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Effects of Metal-Based Montmorillonite Clay and Zeolite Additives on the Fire Retardance and Smoke Suppression of Poly(vinyl Chloride)

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Effects of Metal-Based Montmorillonite Clay and Zeolite Additives on the Fire Retardance and Smoke Suppression of Poly(vinyl chloride)

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Bachelor of Science, Chemistry, The College of William and Mary, 2007

**A Thesis presented to the Graduate Faculty
of the College of William and Mary in Candidacy for the Degree of
Master of Science**

Department of Chemistry

**The College of William and Mary
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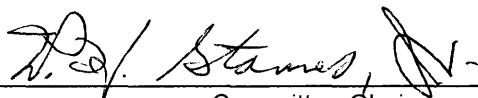
This Thesis is submitted in partial fulfillment of
the requirements for the degree of

Master of Science



Alexander G. Zestos

Approved by the Committee, June 2008

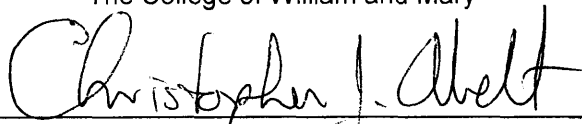


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ABSTRACT PAGE

Poly(vinyl chloride) (PVC) is the second most commonly used thermoplastic produced by the chemical industry. Unfortunately, PVC can undergo thermal degradation relatively easily, a process which generates volatile organic compounds that are smoke producers in fires. This thesis attempts to understand the smoke suppression and fire retardance of poly(vinyl chloride) containing various metal-exchanged montmorillonite and zeolite additives. The additives were blended with PVC and molded into plaques incorporating the resulting formulations. These plaques were burned in a cone calorimeter together with control PVC plaques that contained no metal compounds. By using a computer program, variables such as the time to ignition, specific extinction area, total heat released, total smoke released, etc., were measured and assessed in order to determine the effectiveness of the metal additives in smoke suppression and fire retardance.

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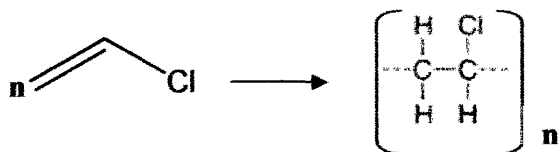
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Introduction

Poly(vinyl chloride) (PVC) is a very commonly used plastic that is an extremely valuable product of the chemical industry. As compared to many other chemical materials, PVC is relatively inexpensive, safe to work with, and easy to manipulate. Some of the many uses for rigid PVC are as replacements for building materials (such as wood and clay), water and sewer piping, siding, magnetic strip cards, window profiles, and various toys.¹ In its softer (plasticized) form, PVC is used to create upholstery, resilient flooring, roofing membranes, electrical cables, and lightweight hobby artillery.¹

Chemically speaking, poly(vinyl chloride) is produced by the free-radical polymerization of the monomer, vinyl chloride (see Figure 1). The polymer is a hard plastic that is made softer and more flexible by the addition of plasticizers, the most widely used of these being phthalates. In the laboratory, we primarily deal with PVC in a white powdery form to which a liquid plasticizer may be added. The polymer was actually discovered accidentally, first in 1835 by Regnault, and then in 1872 by Baumann.¹ It appeared as a white solid inside flasks of vinyl chloride that were exposed to the sun. Many early scientists attempted to use PVC in commercial products, but problems in fabricating the rigid and brittle polymer made such usage quite difficult.

Figure 1: Polymerization of vinyl chloride



Since this study deals with the fire retardance and smoke suppression of PVC, the thermal degradation of PVC at elevated temperatures must be critically examined.

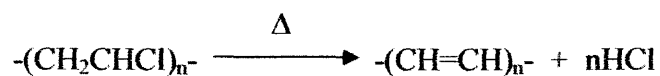
Poly(vinyl chloride) is a relatively unstable polymer that undergoes dehydrochlorination upon heating to form conjugated polyene sequences.¹ Many researchers have spent countless hours examining when and from where in the polymer chains the HCl loss begins and what is the associated step-by-step mechanism of this process.

Since HCl is a strong acid, its release into the environment after heating and thermal degradation is of very serious concern because of its many deleterious effects. Therefore, many studies deal with the prevention - or at least the delay - of thermal degradation. This objective is accomplished by adding various stabilizing additives (frequently, new substances synthesized in the laboratory), which may also help to promote the fire retardance and smoke suppression of PVC.

As already noted, the dehydrochlorination of PVC forms hydrogen chloride (HCl) and a polyene. After the fact, the HCl causes more dehydrochlorination to occur.² A gross simplification of the overall process can be seen in Figure 2.

Figure 2: Release of HCl

a. Release of HCl and formation of a conjugated polyene



b. Catalysis of dehydrochlorination by HCl

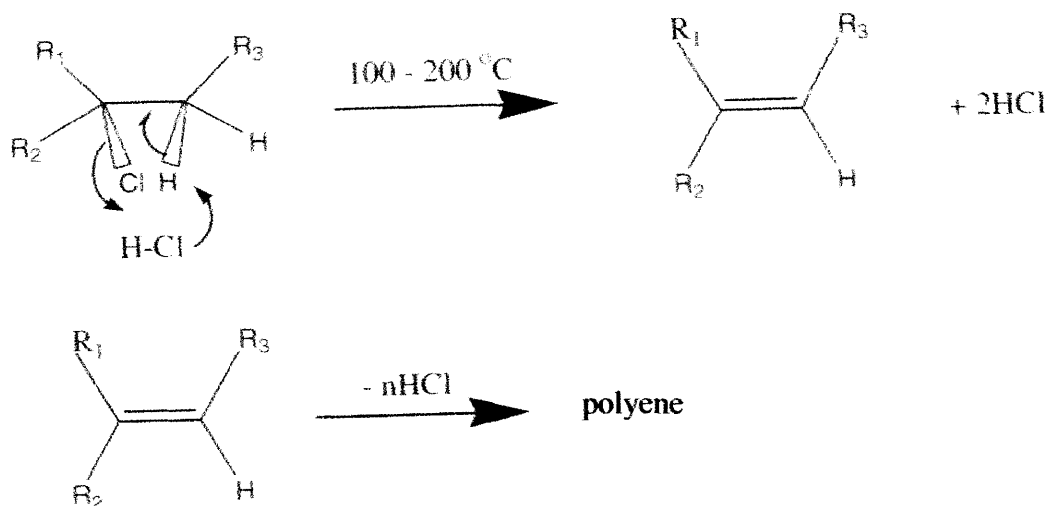
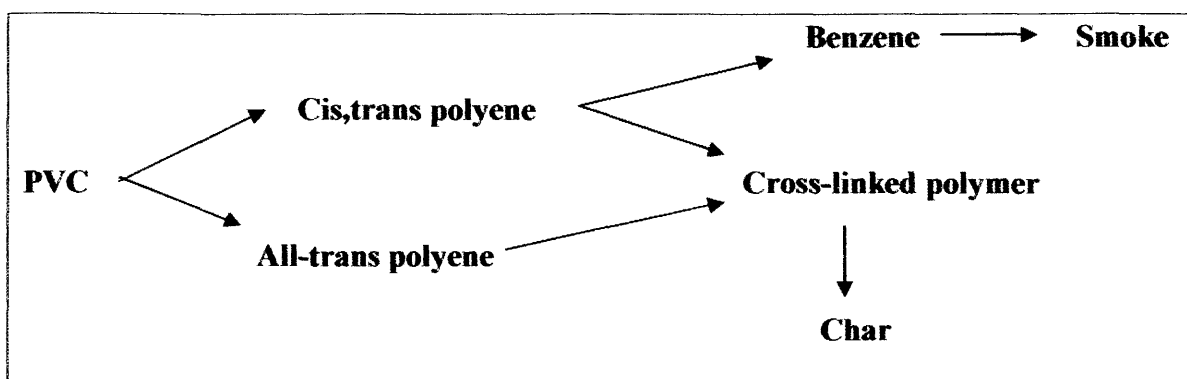


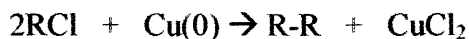
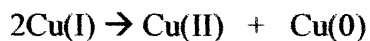
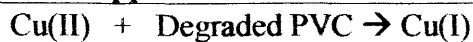
Figure 3 displays the various degradation pathways of PVC in fire situations. Most importantly, the two major byproducts of burning PVC, smoke and char, are shown. In one pathway, when PVC is heated and then burned, it is thermally degraded to form a cis,trans polyene, which then will generate benzene, whose combustion creates smoke. On the other hand, both cis,trans and all-trans polyenes form a cross-linked polymer, which will then form char. From previous studies, it has been determined that plasticized PVC produces much more smoke than char.³ It has been generally seen that adding copper-based additives to plasticized PVC significantly reduces smoke emission and increases the char yield, which is given by $(100)(\text{mass after burn})/(\text{mass before burn})$.³

Figure 3: Degradation of PVC in fires



A major purpose of this thesis is to examine, by means of cone calorimetry, the smoke suppression and fire retardance of PVC that are promoted by some new copper additives. When PVC undergoes combustion, its thermolysis can generate many volatile aromatics in addition to benzene that are smoke producers.³ Also, when it is burned, the cross-linked char that it forms produces aliphatic hydrocarbons in large fires.³ These substances burn without creating much smoke, but unfortunately, they are excellent fuels.⁴ The copper additives being studied by the Starnes group promote the formation of a char which is stable at very high temperatures and is produced without the concurrent formation of volatile aromatic compounds. The cross-linking (charring) mechanism is promoted by zerovalent copper formed *in situ* and is shown in Figure 4, where RCl represents a segment of PVC.⁵ These reactions show the changes in the oxidation state of copper as the PVC is degraded.

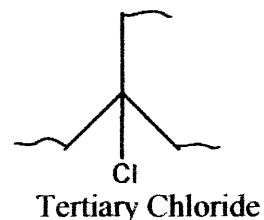
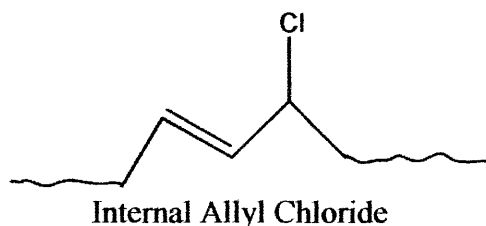
Figure 4: Copper oxidation states during PVC combustion



Orski commented on the structural defects in PVC that cause the thermal instability which leads to dehydrochlorination.⁶ These structural defects arise from multiple “errors” of polymerization during the formation of the polymer.² Though many errors occur, only two will be considered here. The defects that they produce are an internal allyl chloride structure and tertiary chloride groups that result from branching. These two structural defects incorporate a labile chlorine that can be easily removed from the PVC chain.

Figure 5 depicts both of these structural anomalies.

Figure 5: Thermally unstable structural defects in PVC

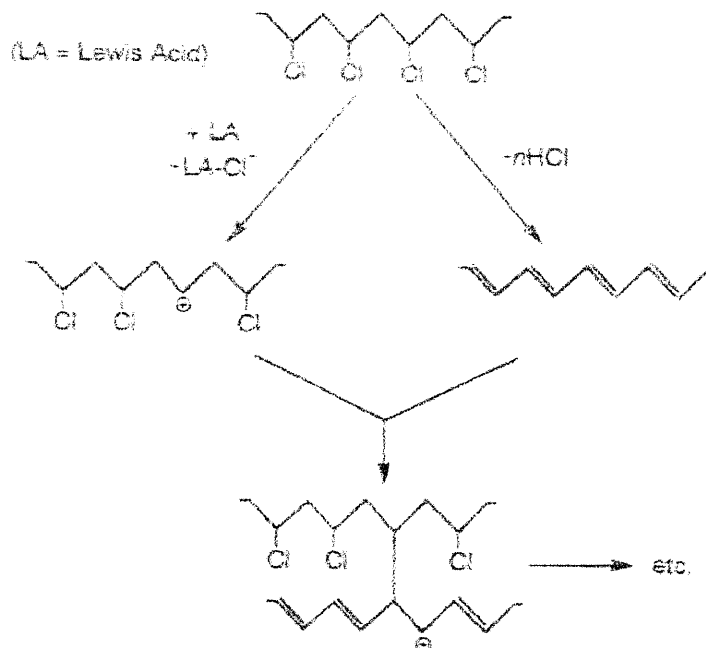


During burning and thermal degradation, a Friedel-Crafts alkylation occurs that promotes cross-linking, especially when a Lewis acid additive is present. By definition, a Lewis acid is any molecule that can accept a pair of electrons and thereby form a

coordinate covalent bond. Lewis acids are electrophiles and are most likely to react in the LUMO (Lowest Unoccupied Molecular Orbital). The reactivity of Lewis acids is primarily assessed in terms of the Hard-Soft-Acid-Base (HSAB) theory. This theory states that “hard” refers to certain species which are relatively miniscule in size, have highly charged states in nature (for acids), and are weakly polarizable. On the other hand, “soft” describes species that are large, have low charge states, and are strongly polarizable. As studied in elementary polymer chemistry, cross-linking (along with entanglement) makes the polymer more rigid and thermally stable and causes it to have a higher melting point, as well.

The specific acid-catalyzed cross-linking mechanism (see Figure 6) occurs when a chloride anion is removed from PVC in order to form a carbocation intermediate.⁷ This intermediate then attacks an alkene double bond to produce the aforementioned cross-link. When this process occurs repeatedly and subsequent extensive dehydrogenation occurs, char is formed. Therefore, after a burn, the higher the char yield from PVC, the better the additive has worked in fire retardance. This mechanism of degradation also tends to prevent the formation of the aromatic smoke producers such as benzene, which is an essential step toward our eventual goal of the smoke suppression of poly(vinyl chloride).

