbent due to its tightly packed sheet structure, its large surface area makes it a good adsorbent which has found wide usage as membrane material in recent times (Marino, Russo, Rezzouk, Bouzid, & Figoli, 2017; Mustapha et al., 2019; Yu et al., 2020).

A less common use of kaolin is its application as a fire retardant. Kaolinite (Al2O3(SiO2)2.2H2O) may have up to four molecules of interstitial water which is released between 300-570oC or between 400oC -700oC in a dehydroxylation reaction as steam, depending on the nature of individual deposits (Daou et al., 2020; Izadifar et al., 2020; Tamar-Agha et al., 2020).. The released steam absorbs heat from its immediate surroundings, creating a heat sink that retards the growth of flame, while the resulting heatresistant alumina-silicate improves the thermal stability of the host system, thereby slowing down thermal degradation. Several researches have looked into the incorporation of kaolin clay as fire retardant filler, either as a supplement for the more common alumina or as an additional filler in intumescing paints, fire-rated plastics, textiles and other flametreated combustible materials (Ou et al., 2021; Tang et al., 2022; Ullah, Ahmad, Shariff, & Bustam, 2014).

For fire-rated plastics, flame retardancy may be improved by incorporating modified kaolin into the polymer matrix. To improve the flame retardancy of low-density polyethylene (LDPE), Ou *et al* (2020) incorporated 3% urea-intercalated kaolin into LDPE. Loss on ignition (LOI) was found to increase from 24.1% to 27.2%. Tang et al (2022) introduced 1.5 wt% glycerine-intercalated kaolin into an intumescent fire-retardant (IFR) formulation, 23.5 wt% of the IFR into polypropylene (PP) was found to decrease the peak heat/ smoke release rate. In a similar experiment, Yuan *et al* (2022) modified the surface of ammonium polyphosphate with kaolinite. Addition of this to PP led to increased thermal stability and char residue. Thus, modification of kaolin either by intercalation or grafting with a polymer moiety is found to improve the thermal stability of the fire-retardant system due to the more uniform dispersion of the kaolinite in the polymer matrix.

For non-plastic materials, fire retardant components are usually incorporated via chemical impregnation or intumescing coating. Intumescing paints are passive firefighting materials which when used as surface coating create a physical thermal barrier to the underlying material on exposure to high temperature or flame. Intumescent formulations consists of a char forming compound, usually pentaerythritol or any of the char forming starch; an acid-based compound, most commonly ammonium poly-phosphate, which triggers the charring reaction; and a fuming agent, which releases gas into the molten char to create an expanded, insulative mass (Hu et al., 2020; Lucherini & Maluk, 2019). Clays, metal oxides and hydroxides such as kaolin are often added as reinforcing filler and as synergistic additives to improve the strength and insulative efficiency of the resulting char (Aglibous, Tretsiakova-McNally, & Fateh, 2020; Ribeiro et al., 2020)..

Xu et al (2021) grafted a phosphate ester on kaolinite surface and blended this into amino resin to prepare a transparent coating which was applied to plywood board. The coating was found to exhibit a 64.9% reduction in flame spread and 45% reduction in smoke density. Hansen-Bruhn et al (2022) in a comparative study reported that unmodified kaolin exhibited a very low expansion factor of 7, compared to barite at 75 and titania at 60. On the other hand, Ulusoy et al (2022) found a blend of kaolin, metakaolin, flyash and calcium carbonate coating to perform better than a commercial coating due to the higher proportion of macro pores displayed by the kaolin-based coating.

Nigerian kaolin from different deposits have been widely studied and characterized for various applications. Mokwa et al (2019) and Labiran et al (2022) characterized some Nigerian kolinite clays for refractory bricks and fireclays; Maciver et al (2020) and Eze et al (2021) characterized some deposits for zeolites and ceramic filters; while Ofunne and Bassey (2019); Okafor et al (2020) characterized others for paints and pharmaceuticals. Though, most have promising properties for commercial applications, blending or modification of the clay structures have been reported to significantly improve the clay properties (Labiran, Ezea, Igba, & Akinyele, 2022; Olugbenga Oludolapo, Amu Igigba, Ehizemhen, Oluyemi-Ayibiowu, & Dorcas, 2022).. However, the idea of flame-retardant formulation is still relatively novel in the African region and no study to the best of our knowledge has been carried out on the suitability of Nigerian kaolin clay as flame retardant material despite its wide abundance. The aim of this study therefore was to determine the suitability of two Nigerian kaolin as alternative fillers in fire retardant coatings. To this end:

- Material characterization of the clay samples were carried out to determine their crystallinity and thermal stability. This was used to explain the behavior of the flame-retardant systems at elevated temperature.
- To determine the effects of clay additives on fireretardant paint, clay-incorporated coated wooden samples were subjected to flame test and their back side temperature recorded and compared to that of the unfilled, controlled sample. Samples of the different coatings were also subjected to thermogravimetric analysis and their residual masses at 800oC compared.
- A blend of the clay samples was prepared and the effect of clay blending on the performance of the fire-retardant coating was investigated.

2. MATERIALS AND METHODS

2.1 Materials

Two 6 kg samples of Kankara kaolin and Darazo kaolin were purchased from the Department of Chemical Engineering, Ahmadu Bello University, Zaria in Nigeria. The kaolin were used as received without further processing. The fire-retardant reagents were of laboratory grade. They were sourced from Aldrich Ltd, Germany. They included pentaerythritol and boric acid, epoxy resin and its curing agent.

2.2 Characterization of Clay Samples

The kaolin samples were characterized for mineral composition using X-ray diffraction analysis (XRD), chemical composition using X-ray florescence analysis (XRF), thermal behaviour using Thermogravimetric analysis (TGA), microstructural analysis using Scanning Electron Microscopy (SEM) and chemical groups using Fourier Transform Infra-Red Spectroscopy (FTIR).

X-ray diffraction analysis was performed on a Rigaku D/Max-IIIC X-ray diffractometer. Diffractions of

pelletized clay samples were collected at scanning rate of 20/min in the 2 to 500 range at room temperature with a CuK α radiation set at 40 kV and 20 mA. The diffraction data (d value and relative intensity) obtained was compared to that of the standard data of minerals from the mineral powder diffraction file, ICDD which contained and included the standard data of more than 3000 minerals.

X-ray fluorescence analysis of pelletized clay samples was carried out on a Philip PW 1210 Diffractometer. The fluorescence rays were generated by bombarding the samples with X-rays emitted from a Cu anode electrode at a wavelength of 1.550Å. The X-rays were produced by passing a stream of electrons generated at 25mA from a heated filament and accelerated at a high voltage of 40kV towards the target electrode. The fluorescence rays were collected in a semi-conductor detector and analyzed in a multichannel spectrum analyzer.

Microstructural analysis of pelletized clay samples was carried out on a JEOL JSM 7600 scanning electron microscope at an accelerating voltage of 15kV and a walking distance of 12 mm to 18 mm at magnifications of 8000, 9000 and 10000 respectively. For the TGA analysis, clay samples were used without prior preparation. 18.7 g of each powdered clay sample was put in a platinum crucible and fired in a closed furnace attached to the TGA 55 – TA Instrument from room temperature to 10000C at a heating rate of 100C/min using nitrogen as inert gas.

2.3 **Preparation of Coatings**

The two clay samples were incorporated into an epoxy matrix as an additive to the main fire retardant ingredients (FRI) of ammonium polyphosphate, melamine and pentaerythriol. The powder clay samples and the FRI were blended together to achieve homogeinety before addition of the epoxy. Shear mixing of the coating slurry was carried out for 20 minutes at 40 rpm before the addition of the curing agent. Shear mixing continued for additional 10 minutes to assist the dispersion of the particles in the resin matrix. The formulation of Yew at al (2015) in which a blend of fire retarding fillers was used was adopted for this study. The control, B1 was without a clay additive, the hybrid sample, B2 had 5.5 wt% each of both clays, B3 had 11 wt% Darazo content while B4 had 11 wt% Kankara content. The paints were applied using a wooden spatula on one face and all edges of 10 cm x 10 cm x 3 cm unlaminated

Runs	KADZ (wt%)	KAKK (wt%)	APP (wt%)	MEL (wt%)	PER (wt%)	EPOXY (wt%)	BINDER (wt%)
B1	0	0	18	9	9	35.33	17.67
B2	5.5	5.5	18	9	9	35.33	17.67
B3	11	0	18	9	9	35.33	17.67
B4	0	11.0	18	9	9	35.33	17.67

Table 1: Chemical Formulations of Darazo and Kankara Intumescing Paints

2.4 Fire Performance Testing

The heat shielding ability of the clay-filled coatings were tested using the Bunsen burner test as shown in Figure 1. The bunsen burner test is a bench scale fire test adapted to ASTME119 for comparing the heat shielding ability of coated samples.