Figure 6: Cross-linking by Friedel-Crafts alkylation



As we have seen, the thermal degradation of PVC involves dehydrochlorination, which removes a hydrogen cation and a chloride anion to form hydrogen chloride (HCl) and a conjugated polyene. However, one must consider that in the presence of a strong Lewis acid at very high temperatures (well above 300°C), cross-linking will not be a significant factor. The char will be broken down through a process of “cationic cracking”, in which the previously beneficial Lewis acid promotes the formation of aliphatics that further exacerbate the situation by burning very readily, though without the production of

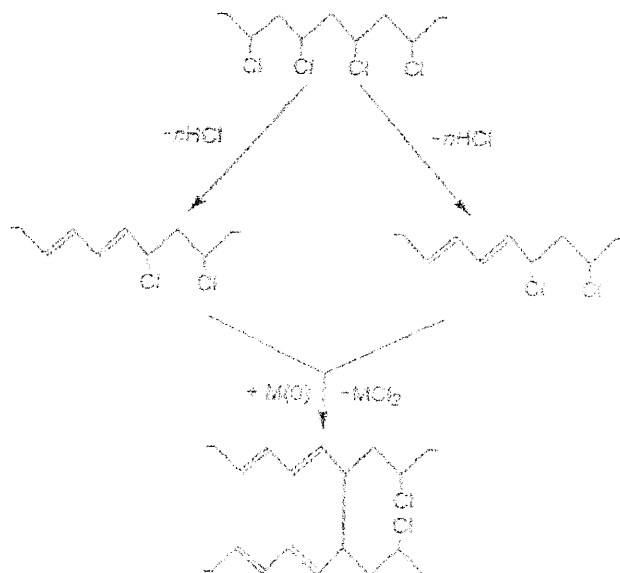
much smoke. This enhanced combustion can be a major problem in large fires.⁷ It has forced the examination of other additives for PVC that are not Lewis acids.

Pike et al. found that high-surface-area oxide-free copper and other zerovalent metals promoted the reductive cross-linking of allylic chloride moieties in PVC.⁷ They found that zerovalent metals that were simply mixed with the polymer as such served as ineffective smoke suppressants, since the metal powders were subject to rapid surface air oxidation. The authors actively researched potential smoke suppressants that were compounds which could decompose thermally to liberate a free metal. Several copper(I) compounds were prepared to be used as effective fire retardants and smoke suppressants. Such compounds are desirable to the chemical industry because they lack color, and the thermal stability of the copper(I) center can be altered with the usage of specific ligands. Simple Cu(I) halides such as CuCl, CuBr, and CuI gave significantly lower mass loss rates in comparison to those obtained with other additives. The importance of this study was underscored by the observation that the cross-linking caused by low-valent metal compounds generally occurred very rapidly with minimal mass losses and little evidence of C=C formation, as opposed to the results obtained with Lewis acidic metal chloride additives. Therefore, these findings corroborated the idea of a mechanism for PVC cross-linking with reductive coupling (mostly at allylic sites) rather than acid catalysis.

The Starnes research group has used many copper-based additives as smoke suppressants and fire retardants for PVC. As implied by Figure 4, a single zerovalent copper atom can prevent the further dehydrochlorination of two long polymer chains.⁷ At extremely high temperatures in degrading PVC, Cu(I) is reduced to Cu(0), which can

abstract two allylic chlorines from two PVC chains and thereby form a carbon-carbon bond (a cross-link) in the reductive coupling process that has already been illustrated (see Figures 4 and 7).⁷ Moreover, both Cu(II) and Cu(I) can accept ligands that modify their reactivity.

Figure 7: Reductive coupling mechanism for cross-linking



Another important consideration is the thermal stability of PVC. Many experimental results have shown that the thermal stability of pure PVC is much lower than it should be had thermal dehydrochlorination commenced only from head-to-tail monomer units.^{2-8, 10} Therefore, anomalous structures (structural defects) that have lower stabilities were proposed to be present in PVC, a situation which means that these defects

act as starting points for the sequential losses of HCl that generate polyene sequences. The virgin PVC polymer contains only four specific types of defects that contribute to its thermal instability. These are the internal allylic, 2,4-dichloro-*n*-butyl branch, long branch, and 1,3-di(2-chloroethyl) branch structures.² The Starnes laboratory previously determined their concentrations by using NMR methods. It was found that the concentrations of the di(2-chloroethyl) defect were so low that its contribution to the loss of thermal stability was negligible.²

The autocatalysis of PVC dehydrochlorination implies that the HCl produced during the process accelerates the rate of thermal degradation. Early on, the degradation is accompanied by an increase in the number of polyene sequences, a situation which involves the initiation of polyene growth from monomer units that were previously stable. This initiation is now known to result from the formation of cation radical intermediates.¹¹ The HCl could also catalyze the growth of existing polyenes or reactions that inhibit cyclizations which shorten polyene lengths.⁸

Additives for PVC that promote stabilization often replace the labile chlorine in an unstable structural defect (including the chloroallylic end of a growing polyene) by groups that are less easily removed by heat.⁸ Many effective thermal stabilizers of PVC are the salts of various metals. They are sufficiently basic to neutralize HCl, which also is a very important function of these additives.⁸ The stabilizers that replace labile halogens frequently are salts represented by the formula MY_2 , where M is a metallic cation, and Y is an organic anion such as thiolate or carboxylate.

In certain cases where strong Lewis acids, such as zinc chloride, are formed *in situ*, these species may catalyze dehydrochlorination during heating. This problem can be

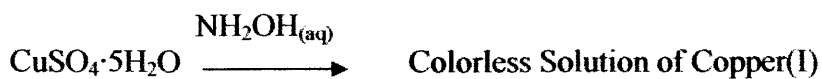
alleviated by using certain mixtures of metal salts whose communal action as stabilizers can be synergistic.⁸

There are specific mechanisms of initiation by internal allylic and tertiary chloride structures in PVC that make them important as labile structures. Evidence has shown that they dehydrochlorinate thermally in the condensed phase by mechanisms involving ion pairs or polar concerted transition states.²

Free-radical mechanisms for the growth of conjugated polyene sequences during the anaerobic thermal degradation of PVC have been studied extensively. However, such a mechanism is now known to be responsible only for the formation of new polyene sequences, rather than for the growth of polyenes *per se*.¹¹

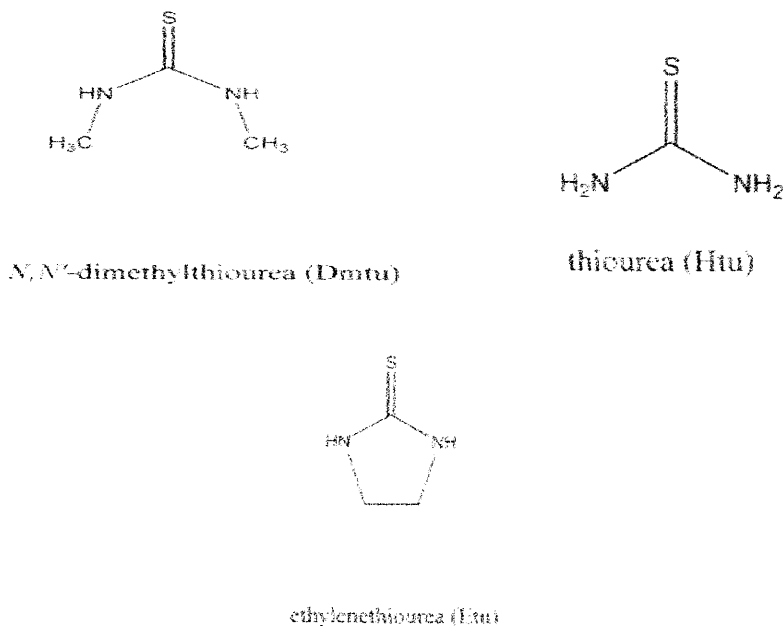
Furthering our discussion of copper, we must distinguish between its two most common valence states, copper(I) and copper(II). Copper(I) is a relatively polarizable species whose stability increases greatly when it is joined with polarizable ligands. On the other hand, copper(II) is more stable than copper(I). However, a problem arises when dealing with copper(II). Copper(II) generally has a strong blue (sometimes blue-green) color, which is not very useful to the polymer industry. For practical reasons, the polymer industry desires colorless additives that are more appealing to the market as a whole. Therefore, the generally colorless copper(I) may be preferred over copper(II) in certain instances, even though it is less thermally stable. The incorporation of various ligands into copper(II) complexes is also utilized to reduce the blue color. In the Starnes laboratory, copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) has been the primary source of copper(II). On the other hand, copper(I) can be obtained from a variety of sources such as

cuprous iodide or cuprous chloride, and also through the reduction of copper(II) by the use of hydroxylamine, as seen below.



Though we did not see a completely colorless copper(I) solution, the color changed from dark blue to a very light blue, a result which allowed us to surmise that NH_2OH served as a satisfactory reducing agent and reduced most of the copper(II) to copper(I). Many other copper additives were utilized, such as CuCl_2 , CuI , Cu(I) thiourea (Htu), Cu(I) ethylenethiourea (Etu), and Cu(I) *N,N'*-dimethylthiourea (Dmtu) (see Figure 8). The data obtained from burning PVC plaques containing these additives were compared to the results obtained from control PVC plaques containing no additives at all.

Figure 8: Structures of ligands for copper(I)



Experimental

Before we repeated the synthesis of the copper compounds in order to obtain enough of them for experimentation, we first produced small amounts to see if we were obtaining acceptable percentage yields.

Additive Synthesis

Drs. Starnes and Pike, Yuichi Matsuyama, and Sara Orski provided instructions regarding the following preparations.

Synthesis of copper(I) ethylenethiourea sulfate [Cu₂(Etu)₆]SO₄

A mixture of 4.0 g (16 mmol) of CuSO₄·5H₂O, 8.178 g (80.05 mmol) of ethylenethiourea (Etu), and 200 mL of UltraFiltered Deionized (UFDI) water was heated and stirred on a hot plate until the blue color of the copper(II) had completely disappeared. The solution was then boiled for approximately 0.5 h, and a yellow precipitate of sulfur formed. Afterwards, the hot mixture was filtered quickly with suction, and the filtrate was cooled in an ice bath and then refrigerated overnight. The resultant white precipitate was recovered by suction filtration, washed well on the filter with ether, methanol, and ethanol in succession, and then dried in an oven at 50°C overnight. The final weight of the complex was 2.30 g (33.5% yield).

Synthesis of copper(I) thiourea sulfate [Cu₂(Htu)₅]SO₄·2H₂O

A mixture of 200 mL of UFDI water, 12.00 g (157.6 mmol) of thiourea (Htu), and 7.87 g (12.0 mmol) of CuSO₄·5H₂O was heated and stirred on a hot plate to produce a white suspension, which eventually yielded a yellow solution containing a yellow precipitate. This mixture was heated under reflux overnight and then filtered while hot through Celite. Afterwards, the filtrate was cooled in an ice bath and stored in a refrigerator overnight. The beige precipitate was collected via suction filtration and

All of our copper(I) molybdate products were obtained from the second synthesis, since, in order to succeed, the first synthesis would actually require a high-temperature furnace. However, there was a problem in using them as smoke suppressants and fire retardants of PVC, in that they were dark brick-red in color. When blended with PVC, they produced very highly colored plaques. Upon knowing this result, the plastics industry would deem Cu_2MoO_4 to be unacceptable as a smoke suppressant or fire retardant for PVC. Therefore, extensive cone calorimeter burns were not conducted with the plaques containing this additive.

Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy (AAS) was utilized as a technique for determining copper content.¹² By using this method, the concentrations of some 62 different metals can be determined in solution. The technique makes use of a flame to atomize the sample. However, other atomizers, such as a graphite furnace, are also used.

There are three definite steps involved in turning a liquid sample into an atomic gas. The first step is desolvation, where the liquid solvent is evaporated, and thus the dry sample remains. The next step is vaporization, in which the solid sample vaporizes into a gas. Lastly, there is atomization, wherein the compounds making up the sample are broken into free atoms. Light focused into the flame is produced by a hollow cathode lamp. Within each lamp, there is a cylindrical metal cathode containing the metal for excitation and an anode. When a high voltage is applied across the anode and cathode, the metal atoms in the cathode are excited into the production of light with a certain emission spectrum. The electrons of the atoms in the flame can be promoted to higher

orbitals by absorbing a set quantity of energy. This amount of energy is specific to a particular electronic transition in a particular element. As the quantity of energy put into the flame is known, and the amount remaining can be measured by the detector, it is possible to calculate how many of these transitions took place and thus to get a signal that is proportional to the concentration of the element being measured. An AAS instrument is shown in Figure 10, and the procedure employed for Cu analysis is described in the next section.

Figure 10: Atomic absorption spectrometer



AAS Procedure and Results¹³

Weigh out 11-13 mg (exact to 0.1 mg) of sample in a 2-dram vial. Add about 25 drops of concentrated nitric acid. Warm the mixture on a hot (not boiling) water bath for about 5 min. Rinse a 100-mL volumetric flask twice with ultrafiltered deionized (UFDI) water. Add about 2 mL of UFDI water to the vial. Quantitatively transfer the copper/water/nitric acid mixture to the volumetric flask with a Pasteur pipet. Rinse the vial with UFDI water by using the same pipet three times; be sure to transfer the liquid quantitatively. Fill the volumetric flask exactly to the mark with UFDI water. Invert the volumetric flask thrice to mix. If solids are present, sonicate the volumetric flask mixture for 10 min.

Rinse a 25-mL volumetric flask twice with UFDI water. (If suspended solids are present in the 100-mL volumetric flask, filter about 15 mL of the mixture through a pipet filter containing Celite into a vessel which has been pre-rinsed with the solution.) Rinse a 1-, 2-, 3-, or 5-mL (see below) volumetric pipet with the solution (filtered if necessary) from the 100-mL volumetric flask. Volumetrically pipet 1.0, 2.0, 3.0, or 5.0 mL from the 100-mL flask into the 25-mL flask. The volumetric pipet is calibrated to deliver (not to contain), so do not blow out the remaining drop in the tip. Fill the 25-mL volumetric flask exactly to the mark with UFDI water. Invert the volumetric flask thrice to mix.

Note on the choice of 1, 2, 3, or 5 mL to pipet into the 25-mL volumetric flask: The choice depends on the theoretical copper content of the sample. The table below should be used to guide in the choice.

<u>Theoretical copper content (%)</u>	<u>Pipet volume of choice (mL)</u>
20-50	1
10-20	2
6-10	3
2-6	5

Preparation of Standards:

Rinse six 100-mL volumetric flasks thrice each with UFDI water. Rinse a 1.0-mL volumetric pipet with the commercial 1000-ppm copper standard solution.

Volumetrically pipet 1.0 mL of the 1000-ppm copper standard into a rinsed 100-mL volumetric flask. (Note the proper use of the volumetric pipet as described above.) Add two drops of concentrated nitric acid. Fill the volumetric flask exactly to the mark with UFDI water. Invert the volumetric flask thrice to mix. This is now a 10-ppm(10,000-ppb) standard stock solution.

Rinse 5.0-, 10.0-, 15.0-, 20.0-, and 25.0-mL volumetric pipets with the 10-ppm standard. Pipet these amounts of the 10-ppm standard into the five remaining volumetric flasks. Add two drops of concentrated nitric acid to each. Dilute each flask to the mark by using UFDI water. These are now 500-, 1000-, 1500-, 2000-, and 2500-ppb standards, respectively.

The standards were used in order to form a calibration curve that allowed us to calculate the concentration of each metal solution. Once each concentration was determined, that allowed us to calculate the experimental percentage of copper in the

starting sample. This percentage was then compared to the theoretical percentage of copper in a compound. Table 1 shows that the agreement was satisfactory in every case.

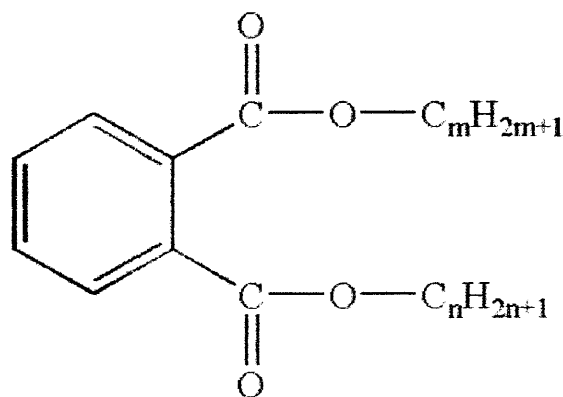
Table 1: Copper analysis using AAS

<u>Compound</u>	<u>Experimental % Cu</u>	<u>Theoretical % Cu</u>	<u>% Difference (Error)</u>
$[\text{Cu}_2(\text{Htu})_5]\text{SO}_4 \cdot 2\text{H}_2\text{O}$	19.10	20.44	5.29
$[\text{Cu}_2(\text{Etu})_6]\text{SO}_4$	14.87	14.99	0.81
Cu_2MoO_4	45.00	44.25	1.67

Palatinol 79P

Palatinol 79P is an excellent commercial plasticizer for PVC. It was obtained from BASF as a colorless viscous liquid. Figure 11 shows that it is a mixture of esters derived from trimellitic acid and a mixture of alkanols containing 7 or 9 carbon atoms.

Figure 11: Structure of Palatinol 79P



Where $n, m = 7$ or 9

Preparation of PVC Plaques

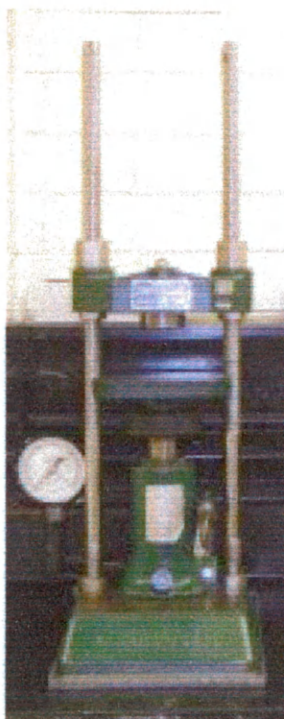
The standard procedure involved blending 40 g of pure PVC (containing no additives and from a commercial source) with 30 phr (parts by weight per hundred parts

of PVC), or 12 g, of Palatinol 79 P. The mixture was thoroughly homogenized by using a mortar and pestle. Such mixtures were made into plaques, as described below, and used as control samples for comparison with our other plaques that contained the copper-based additives. For those plaques, 4 g (10 phr) of each additive was added to the PVC-plasticizer mixture. Heating and shearing (which will be discussed later), using a Biomixer®, was conducted with mixtures of plasticizer and copper-exchanged clay before combining these materials with the polymer.

The mixture containing the PVC, the additive, and the plasticizer was evenly distributed across the bottom plate of a stainless steel mold whose dimensions were 100 mm x 100 mm x 3 mm (thickness). A corresponding stainless steel top plate was attached, and the mold was then placed on a Model C Carver press (see Figure 12). The press heated the mold at approximately 300°F and compressed it at 20,000 pounds per square inch (psi). Pressure and heat were applied for approximately 9 minutes, and the mold was then removed and allowed to cool. Frequently, the two parts of the mold were very difficult to separate from one another. A metal spatula was utilized to facilitate their separation. The cooled PVC plaque was trimmed around its edges with scissors in order to remove any excess material and to maintain a symmetrical shape.

After being heated and pressed for 9 minutes, the plasticized PVC plaque is brownish/beige in color and relatively transparent. Before cooling to room temperature, the plaque is very flexible, but once it cools, it becomes very rigid and brittle.

Figure 12: Carver press



Copper-Exchanged Clay

For purposes of practicality, copper(II) additives usually are not added as such to PVC, owing to their bluish colors, which are undesirable for commercial products. Instead, the Cu(II) can be exchanged into natural clays. The particular clay that we used is sodium montmorillonite (Na-MMT). The basic procedure for forming the copper-exchanged clays involves heating and stirring a mixture of Na-MMT (50 g) with a solution of a copper compound (4-5 g) in 200 mL of UFDI water. The mixture is stirred and heated at 90-95°C overnight by using a magnetic stirrer and a hotplate. Many methods exist for isolating the exchanged clay. Most commonly, it is collected by suction filtration, washed repeatedly on the filter with water, and dried in an oven overnight at

40-50°C. Figure 13 shows pictures of the powdery Na-MMT and the hard and brittle Cu-exchanged MMT.

Figure 13: MMT

a. Na-MMT



b. Cu-Exchanged MMT



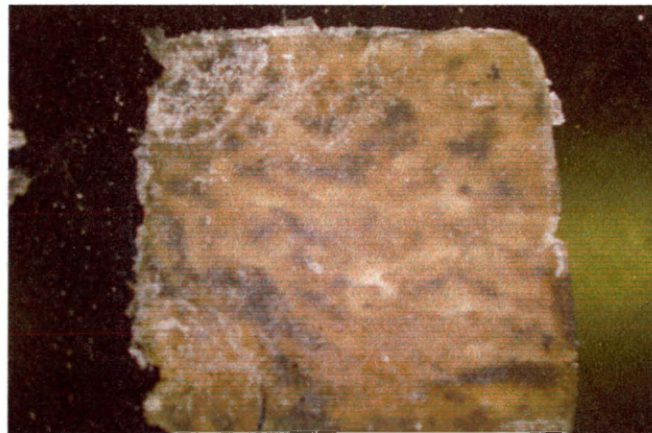
As a result of this process, a copper-sodium cation exchange takes place in the gallery space that separates the aluminosilicate layers of the clay. This chemical reaction

leads to noticeable changes in physical properties. First, the color of the copper-exchanged clay frequently is a dark brown, as opposed to a very light yellowish-brown for the unexchanged clay. Also, the unexchanged clay is a very finely divided powder, while the exchanged clay is very hard and brittle. Figure 14 shows visual representations of how plaques appear upon being removed from the press. The Starnes research group observed that Cu-MMT-containing PVC plaques that had been made without heating and shearing were very heterogeneous, with pieces of clay dispersed throughout the plaques randomly. In contrast, similar plaques that had been prepared with heating and shearing appeared very homogeneous, with the additive dispersed uniformly in the plasticized polymer. Intercalation of plasticizer into the gallery space of the clay also is believed to take place primarily during heating and shearing.

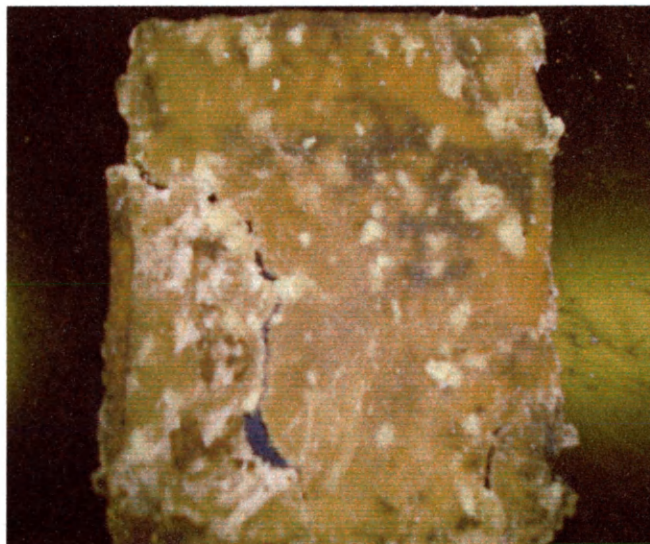
Figure 14 also contains a picture of the remains of a PVC plaque with a Cu-MMT additive after burning. The char after burning has a distinct red color that is believed to signify the reduction of Cu(II) to Cu(I) during burning to form reddish cuprous oxide.

Figure 14: PVC plaques

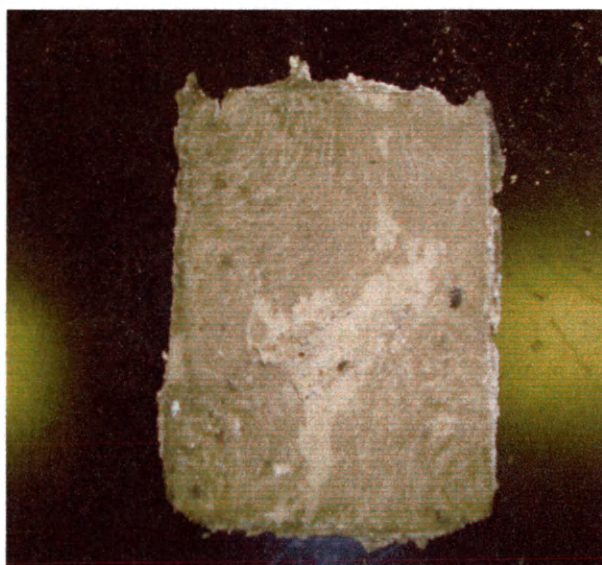
a. Control PVC plaque



b. PVC plaque with Cu-MMT (no heating and shearing)



c. PVC plaque with Cu-MMT (heating and shearing)



d. Char remains of Cu-MMT PVC plaque after burn



The Na-MMT clay can be copper-exchanged with many copper additives. For our experimentation, we exchanged the Na-MMT clay with Cu(II) from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and with Cu(I) from Cu(I)Htu and Cu(I)Etu. Copper analysis by atomic absorption spectroscopy was used in order to determine if the desired exchange was complete. Scheme 1 shows a calculation from the Starnes laboratory that allows us to determine the theoretical percentage of Cu(II) in a completely exchanged MMT clay.

Scheme 1: Calculation of theoretical copper content

The manufacturer tells us that the Na-MMT clay has a cation exchange capacity (cec) of 92.6 meq/100 g = 0.0926 equiv/100 g.

$0.0926 / [(2)(100)] = 0.000463$ equiv/g (for Cu^{2+}), where the “2” in the denominator denotes a +2 charge for copper.

Multiply by the atomic mass of copper: $(0.000463)(63.55) = 0.0294$ g of Cu^{2+} .

Now take the cation exchange capacity and multiply it by the atomic mass of sodium: $(0.0926/100) = 0.000926(22.99) = 0.0213$ g of Na^+ .

Subtract the mass of Na^+ from 1 to get the mass of the aluminosilicate:
 $1 - 0.0213$ g = 0.9787 g of aluminosilicate.

0.9787 g aluminosilicate + 0.0294 g Cu = 1.0081 g total mass.

Now find the percentage of copper by dividing the mass of the copper by the total mass:
 $\% \text{Cu}^{2+} = (100)(0.0294)/(1.0081) = 2.92\%$ (after complete exchange).

In order to verify complete exchange, the AAS instrument was once again utilized. In this particular example, 4 replicate Cu^{2+} ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)-exchanged clay samples were created for this purpose. The AAS procedure was the same as that described above, with the exception that 10 more drops of nitric acid was used in order to break down the copper-exchanged clays, which are very hard. Also, it was necessary to sonicate for a longer time in order to ensure the absence of suspended solid particles from the solution.

As shown by Table 2, the percentage errors were relatively small but large enough to be noticeable in some cases. This result can probably be accounted for by the presence of small amounts of solid particles containing undissolved copper.