Figure 1: Bench-scale fire test set-up

This was done by impacting flame from a butane gas burner on the coated surface and measuring backside temperature of the wood by taking the average readings of three thermocouples attached to the uncoated surface. The thermal stability of the clayfilled coatings were evaluated by obtaining residual masses of the coated film samples on a TGA 55 – TA machine.

3 RESULTS AND DISCUSSION

3.1 Mineral Composition

The XRD graphs of the clay samples are presented in Figure 2. Both the Kankara kaolin clay and the Darazo kaolin clay showed several peaks for kaolinite, anatase, quartz, hematite and illite. However, Darazo clay shows highly prominent peaks for kaolinite, the desired mineral, while the peaks are less clearly defined in Kankara clay except the peak at 28 20. This indicates that Darazo is populated by highly crystalline kaolinite while Kankara is populated by poorly crystalline kaolinites. Li et al (2019) and Belmokhtar et al (2018) have reported in earlier works

that the physicochemical properties of kaolin-group minerals are strongly dependent on their crystallinity(;). Poorly crystalline aluminosilicates are known to be characterized by small particle sizes, high specific surface area and excellent ion exchange rates while crystalline aluminosilicates have relatively bigger particles and are more electronically stable(;)



Figure 2: Comparison of the mineralogy of Darazo clay and Kankara clay

Christian et al (2018) recently reported the high specific surface area and excellent ion exchange rates of Kankara clay as a promising adsorbent in the local pharmaceutical industry(). The high ion exchange rate of Kankara clay will ease the incorporation of polymer ions in synthesizing organoclays necessary for the production of high performing intumescent paints. Other works have also shown that intercalation of ions its easier in more crystalline kaolinite(). Again, both clay types may still play heat shielding roles by migration of the particles to the surface of the intumescing char to create a physical barrier and reinforce the char strength(;). Thus, each clay type may have its own unique mechanism for improving fire retardation based on their overriding properties.

3.2 Chemical Composition

The elemental compositions of both clays are presented in Table 2. The chemical oxide components analyzed for each sample were silica (SiO_2) , alumina (Al_2O_3) , iron oxide (Fe_2O_3) , titanium oxide (TiO_2) , calcite (CaO), potassium oxide (K_2O) , sodium oxide (Na_2O) , magnesium oxide (MgO) and manganese oxide (MnO).

Table 2: Chemical compositions of the Darazo and Kankara Clays (wt%)

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Sample ID	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	K ₂ O	Na ₂ O	MgO	MnO
Sample DZ	49.53	33.50	0.15	0.09	0.25	1.60	0.21	0.75	0.01
Sample KK	49.71	34.80	0.72	0.66	0.09	1.21	0.06	0.21	0.01

Silica was found to be the most abundant oxide in both clays with almost 50% weight content in both clays. Alumina had a percent composition of about 33-35% in both clays with Kankara clay having slightly more alumina content than Darazo clay. All other components existed as trace elements with compositions between 1.6 to 0.01%. Kankara showed greater content of iron oxide impurity than Darazo, implying Darazo may be better suited for paper production as less bleaching will be needed. Kankara clay also possessed slightly higher content of titanate than Darazo while the Darazo clay shows greater percent of the alkali oxides. This analysis confirms both clays to be aluminum -silicate minerals with trace impurities. Many works, including those of Xu et al (2022) and Laoutid et al (2021) have reported that metal oxides such as titanium oxide, iron oxide and calcite as found in both clay types offer additional flame diluting effects as a result of their noncombustibility and high thermal stability.

3.3 Microstructural Analysis

The micrographs of Kankara and Darazo clay samples are presented in Figure 3. The micrographs of both clay samples reveal sheet-like structures characteristic of layered aluminum-silicate minerals. The Kankara micrographs reveal flaky sheets with more rounded edges while the Darazo micrograph reveal crystal platelets with sharper outlines. Both clay particles showed high degree of agglomeration. The particle size from the micrographs could be estimated to be in the range of 50 µm to 200 µm for both clay types. Generally, clays act in the condensed phase by migrating to the polymer surface at high temperature to provide additional viscosity which reduces the release of free radicals to the flame front and encourages the thickening and strengthening of the char bulk. The Kankara clay again because of the greater surface area provided by the flaky structure may provide greater barrier and labyrinth effect, than the Darazo platelets, leading to greater delay in material decomposition and smoke generation, and inhibition of heat and mass transfer (Chen et al 2019; Liu et al 2020).