Table 2: Percentage of copper in Cu(II)-exchanged clays

<u>Trial</u>	<u>Experimental % Cu</u>	<u>Theoretical % Cu</u>	<u>% Difference</u>
1	2.875	2.92	1.5
2	2.753	2.92	5.6
3	2.721	2.92	6.6
4	2.856	2.92	2.1

Usage of Other Metals

In addition to utilizing copper(II) sulfate for cation exchange in a montmorillonite, we experimented with two other metals, zinc and aluminum. We accomplished their exchange by using zinc sulfate and aluminum sulfate, respectively. The usage of other metals allowed us to see if copper were unique in its ability to be used in clay as a fire retardant and smoke suppressant, or if other metals could be employed with similar results.

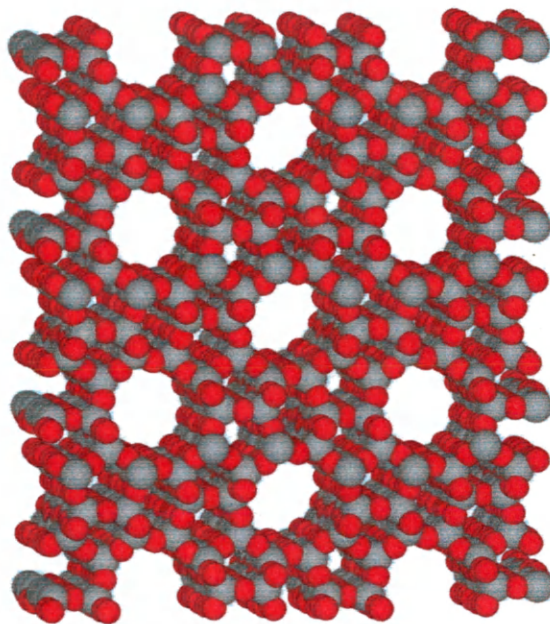
The zinc and aluminum cations are strong Lewis acids. This property may cause the zinc and aluminum additives to “tear up the polymer” by promoting premature degradation (dehydrochlorination) during heating with the Carver press. Therefore, deleterious effects could result that were counter to our original goals. However, our research also used mixtures containing two different metals. In such cases, we tested for synergism to see if the actual results were more beneficial than just the sum of the parts. In other words, we explored whether mixtures of metal additives were more advantageous as smoke suppressants and fire retardants than single additives containing just one metal.

Zeolites

One problem with using copper-exchanged montmorillonite clay was that the starting clay had a relatively low cation exchange capacity. Therefore, we attempted to find other media that could be substituted for sodium montmorillonite, and had considerably higher cation exchange capacities. Zeolites occur naturally throughout the world and can be synthesized in the laboratory as well.¹⁴ The framework of zeolites is made up of aluminosilicates. Usually, a silicon atom is in the middle, and oxygen atoms are at the corners. These tetrahedra can link together by their corners (see Figure 15) to form a rich variety of structures. The framework structure may contain linked cages, cavities, or channels which are of the right size to allow small molecules to enter; i.e., the limiting pore sizes are roughly between 3 and 10 Å in diameter. With respect to our research, many synthetic zeolites are ideal for ion exchange. The loosely bound nature of their extra-framework metal ions (such as in zeolite NaA) means that these ions are often readily exchanged with other metal cations when in aqueous media. This property allows us to exchange easily and efficiently by using copper sulfate pentahydrate (as well as compounds of other metals) and heating and stirring overnight.

Our research led us to utilize synthetic zeolites, which are advertised to have higher cation exchange capacities. These zeolites are microporous crystalline solids with well-defined structures. They contain silicon, aluminum, and oxygen in their framework and cations, water, and/or other molecules within their pores.¹⁴ However, in this particular case, because of the presence of various cations, sodium-copper cation exchange was not necessarily taking place. Therefore, our structural understanding of copper-exchanged zeolites is incomplete.

Figure 15: Zeolite structure¹⁴



The Starnes group used three specific zeolites, BRZ zeolite, Z-Ultra zeolite, and St. Cloud zeolite. Each zeolite was heated and stirred overnight in order to accomplish exchange with copper(II) in an aqueous solution of copper sulfate. Atomic absorption spectroscopy (AAS) was performed on the samples to determine the percentage of copper in each zeolite after exchange. The percentages are recorded below.

Zeolite	% Copper
St. Cloud	3.11
Z-Ultra	3.23
BRZ	3.77

Since the BRZ zeolite had the highest percentage of copper, we used it first and most frequently in our experimentation. However, we also tested the other exchanged zeolites as smoke suppressants and fire retardants for PVC.

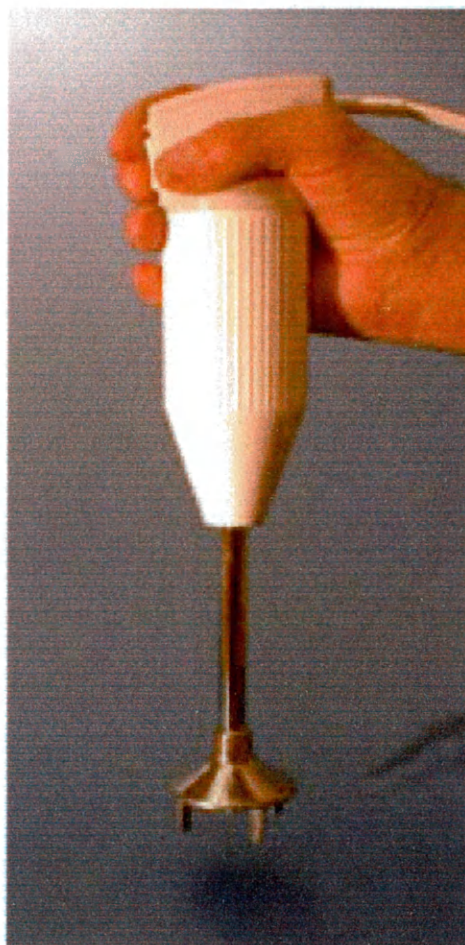
It is important to note that the copper-exchanged zeolites produce less color in PVC than copper montmorillonite additives. This is a significant result, because the chemical industry desires colorless additives for commercial viability.

Heating and Shearing

One of the most important aspects of this research has been the heating and shearing of mixtures of clay (or zeolite) and plasticizer before these two constituents are blended with PVC. In this case, all of the clay samples used were copper-exchanged sodium montmorillonite. Heating and shearing are believed to be important because they accelerate the incorporation of plasticizer into the gallery space of the clay. The plasticizer greatly increases the organophilicity of this space and thus should facilitate the subsequent intercalation of PVC between the aluminosilicate sheets. Combustion of the nanocomposite thus formed should produce less heat and smoke than the combustion of plasticized PVC that has not been nanocomposited.¹⁵

Preliminary heating and shearing also increase the homogeneity of the PVC formulation. This result has been observed just by looking at the PVC/plasticizer/additive mixtures with the naked eye. Mixtures that were prepared with a mortar and pestle contained a plethora of small dark brown specks of the clay. On the other hand, when the Cu(II)-MMT clay had first been heated and sheared with the plasticizer for 5-10 minutes at 10,000 rpm by using the BioSpec BioMixer® shown in Figure 16, the final formulation appeared to be very homogeneous.

Figure 16: Biomixer® with blade



Both heating and shearing are important for increasing homogeneity. When the clay and the plasticizer are heated and sheared simultaneously, even more homogeneity is observed than when heating is omitted. Simultaneous heating and shearing also are expected to maximize the incorporation of the plasticizer into the gallery space of the MMT.

Cone Calorimetry

All of the plaques were burned by using a Fire Testing Technology cone calorimeter. A cone calorimeter is an instrument that burns relatively small samples of various materials and collects data on smoke emitted, heat release rate, and other parameters related to combustion. The net heat of combustion of any organic material corresponds to the amount of oxygen required. Approximately 13.1 megajoules of heat is released per kilogram of oxygen consumed.¹⁶ A radiant electrical heater in the shape of a cone irradiates the sample and thus causes it to burn. Smoke measurements are made in the exhaust duct by a neon laser, using main beam and reference detectors. All of the data are transferred to a compatible computer program that records and organizes the information for each burn. The most important variables measured are total smoke released (TSR), heat release rate (HRR), total heat released (THR), and mass loss rate (MLR). A variable that is calculated manually (with information from the cone calorimeter, of course) is the char yield (CY). The char yield tells us how much char is left after the burn with respect to the mass of the unburned sample. The char yield is obtained from the following equation:

$$\text{Char Yield (CY)} = \frac{(\text{final mass})}{(\text{initial mass})} * 100\%$$

For our purposes, a higher char yield means a better fire retardant.

Table 3 provides a summary of the variables that the cone calorimeter measures,¹⁷ while Tables 4-6 and Figure 17 present some representative results of our cone calorimeter experiments. The results from many other burns supported the conclusions that could be reached from the data presented here.

Table 3: Cone calorimeter variables

Parameter	Abbreviation	Unit	Description
Time to ignition	TTI	S	Time of sustained (>10 s) flaming
Specific extinction area (avg. and peak)	SEA _{av} , SEA _{pk}	M ² kg ⁻¹	Smoke produced per unit mass being volatilized
Total smoke released	TSR	(unitless)	Cumulative smoke produced
Heat release rate (avg. and peak)	HRR _{av} , HRR _{pk}	kW m ⁻²	Rate of heat release per unit sample area
Total heat released	THR	MJ m ⁻²	Cumulative heat energy released per unit sample area
Mass loss rate (avg. and peak)	MLR _{av} , MLR _{pk}	g s ⁻¹	Mass of sample being volatilized per unit time
Effective heat of combustion (avg.)	EHC _{av}	MJ kg ⁻¹	Heat released per unit mass volatilized
Char yield	CY	%	Percentage of sample mass remaining after burning

Table 4: PVC burn data

Additive*	TTI (s)	SEA _{av} (m ² /kg)	SEA _{pk} (m ² /kg)	TSR	HRR _{av} (kW/m ²)	HRR _{pk} (kW/m ²)	THR (MJ/m ²)	MLR _{av} (g/s)	MLR _{pk} (g/s)	EHC _{av} (MJ/kg)	CY (%)
None (PVC-1)	34	863	1138	4435	53.1	175.6	16.7	0.140	0.343	3.35	2.1
None (PVC-2)	34	934	1395	4623	46.2	75.8	12.2	0.166	0.382	2.45	2.1
Na-MMT-1	20	953	1731	4766	110.6	267.2	40.8	0.117	0.364	8.37	2.2
Na-MMT-2	14	1003	3442	4251	74.2	132.5	21.4	0.128	0.498	5.17	3.3
Cu(II)-Clay-1	14	973	2368	3906	21.0	31.3	6.2	0.121	0.252	1.52	13.0
Cu(II)-Clay-2	8	952	1478	4074	17.2	29.0	7.2	0.092	0.272	1.66	3.2
Cu(II)-Clay ^A	19	1027	1749	4533	18.3	28.3	6.2	0.117	0.285	1.38	9.1
Cu(II)-Clay ^B	19	959	1944	4329	19.4	36.1	6.2	0.131	0.257	1.31	13.5
Cu(I)-Htu-Clay-1	8	938	1446	3661	15.4	20.0	3.8	0.145	0.257	0.93	10.0
Cu(I)-Htu-Clay-2	29	1012	2840	3723	12.8	19.0	3.6	0.132	0.291	0.85	13.1
Cu(I)-Htu-Clay-1 ^B	35	978	2003	4460	33.6	87.6	9.2	0.141	0.286	2.10	4.7
Cu(I)-Htu-Clay-2 ^B	24	1000	2086	4212	47.0	67.1	12.0	0.136	0.335	3.06	11.1
Cu(I)-Etu-Clay-1	8	987	2154	4665	17.1	34.4	5.2	0.140	0.498	1.07	6.7
Cu(I)-Etu-Clay-2	9	913	1674	4206	15.6	28.2	5.1	0.129	0.381	1.07	6.8
Cu(I)-Etu-Clay ^B	6	1021	2091	4712	12.1	24.1	3.3	0.150	0.334	0.71	6.7

* All additives were heated and sheared for 10 minutes at 80-85°C unless otherwise noted.

^A Additive was heated and sheared for 5 minutes.

^B These additives were mixed without heating and shearing.

Table 5: PVC burn data

Additive*	TTI (s)	TSR	HRR _{av} (kW/m ²)	HRR _{pk} (kW/m ²)	THR (MJ/m ²)	MLR _{av} (g/s)	MLR _{pk} (g/s)	EHC _{av} (MJ/kg)	CY (%)
None	25	5677	99.1	145.5	35.7	0.210	0.700	3.3	1.0
Cu(I)-Clay-1	12	3658	12.7	36.0	4.9	0.130	0.410	2.1	3.1
Cu(I)-Clay-2	15	3409	16.3	35.8	7.0	0.121	0.381	2.9	4.0
Cu(II)Cl ₂ -Clay-1	14	4000	32.1	44.0	13.3	0.190	0.562	5.0	3.1
Cu(II)Cl ₂ -Clay-2	25	4113	17.1	44.5	7.1	0.154	0.440	4.9	3.0

*All additives were heated and sheared for 10 minutes at 80-85°C.

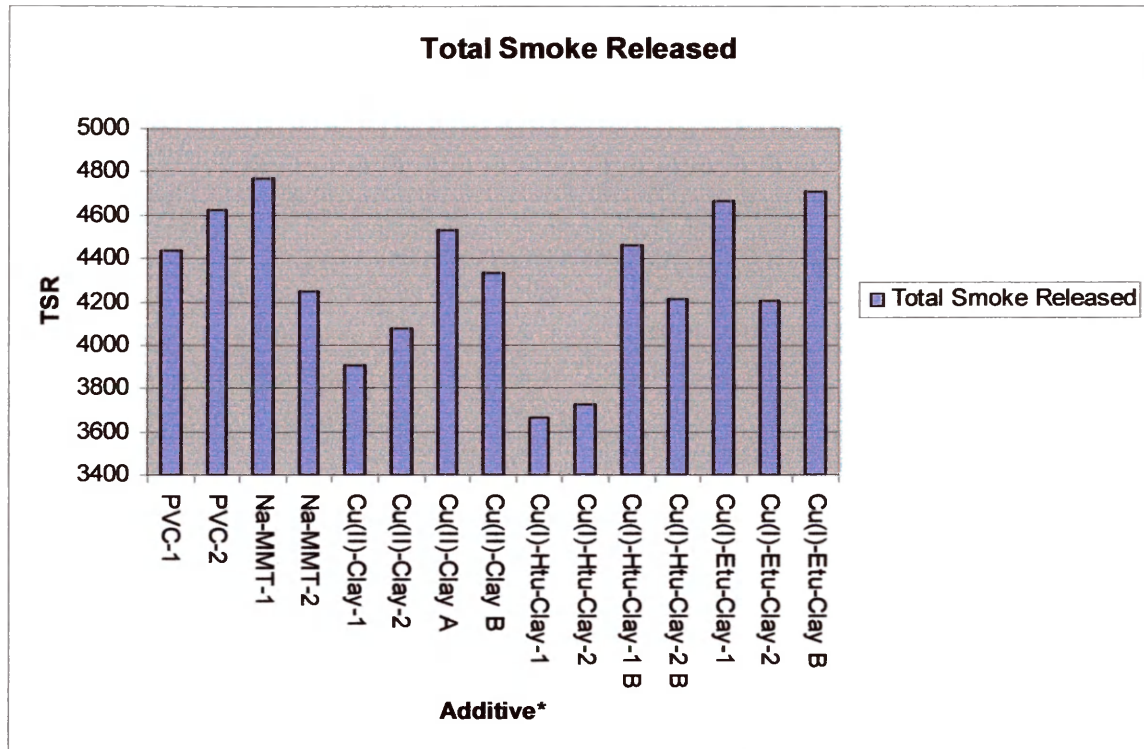
Table 6: PVC burn data for Sherwin-Williams samples

Sample	TTI (s)	SEA _{av} (m ² /kg)	SEA _{pk} (m ² /kg)	TSR	HRR _{av} (kW/m ²)	HRR _{pk} (kW/m ²)	THR (MJ/m ²)	MLR _{av} (g/s)	MLR _{pk} (g/s)	EHC _{av} (MJ/kg)	CY (%)
No additive	33	964	1631	4169	83.3	97.0	31.0	0.091	0.270	7.6	7.4
82Na+1	50	476	1059	1390	38.0	120.5	10.8	0.082	0.132	4.3	40
82Na+2	49	274	2702	1621	32.1	54.1	18.3	0.062	0.561	3.5	60
82b-1*	15	465	1023	N/A	37.0	54.9	7.2	0.040	0.012	7.6	31
82b-2	29	469	922	1676	30.0	73.3	14.0	0.071	0.151	4.1	22
82c-1	20	394	1055	1029	28.8	32.2	11.1	0.060	0.113	4.5	40
82c-2	46	474	1128	1676	25.9	40.9	11.4	0.073	0.121	3.5	51
82d-1	16	447	1157	1630	38.6	77.8	10.8	0.062	0.132	5.4	53
82d-2	25	471	1161	1489	29.8	52.7	10.9	0.071	0.141	3.6	50

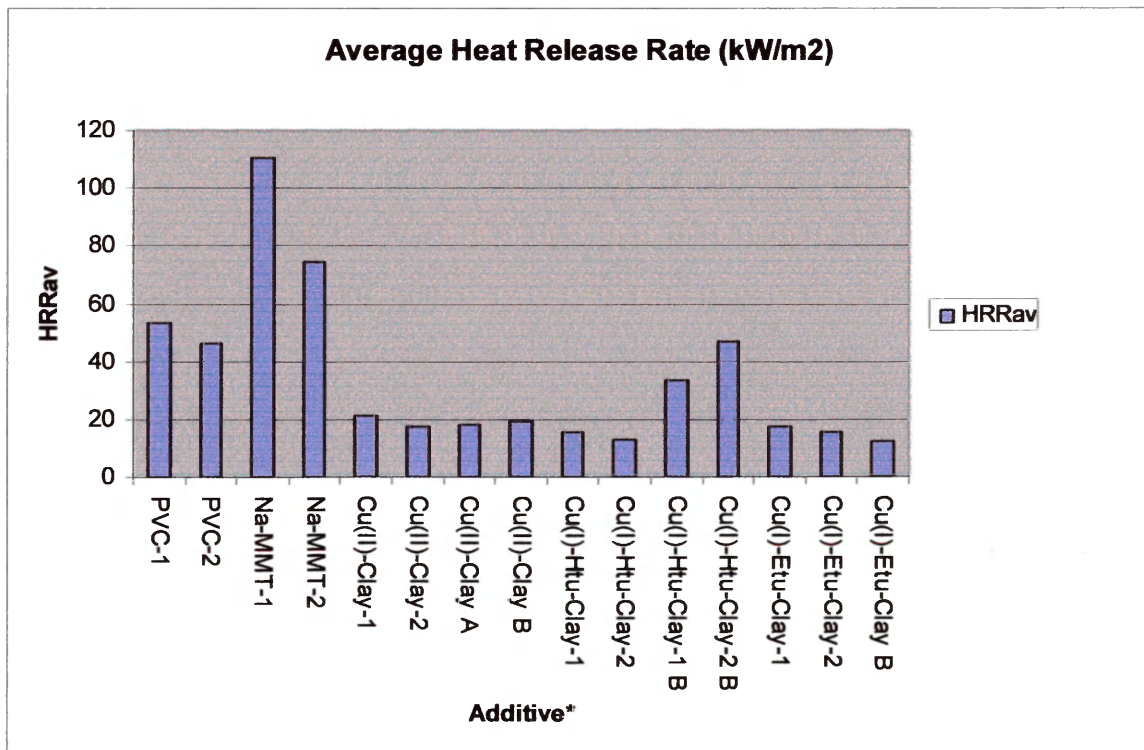
*During this run, the computer froze, and thus no smoke values were recorded.

Figure 17: Graphs of data from Table 4

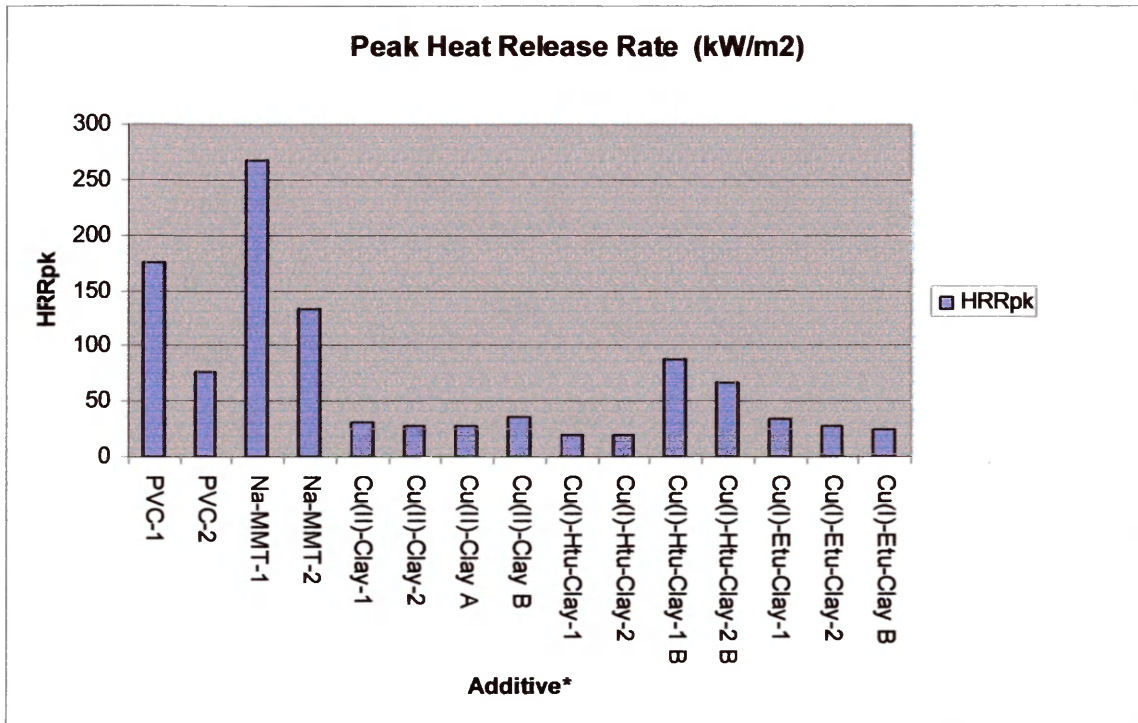
a.



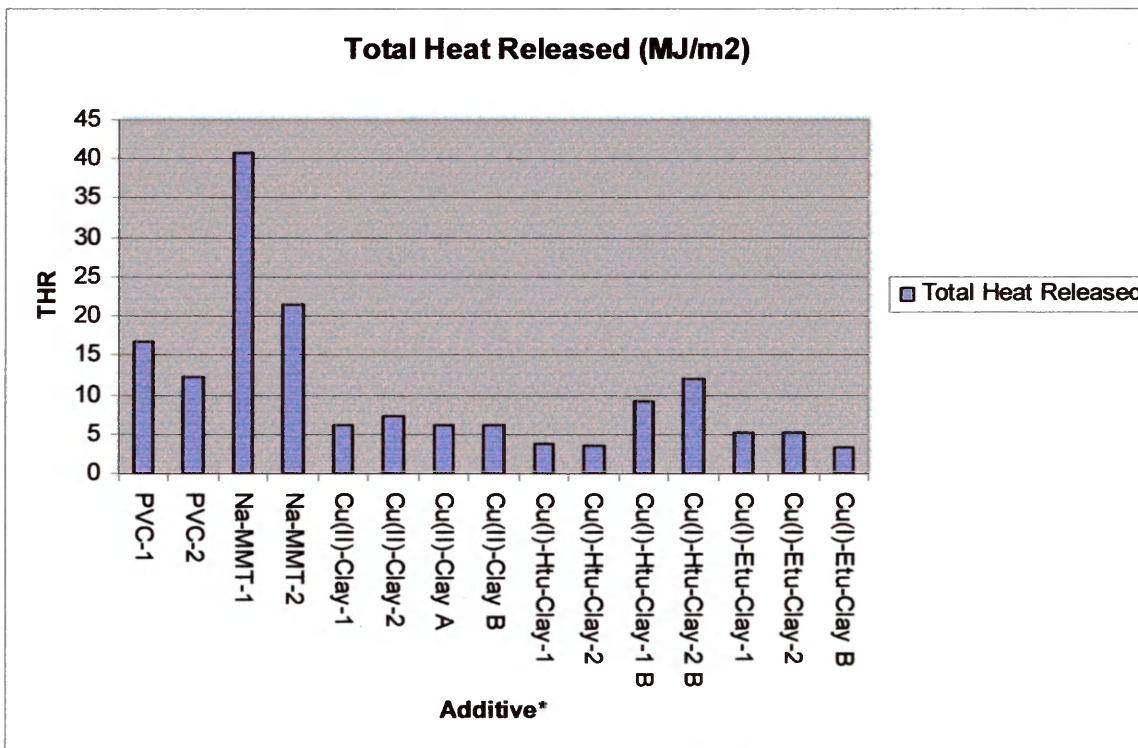
b.



c.



d.



* All additives were heated and sheared for 10 minutes at 80-85°C unless otherwise noted.

^A Additive was heated and sheared for 5 minutes.

^B These additives were mixed without heating and shearing.

Cone Calorimetry Results and Data Analysis

According to the data in Tables 4 and 5 and Figure 17, the copper additives were indeed very effective for both the smoke suppression and the fire retardance of PVC. The PVC plaques that contained the best copper-clay additives exhibited a total smoke release reduction of about 20% with respect to the control (additive-free) PVC. Average heat release rates were usually reduced by 60-70% for plaques that contained the copper clays, and their peak heat release rates also were greatly lowered in most cases. Total char yields increased by factors of ca. 1.5 to 6; the effective heat of combustion usually decreased by about a factor of 2; and the average mass loss rate decreased by some 10-30% as well. Overall, the data were very impressive in showing that the copper-clay additives promoted smoke suppression and fire retardance with respect to most of the important variables that the cone calorimeter measured.

In addition to burning control plaques with no metal-containing additive, we burned plaques that contained 10 phr of unexchanged sodium montmorillonite clay. The latter plaques fared just as poorly as the additive-free PVC controls and had even higher heat release rates.

On the basis of our data, specific additives were noteworthy for their excellent performance in smoke suppression and fire retardance. The Cu(I)-Htu-clay plaques with 10 minutes of heating and shearing provided the lowest total smoke released values, with an average at around 3700 in comparison to the controls, which averaged out at about 4500. These plaques were outstanding in several other respects as well. The Cu(II)-clay plaques also gave very good results, overall, particularly after heating and shearing. For

several additives, heating and shearing had especially beneficial effects on the total amount of smoke produced.

Table 5 contains data for some additional copper-clay additives that were prepared by exchanging Cu(I) or Cu(II) into Na-MMT. The data are encouraging, but unfortunately, these clays gave highly colored plaques and thus cannot be incorporated into commercial PVC products.

The data in Table 6 are for samples prepared by Sherwin-Williams from Cu(II)-exchanged clay and sodium montmorillonite. All of these samples contained a lead stabilizer, antimony trioxide, alumina trihydrate, and a phosphate ester plasticizer. The only differences among the samples were that 82Na⁺ contained 6 phr of sodium montmorillonite that had not been heated and sheared with the plasticizer, while 82b,-c, and -d contained 4, 6, and 8 phr, respectively, of Cu(II) clay that had been sheared (but not heated) with the plasticizer for 15 min at 3000 rpm. The tabulated results show no consistent effects that can be related to the type or amount of clay. The reasons for this observation are unclear but may be connected with the lack of heating and the use of a shearing method that was less effective than ours.