Figure 3: (a) Micrograph of Kankara clay @ 9000x (b) Micrograph of Darazo clay @ 9000x 3.4 Functional Group Analysis The FTIR graphs of the two clays are presented in Figure 4. Both Kankara and Darazo clays show very identical peaks, however Darazo shows lower transmittance for all the functional groups considered, this is in keeping with its more crystalline nature which absorbed more of the waves compared to Kankara. Characteristics peaks of silicate minerals at around 920 to 980 cm⁻¹ are very prominent in both minerals. Also, the O-H hydroxide peaks around 3600 cm⁻¹ reported by Agbendeh et al (2021) and Mgbemere et al (2018) are quite prominent in both clays. The H-O-H bending of water around 1637 cm⁻¹ earlier reported by Ayeni et al (2019) is observed to have much greater absorbance for water molecules in Darazo than Kankara, implying stronger water bonds in Darazo than in Kankara. The aluminum peaks at around 650 cm⁻¹ are also identified. These results are in tandem with the other analyses and confirm these clays as aluminum silicate-based materials or aluminum-silicate hydroxide minerals with varying degree of crystallinity.



Figure 4: Comparing the FTIR Spectra of Kankara and Darazo Clays

3.4 Thermal Analysis

The TGA graphs of both clays are presented in Figure 5. The thermal analysis which was run from approx. 20°C to 1000°C show a weight loss of about 6.5 % for Darazo clay occurring between 450°C and 650°C due to the dehydroxylation of the minerals in the clay as shown in Figure 5a. Figure 5b show that Kankara clay has a total mass loss of 8.9 % at around the same range due to dehydroxylation and initial loss of water of crystallization at 200°C. The ability of Kankara to lose water faster is already evident in the weaker H-O-H bonds of Kankara as observed in the IR peaks of Figure 4. While Darazo appear to be more thermally stable, Kankara has the potential of a better hydrant due to about 2.5% water released around 200°C. This may contribute to delaying ignition time of the treated wood material. Both clays are shown to be endothermic in their reaction absorbing between 14 W/g to 18 W/g of heat at the elevated temperature of about 400°C to 950°C. This endothermic reaction will help draw heat away from the coated substrate creating a cooling effect that will reduce flame spread.



Equally important also is the residual mass of the clays. Both clays are able to maintain high residual masses at the elevated temperature of 1000°C, with Kankara having a residual mass of about 90% and Darazo, a residual mass of about 93%. This is very important, since these noncombustible residues reduce the total amount of volatile elements available to the flame front, thereby thermally stabilizing the wood bulk long after the flame retardants components have degraded. Darazo slightly greater residual mass is as a result of its greater crystallinity which has already observed above conferred on its greater thermal stability than Kankara clay.

3.6 Fire Performance of Test Samples

3.6.1 Heat Shielding Ability

The results of the fire tests for the four coated samples without any clay additives (B1), with 5.5 wt% of each clay type (B2), with 11 wt% of Darazo (B3) and Kankara (B4) respectively are presented in Figure 6.



Figure 6: Comparing the heat curves for the wood samples without any clay additive, B1; 5.5 wt% of each clay type, B2; with 11 wt% Darazo, B3; and 11 wt% Kankara B4 when exposed to a Bunsen flame at $750^{\circ}C \pm 50^{\circ}C$ for 12 minutes.