Tables 7-12 and Figures 18 and 19 provide the results of repeated trials for previous burns and expand on many new variables that are involved in the smoke suppression and fire retardance of PVC. Zeolites and other metals (Al and Zn) were used in addition to the Cu-MMT additives. These tables further corroborate the hypothesis that, at least in some cases, heating and shearing both contribute to the formation of a homogeneous plaque where both intercalation and exfoliation may occur.

Table 7 and Figure 18 present data for plasticized PVC plaques containing MMT additives that had been exchanged with Cu and Zn. Some plaques containing MMT additives that were heated and sheared showed a marked decrease in heat release and/or total smoke emitted with respect to control PVC plaques that contained no MMT additive. The plaques that contained the Zn-Cu mixture fared the best, with an average smoke release value of ca. 3100. We had hypothesized that synergism of a mixture of MMT additives containing the two metals might lead to a superior additive for smoke suppression.

Table 7: PVC burn data (MMT additives)

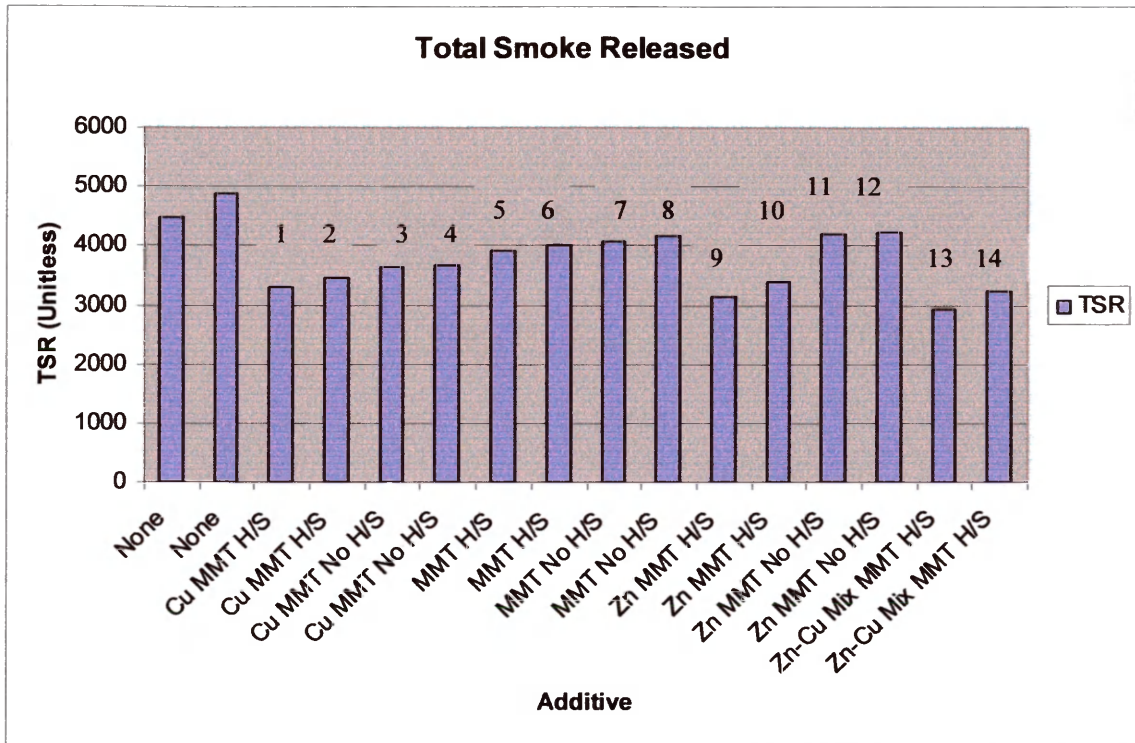
Additive	TTI (s)	SEAAv (m ² /kg)	SEApk (m ² /kg)	TSR	HRRav (kW/m ²)	HRRpk (kW/m ²)	THR (MJ/m ²)	MLRAv (g/s)	MLRpk (g/s)	EHCav (MJ/kg)	CY (%)
None	76	868	1860	4481	56.1	306.0	18.8	0.126	0.330	3.93	0.0
None	36	989	1926	4879	57.0	231.9	39.6	0.158	0.331	8.07	2.6
1	15	738	1495	3281	18.9	164.7	22.7	0.102	0.277	5.11	21.8
2	12	792	2175	3454	15.4	31.4	5.3	0.113	0.267	1.21	20.8
3	45	813	1898	3652	27.7	73.0	10.8	0.101	0.277	2.42	19.5
4	22	818	1351	3671	10.0	120.9	3.3	0.107	0.245	0.74	19.5
5	24	821	2175	3906	17.2	36.0	5.9	0.093	0.254	7.97	12.6
6	31	806	2017	4021	27.9	46.0	9.4	0.105	0.238	2.35	12.7
7	33	966	2007	4057	20.2	132.2	29.0	0.104	0.289	7.00	11.9
8	17	918	2070	4168	43.7	66.4	14.2	0.121	0.248	3.19	17.8
9	10	782	5686	3137	12.6	31.0	4.1	0.111	0.200	1.00	23.7
10	12	851	2084	3391	11.3	60.1	3.4	0.117	0.226	0.85	24.7
11	24	921	2540	4209	15.0	35.7	3.8	0.160	0.377	0.83	12.0
12	15	961	2781	4214	23.7	35.5	5.9	0.133	0.353	1.57	12.1
13	12	778	1462	2921	12.9	29.7	4.0	0.106	0.246	1.07	14.8
14	16	779	2175	3234	21.5	40.3	7.6	0.103	0.228	1.84	18.4

Key

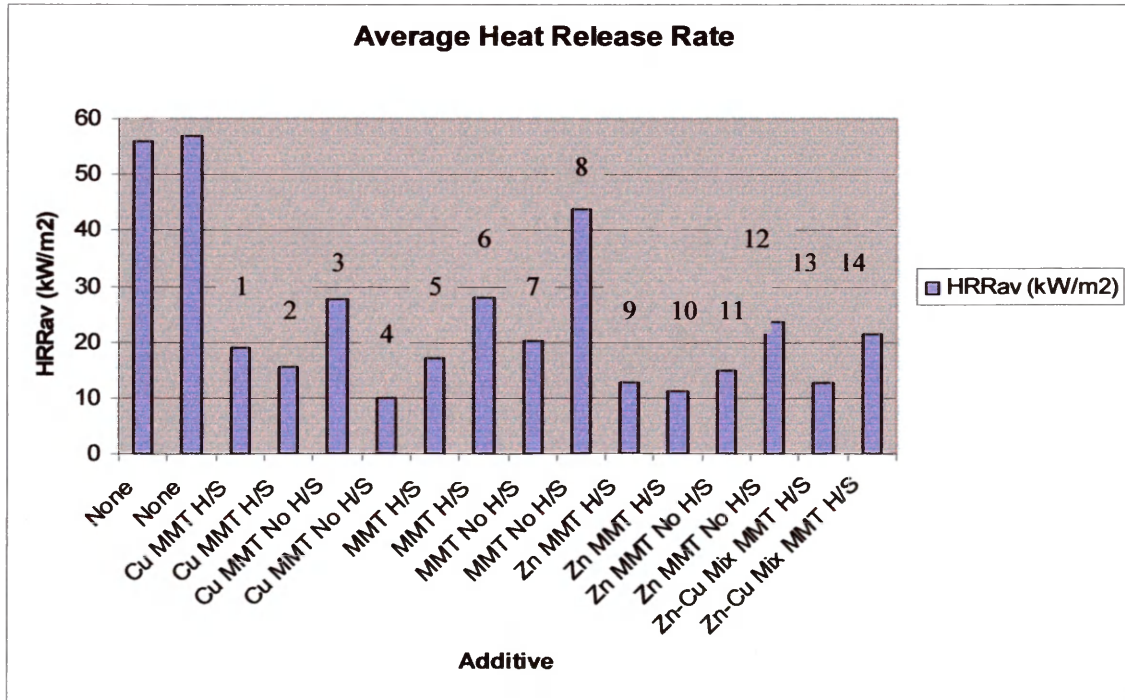
- 1,2 – Cu MMT, heat/shear
- 3,4 – Cu MMT, no heat/shear
- 5,6 – MMT, heat/shear
- 7,8 – MMT, no heat/shear
- 9,10 – Zn MMT, heat/shear
- 11,12 – Zn MMT, no heat/shear
- 13,14 – Zn-Cu Mix, heat/shear

Figure 18: Graphs of data from Table 7

a.



b.



c.

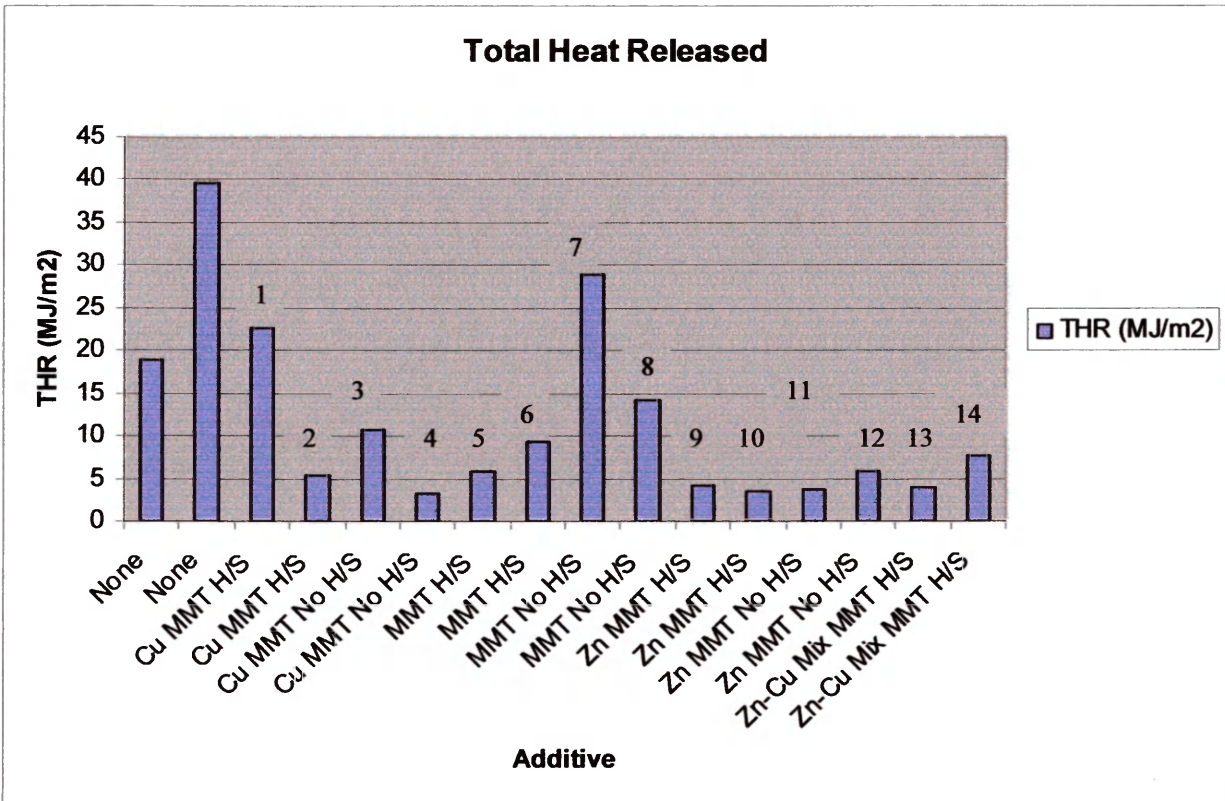


Table 8: PVC burn data (MMT additives)

Additive	TTI (s)	SEAvv (m2/kg)	SEApk (m2/kg)	TSR	HRRav (kW/m2)	HRRpk (kW/m2)	THR (MJ/m2)	MLRav (g/s)	MLRpk (g/s)	EHCav (MJ/kg)	CY (%)
None	34	953	1643	4734	47.5	92.5	20.2	0.102	0.275	4.09	2.0
1	22	788	1585	3346	29.3	32.0	11.0	0.099	0.264	2.62	14.3
2	23	914	2011	3737	29.6	32.3	10.4	0.102	0.317	2.57	14.5
3	47	820	2124	3343	24.9	46.4	10.6	0.083	0.214	2.64	13.7
4	30	1006	4507	3478	25.4	63.1	10.6	0.093	0.282	2.40	12.0
5	37	672	1100	3303	17.1	48.6	7.6	0.095	0.266	1.58	6.1
6	37	758	3958	2909	15.3	28.6	6.1	0.081	0.217	1.66	21.5
7	57	698	1480	2697	30.1	34.2	7.1	0.073	0.237	3.63	18.6
8	35	740	6557	2730	12.9	34.9	6.2	0.030	0.234	1.00	16.0
9	28	827	2361	2996	24.6	28.0	8.5	0.091	0.238	2.39	6.7
10	16	729	3105	2995	22.6	25.4	10.2	0.080	0.193	2.49	26.3
11	36	815	9000	3415	13.9	38.1	5.8	0.087	0.231	1.42	17.3
12	24	818	3046	3339	16.0	18.4	5.4	0.107	0.274	1.32	23.7
13	19	682	1641	2663	14.0	30.0	4.8	0.101	0.247	1.23	21.8
14	21	587	2115	2132	11.9	15.6	5.3	0.071	0.299	1.49	22.6

Key

- 1,2 – Al MMT, 10 phr, no heat/shear
- 3,4 – Al MMT, 10 phr, heat/shear
- 5,6 – Al-Cu Mix MMT, 10 phr, heat/shear
- 7,8 – Al-Cu Mix MMT, 15 phr, heat/shear
- 9,10 – Al-Cu Mix MMT, 20 phr, heat/shear
- 11,12 – Zn-Cu Mix MMT, 15 phr, heat/shear
- 13,14 – Zn-Cu Mix MMT, 20 phr, heat/shear

Table 9: PVC burn data (zeolite additives)

Additive	TTI (s)	SEAvv (m ² /kg)	SEApk (m ² /kg)	TSR	HRRav (kW/m ²)	HRRpk (kW/m ²)	THR (MJ/m ²)	MLRav (g/s)	MLRpk (g/s)	EHCav (MJ/kg)	Char Yield (%)
None (PVC)	40	1199	9999	5417	41.8	89.5	10.2	0.162	0.386	2.28	1.1
1	16	891	1556	3713	11.4	23.6	5.1	0.084	0.153	1.21	16.6
2	38	832	1601	3813	15.9	29.5	7.3	0.088	0.209	1.59	14.2
3	33	1037	1825	4746	22.8	37.3	8.3	0.116	0.279	1.74	14.9
4	19	935	2044	3995	19.9	29.4	8.0	0.094	0.227	1.87	18.1
5	13	945	1610	4439	20.1	35.0	7.2	0.117	0.330	1.52	18.2
6	33	1037	1825	4746	22.8	37.3	8.3	0.116	0.279	1.74	16.2
7	26	1000	2035	4336	20.0	29.4	6.8	0.118	0.293	1.50	17.9
8	20	984	2206	4588	15.0	32.8	7.1	0.090	0.324	1.48	17.4
9	23	867	1915	3835	15.1	29.6	6.2	0.097	0.221	1.38	19.2
10	22	865	1419	3811	19.9	47.6	8.3	0.095	0.219	1.85	18.8
11	13	874	2916	3709	21.2	41.9	9.2	0.088	0.222	2.12	37.7
12	22	911	3596	3648	20.0	33.9	7.8	0.096	0.223	1.84	20.9
13	25	1048	2573	4945	22.6	39.3	7.1	0.134	0.306	1.49	17.1
14	31	937	5852	4382	21.9	38.3	8.3	0.121	0.299	1.75	17.5
15	32	993	1717	4609	26.5	38.0	8.2	0.135	0.338	1.74	12.2
16	21	1044	4134	3929	26.3	38.8	7.5	0.122	0.289	1.91	21.1
[2] 1	58	1016	1592	4882	16.0	42.7	6.9	0.095	0.234	1.49	13.9
[2] 2	47	1072	1889	4872	25.0	63.9	4.4	0.111	0.226	1.01	19.4
[2] 3	47	981	1547	4803	15.6	41.5	7.7	0.091	0.233	1.52	16.2
[2] 4	42	916	1678	3954	13.5	51.4	6.4	0.119	0.229	1.55	18.0
[2] 5	Computer Froze	No Data Recorded									
[2] 6	22	888	1670	4020	14.5	45.7	7.1	0.082	0.163	1.57	17.3
[2] 7	58	823	2311	3497	10.0	33.8	5.4	0.069	0.169	1.28	16.6
[2] 8	10	997	2985	4201	19.9	37.4	8.9	0.084	0.198	2.08	22.7

Key:

- 1,2 – Cu-BRZ, heat/shear
- 3,4 – Cu-BRZ, no heat/shear
- 5,6 – BRZ, heat/shear
- 7,8 – BRZ, no heat/shear
- 9,10 – Cu-Z-Ultra, heat/shear
- 11,12 – Cu-Z-Ultra, no heat/shear
- 13,14 – Z-Ultra, heat/shear
- 15,16 – Z-Ultra, no heat/shear
- [2]1, [2]2 – Cu-St. Cloud, heat/shear
- [2]3, [2]4 – Cu-St. Cloud, no heat/shear
- [2]5, [2]6 – St. Cloud, heat/shear
- [2]7, [2]8 – St. Cloud, no heat/shear

Table 10: PVC burn data (BRZ zeolite additives)

Additive	TTI (s)	SEAvv (m2/kg)	SEApk (m2/kg)	TSR	HRRav (kW/m2)	HRRpk (kW/m2)	THR (MJ/m2)	MLRav (g/s)	MLRpk (g/s)	EHCav (MJ/kg)	CY (%)
None	36	885	2598	4729	48.5	52.7	21.0	0.103	0.273	4.17	0.0
1	25	894	1360	4648	27.1	31.3	12.3	0.097	0.245	2.40	2.7
2	39	804	1894	3903	27.1	32.7	13.0	0.087	0.236	2.76	9.4
3	31	916	1617	4603	27.9	50.1	12.3	0.100	0.299	2.46	7.5
4	42	855	1330	4113	27.9	33.6	13.3	0.087	0.281	2.84	11.8
5	29	978	6258	4555	37.7	45.0	17.0	0.089	0.264	3.73	14.7
6	49	901	1463	3879	16.8	32.8	13.5	0.099	0.198	1.66	18.9
7	27	867	1830	3497	17.6	28.1	12.1	0.128	0.229	1.53	17.7
8	30	956	1609	4212	22.5	27.0	8.6	0.101	0.248	1.97	16.4
9	41	947	1882	4335	24.8	29.1	11.2	0.086	0.299	2.54	9.1
10	19	986	2060	4209	20.5	24.1	7.1	0.112	0.250	1.63	14.3
11	23	1025	2189	3795	13.4	15.8	3.8	0.115	0.316	1.03	24.2
12	43	796	5652	3437	11.5	27.9	4.3	0.103	0.188	1.98	21.6
13	17	747	1186	3129	18.5	28.4	5.9	0.119	0.236	1.37	19.3
14	62	803	1588	3217	36.7	59.8	15.1	0.082	0.188	3.94	11.7
15	42	768	6300	3395	52.7	149.7	26.9	0.075	0.186	6.22	23.0
16	15	762	2835	3330	46.1	75.3	42.3	0.087	0.229	9.70	19.8
17	35	851	1482	3236	39.4	168.0	27.3	0.120	0.221	7.31	20.0
18	17	745	1693	3390	60.0	172.0	37.1	0.064	0.210	8.32	6.3
19	14	848	2123	3733	57.5	152.3	32.5	0.067	0.285	7.60	5.9

Key: BRZ Zeolite Burns

- 1 – Zeolite, no heat/shear
- 2 – Cu Zeolite, no heat/shear
- 3 – Al Zeolite, no heat/shear
- 4,5 – Zn Zeolite, no heat/shear
- 6,7 – Al-Cu Mix Zeolite, 10 phr, heat/shear
- 8,9 – Zn-Al Mix Zeolite, 10 phr, heat/shear
- 10,11 – Al Zeolite, 10 phr, heat/shear
- 12,13 – Zn-Cu Mix Zeolite, 10 phr, heat/shear
- 14,15 – Zn-Cu Mix Zeolite, 15 phr, heat/shear
- 16,17 – Zn-Cu Mix Zeolite, 20 phr, heat/shear
- 18,19 – Al-Cu Mix Zeolite, 15 phr, heat/shear

Table 11: PVC burn data (BRZ zeolite additives)

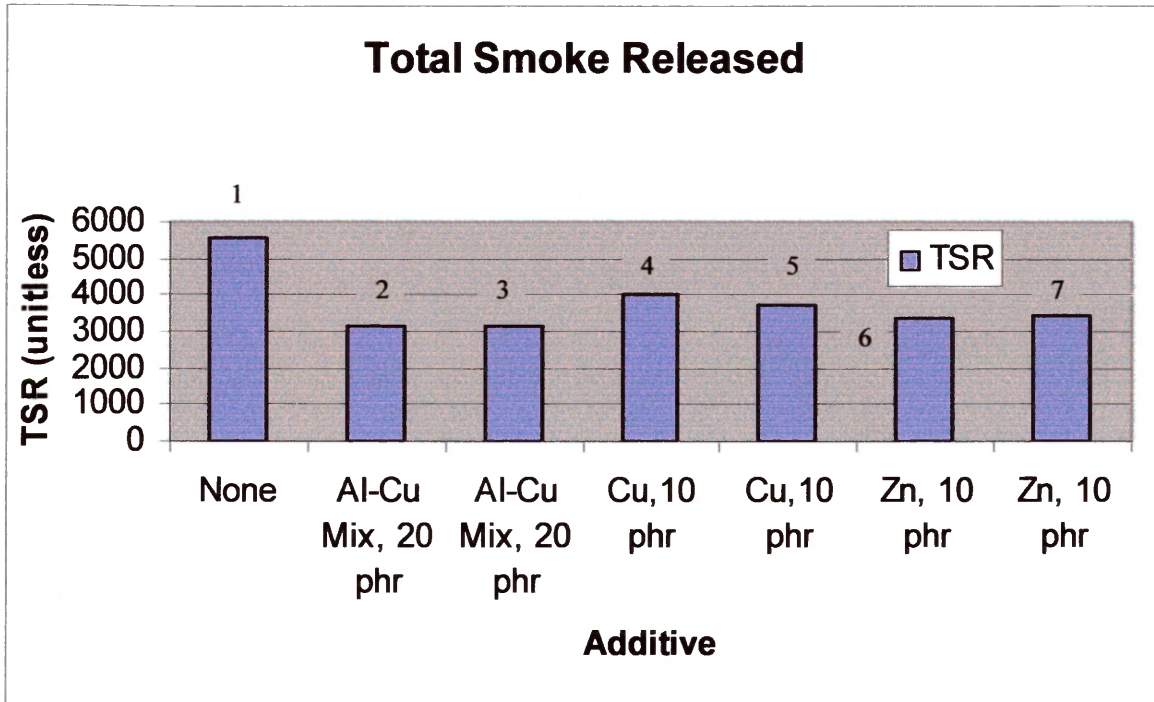
Additive	TTI (s)	SEAv (m ² /kg)	SEApk (m ² /kg)	TSR	HRRav (kW/m ²)	HRRpk (kW/m ²)	THR (MJ/m ²)	MLRav (g/s)	MLRpk (g/s)	EHCav (MJ/kg)	CY (%)
1	25	1099	1675	5584	83.4	89.5	30.1	0.118	0.289	6.27	0.0
2	29	853	1913	3112	14.4	81.2	12.9	0.074	0.204	2.92	20.1
3	22	709	1653	3134	15.5	57.9	8.2	0.074	0.178	1.85	20.2
4	21	986	1808	4032	12.1	33.4	5.6	0.080	0.212	1.33	19.1
5	23	935	5458	3702	12.4	48.5	4.9	0.087	0.189	1.25	21.3
6	47	1018	1639	3354	15.4	39.0	7.1	0.085	0.218	1.61	14.6
7	25	1002	1784	3445	15.3	34.7	5.9	0.077	0.190	1.76	25.4

Key: BRZ Zeolite Burns (Heating/Shearing)

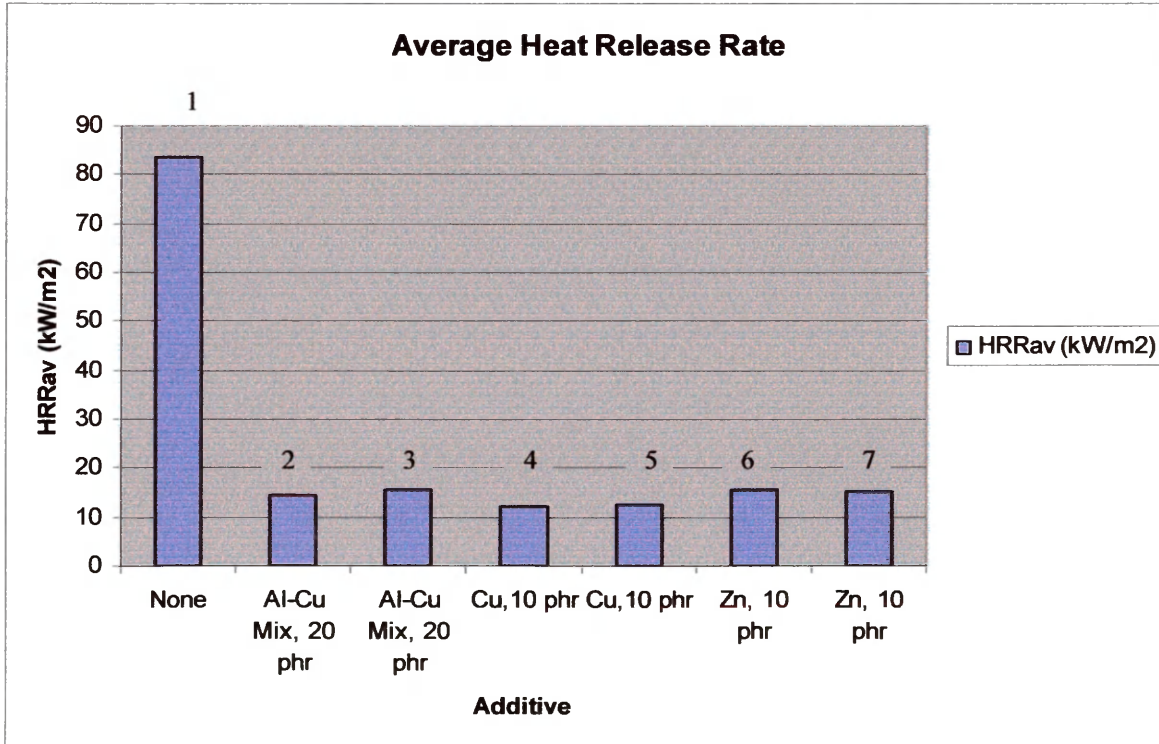
- 1 – None
- 2,3 – Al-Cu Mix Zeolite, 20 phr
- 4,5 – Cu Zeolite, 10 phr
- 6,7 – Zn Zeolite, 10 phr

Figure 19: Graphs of data from Table 11

a.



b.



c.