At the start of the experiment, all sample temperatures rose rapidly from room temperature to about 68°C in 2 minutes, except for B4 (containing semi-crystalline kaolinite) which reached a higher temperature of 79°C as less crystalline surface water was released as steam. Thereafter, B4 was able to maintain a thermal plateau of $80 \pm 2^{\circ}C$ as the endothermic reaction continuously drew heat away from the wood surface. It may be observed that the rate of degradation of each sample correlates with the thermal stability of the clay additive as reported in the TGA analysis. Therefore, B3 which contained more thermally stable Darazo clay gradually rose to 80°C in 7 minutes, while B2 which is a hybrid of B3 and B4 displayed delayed, but greater endothermic reaction due to the combined effect of the semi and fully crystalline water molecules. Thus, the temperature was seen to rapidly rise to around 85°C in the 3rd minute and then drop to around 73°C in the 6th minute. The control sample, B1 maintained the initial temperature rise of 68°C for a longer time implying the immediate setting in of intumescing action. Beyond the 6th minutes, all samples showed varying increase in temperature. The filled coated samples showed slower temperature increase probably due to the diluting effect of the noncombustible residual masses. The hybrid sample, B2 showed the lowest temperature of 102°C at the 10th minute followed by B4 with 110.9°C and B3 with 118.5°C. The control sample had the highest temperature increase of 128.4°C after 10 minutes of flame contact. Thus, incorporation of either clay led to an improvement in the fire retardancy of the intumescing paint. 11 wt% addition of Kankara gave a greater reduction of 13.6% compared to 11 wt% addition of Darazo at 7.7% reduction. The combined effect of both clays gave the highest cooling effect at 20.56% reduction compared to the unfilled paint.

3.6.2 Resistance to Flame Propagation

Flame spread may be described as the extent of travel of the flame point over the surface of the solid combustible. The area of the uncharred, coated wood samples could be taken as a measure of the coating resistance to flame spread. Measured with a scale ruler to the nearest millimeter, the length of the uncharred region in B2 representing the hybrid formulation was found to be 12 mm while that of the control, B1 was found to be 5 mm. B3 had an uncharred length of 8 mm while B4 had an uncharred length of 10 mm. This is seen to correlate with the heat shielding ability of the systems, where the highest temperature reduction is observed in the hybrid sample. These are shown in Figure 8. No intumescence was observed in either the control sample or the filled samples. This lack of intumescence may be due to several factors including agglomeration of the fillers, and the presence of other non-intumescing minerals such as quartz and illinite within the clay samples. The presence of these minerals is however not detrimental to the fireretardant ability as they increase the non-combustible component of the system. Nevertheless, further work will be needed to modify the clay surface for uniform dispersion within the resin matrix for enhanced performance.



Figure 7: Test samples after fire test showing extent of flame propagation

3.6.3 Percent Mass Loss

The weights of the samples taken before and after the fire test were used to compute the percent mass loss during burning. This is presented in Table 3.

Table: Percent mass loss during fire test.

Samples	Mass before fire test (g)	Mass after fire test (g)	Mass loss (%)
B0	104.73	71.68	31.55
B1	118.62	90.54	23.67
B2	118.54	90.84	23.36
B3	118.50	93.45	21.14
B4	118.24	92.81	21.51

From the Table, B0 represents the uncoated wood, B1, the coated wood without filler, B2, the coated wood with hybrid filler; B3, Darazo clay-filled coating and B4, Kankara clay-filled coating. The uncoated wood had the highest mass loss of 31.55 %, confirming that the fire-retardant paints improved the fire-resistance of the wooden material. The clay-filled samples both had a mass loss of approximately 21%, the hybrid formulation had a slightly higher mass loss of 23.36%, while the unfilled sample B1 had a mass loss of 23.67%. From this, it can be seen that incorporation of the kaolin clay slowed down thermal degradation of the coated wood.

4. CONCLUSION

This work investigate the suitability of two of the numerous Nigerian kaolin deposits as fillers in fire retardant paints.

- It was found that Kankara clay consisted of semi crystalline kaolinite while Darazo clay contained fully crystalline kaolinite.
- Kankara clay displayed a 2-step dehydroxylation process with the first endothermic reaction occurring at around 200°C and the second one beginning at around 450°C. Darazo clay had a single dehydroxylation stage starting around 400°C. Thus, Darazo clay exhibited greater thermal stability while Kankara clay showed greater tendency to decompose and release more water of dehydroxylation.
- The material properties of each clay type affected the overall performance of the paint when the clay was incorporated as additive. The performance of the Kankara-filled paint appeared to depend mainly on thermal cooling as the endothermic reaction drew heat away from the wood surface creating a

thermal plateau on the wood surface. For the Darazo-filled paint, performance appeared to depend more on the thermal stability created by the bulk effect of the filler itself, therefore the temperature had a slower, but steadier rise. The addition of either clay led to improvement in the heat shielding ability, flame propagation and thermal degradation of the coated wood, while the combined effect created even greater synergy. The high percentage of noncombustible residual masses found in both clays added to the thermal stability of the system.

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