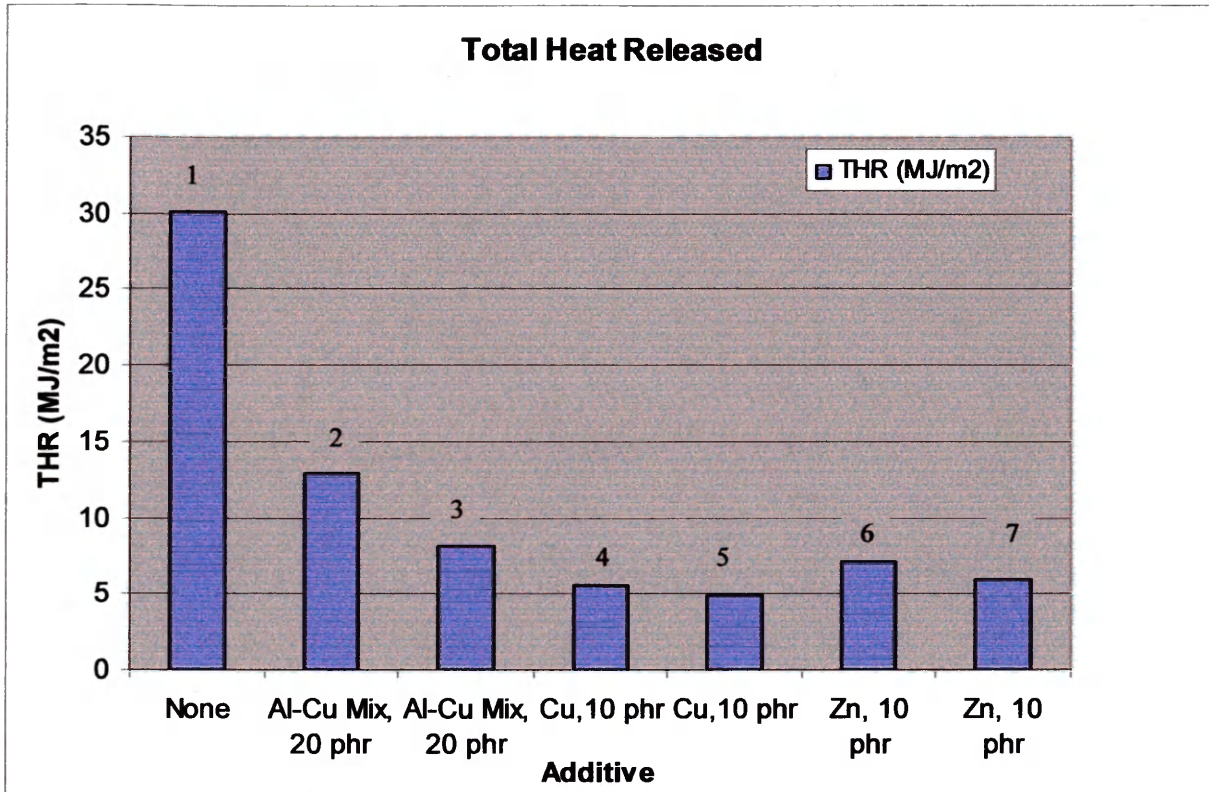


Table 12: PVC burn data (Z-Ultra and St. Cloud zeolite additives)

Additive	TTI (s)	SEAvv (m2/kg)	SEApk (m2/kg)	TSR	HRRav (kW/m2)	HRRpk (kW/m2)	THR (MJ/m2)	MLRav (g/s)	MLRpk (g/s)	EHCav (MJ/kg)	CY (%)
None	30	780	1533	4971	87.4	94.2	39.6	0.154	0.350	3.31	0.0
1	29	790	1997	4722	55.7	76.0	5.9	0.093	0.235	2.43	5.5
2	16	869	1602	4537	57.9	94.3	7.9	0.101	0.236	1.56	10.7
3	23	760	1382	3088	15.3	49.1	6.4	0.085	0.206	1.58	14.8
4	Computer Froze, No Data										
5	14	803	1367	3592	46.9	223.0	5.8	0.123	0.297	3.38	12.5
6	19	811	2920	3577	64.5	250.5	15.3	0.083	0.266	6.84	15.4
7	21	799	2021	3401	47.1	187.5	21.7	0.081	0.227	5.15	14.3
8	25	766	2251	3553	60.0	155.0	27.0	0.078	0.204	6.86	16.7
9	19	763	6342	2791	57.4	168.0	25.0	0.089	0.244	5.71	15.8
10	20	675	1160	2659	58.1	150.5	13.8	0.078	0.187	6.55	20.7
11	12	783	1701	3310	74.6	173.0	26.7	0.104	0.243	6.30	14.8
12	Computer Froze, No Data										
13	17	740	2762	3057	54.1	197.1	17.9	0.110	0.282	4.36	17.3
14	14	825	3928	3262	50.7	174.5	16.0	0.110	0.248	4.05	18.4
15	17	778	3997	2771	76.2	165.6	30.6	0.077	0.179	8.74	18.3
16	19	678	1540	2737	75.3	188.2	29.4	0.091	0.202	7.35	18.5
17	24	719	1501	3175	25.9	66.2	23.1	0.093	0.220	5.46	23.7
18	17	742	2314	3205	36.3	104.2	19.3	0.067	0.227	4.79	6.3
19	10	598	1552	2409	20.9	45.5	10.7	0.083	0.217	1.15	5.9
20	6	674	1732	2880	30.2	92.0	9.4	0.081	0.191	2.45	19.4

Key: Z-Ultra Burns

- 1,2 – Zeolite, no heat/shear
 - 3,4 – Cu Zeolite, heat/shear
 - 5,6 – Al Zeolite, no heat/shear
 - 7,8 – Zn Zeolite, no heat/shear
 - 9,10 – Al-Cu Mix Zeolite, heat/shear
 - 11,12 – Zn-Al Mix Zeolite, heat/shear
 - 13,14 – Al Zeolite, heat/shear
 - 15,16 – Zn-Cu Mix Zeolite, heat/shear
- St. Cloud Zeolite Burns**
- 17,18 – Cu Zeolite, no heat/shear
 - 19,20 – Cu Zeolite, heat/shear

Table 8 shows effects of additive mixtures that can be compared with the results in Table 7. In this case, the amount of additive in some plaques was increased significantly. Instead of the standard amount of 10 phr (or approximately 4 g of additive), 15 phr and 20 phr of the additives were used (6 g and 8 g of additive, respectively). It was found that increases in the amount of additive were accompanied by reductions in both smoke released and heat release. For example, plaques that contained 20 phr of the Zn-Cu MMT had an average smoke value of 2400, which was markedly less than the average smoke value of 3400 for plaques with 15 phr of this additive. On the other hand, the suppression effects tended to level off at the highest additive levels used.

Tables 9-12 and Figure 19 vary from the preceding tables in that they contain data for plaques having zeolite additives instead of MMT additives. Unlike MMT, zeolites do not contain aluminosilicate layerings. Instead, the microstructure of zeolites is made up of linked cages or cavities. Therefore, the effects of heating and shearing that presumably help to disrupt the layering of the MMT and promote a blocking mechanism¹⁵ of smoke and heat release are not expected with zeolite additives. On the other hand, BRZ zeolite has a cation-Cu(II) exchange capacity of at least 3.77% in comparison to the 2.92% of MMT. Therefore, the presence of more Cu in the additive should further promote the reductive coupling mechanism, which leads to the crosslinking of PVC, and to the formation of more char and less smoke.

Table 9 provides a general overview of the use of all three zeolites, BRZ, Z-Ultra, and St. Cloud. As expected after heating and shearing, the average smoke values of PVC plaques that contained the Cu-exchanged zeolites correlated directly to

cation-exchange capacities with values of 3760, 3820, and 4880 for BRZ, Z-Ultra, and St. Cloud, respectively. Reductions in the heat release of PVC plaques with Cu-exchanged zeolite additives also were observed, though they were not as dramatic as those produced by the metal-exchanged MMT additives.

Unexpectedly, Table 10 shows that increasing the amount of BRZ zeolite additive above 10 phr did not necessarily have beneficial effects in reducing both heat release and smoke. However, in both respects, there is good evidence for synergism in Table 10 for the Zn-Cu mixed additive, which gave TSR values close to 3000.

Tables 11 and 12 contain additional data for mixtures of metal-exchanged zeolite additives. Figure 19 shows that the reproducibility of the smoke and heat release values was ordinarily within an acceptable range ($\pm 10\%$).

The aforementioned experiments may create some confusion because of the multitude of variables involved. The variables include the type of medium used for metal exchange (MMT or zeolite), the amount of additive used (10-20 phr), the use or avoidance of heating and shearing, and the metals and metal combinations, if any, exchanged into the media. The investigation of these variables led to hundreds of experiments involving the formation and burning of plaques.

Despite the multitude of variables, several conclusions can be reached from the analysis of the burn data. First and foremost, the use of metal-exchanged clay or zeolites significantly reduces the smoke emitted and heat released from PVC plaques. The use of unexchanged MMT or zeolites as additives for PVC generally produces effects that are less beneficial. Heating and shearing of mixtures of plasticizer and metal-exchanged MMT increases homogeneity and may facilitate intercalation and

exfoliation that result from the entry of PVC into the gallery space of the clay. The use of zeolites is important owing to their higher cation-exchange capacities with respect to MMT, which bring more metal into the system. As expected, as the amount of metal-exchanged MMT additive is increased, the heat release and smoke release values tend to drop concurrently. Synergism for heat and smoke reduction was observed with a mixture of Zn- and Cu-exchanged zeolites.

Future Studies

Currently, the Starnes group is looking for more efficient materials to replace Na-MMT. More specifically, we are attempting to identify other zeolites with considerably higher cation-exchange capacities, which can incorporate more copper introduced by exchange.^{18,19} Because of their higher copper contents, such zeolites could be much more effective than our copper clays as smoke suppressants and fire retardants.

Conclusion

The objectives of this research are to make PVC much more flame-resistant and a source of much less smoke when burning. The smoke produced by fires actually causes more fatalities than the fires themselves. Since PVC is used in so many commercial products, its fire retardance and smoke suppression can save many lives. Through the guidance of Dr. Starnes, I would like to think that I am making a difference with my research.

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Appendix: Daily Calibrations of the Cone Calorimeter

- Leave Machine, Power, Analyzers, and Smoke ON for 24 h before each run.
- Turn on water faucet and check pinwheel.
- Drain coldtrap into beaker and close valve (parallel w/ ground is closed).
- Check Drierite (remove when pink) and Ascarite (remove when white or solidified).
- Check soot filters and change when dirty more than halfway through.
- Turn on computer and start program.
- Calibrate gas analyzer
 - Zero Oxygen Analyzer
 - Be sure pump is off.
 - Turn on nitrogen tank and adjust the 2 switches.
 - Check flow rate (200 mL/min).
 - Click Calibrate Gas Analyzers on PC.
 - Select “Oxygen” and press “Zero”.
 - Adjust front of machine so it reads “Zero”.
 - Spanning
 - Turn off nitrogen cylinder and turn on pump.
 - Turn switch to “sample gas” and check flow rate (200 mL/min).
 - Allow time to stabilize (20.5% oxygen on cone calorimeter).
 - Adjust cone manually to agree.
 - Select Oxygen and press “Ambient”.
 - Press OK.
- Calibrate Smoke System
 - Zeroing
 - Go to calibrate/smoke, then block off the laser (paper block) at the compensating diode (near laser).
 - Allow system to stabilize, then press zero.
 - Remove block and close diode door.
 - Balancing
 - With laser unblocked and both diode doors closed, press balance.
 - Calibrate
 - Press calibrate and select the calibration filter (.304) and place it in front of the main diode (away from laser), then press OK.
- Zero DPT and MFM
 - Turn off exhaust fans and hood and try to block the smokestack.
 - Ensure that all methane valves and tank are turned off.
 - Select “Zero” on PC and zero methane and DPT.
- Set flow rate for exhaust and Soot Sampler
 - Check [Status] on PC.
 - Flow rate should be 30.0 g/s cold or approximately (25 L/s).
 - Adjust exhaust control knob after turning on exhaust and hoods.

- Check height of sample with respect to the cone; there should be 25 mm between the two.
- Heat Release (C-factor) Calibrations
 - Turn sample pump “ON”.
 - Insert methane burner into holder.
 - Turn methane valve to “OFF”.
 - Check that exhaust is ON.
 - Open door below cone.
 - Put sparker arm above burner.
 - Turn on *Ignition*.
 - Slowly turn on methane first at tank, then “methane on” switch, adjust flow to allow approximately 5 kW methane heat output.
 - Turn off *Ignition* when steady flow is achieved and move sparker arm to original position.
 - Be sure flame travels through cone to exhaust.
 - Go to Calibrate/Heat Release.
 - Let stabilize for 60 seconds.
 - Hit OK when C-Factor is stabilized.
 - Turn off methane at tank and allow to burn out.
- Calibrate Heat Flux
 - Check the temperature for the desired irradiance (heat flux). Check chart for calibration curve.
 - Be sure that water is on and that a ceramic tile is on the Load Cell.
 - Calibrate with heat flux meter
 - Do not touch the black surface under the red cap.
 - Ensure that the distance is 25 mm from the bottom of the cone.
 - Turn up the temperature for the desired heat flux with cone doors closed.
 - Open the doors to record/adjust the irradiance (i.e., temperature or heat flux).
 - Close the doors when finished and remove the sensor. Recap when the tip is cool and prepare to run a sample.
- Running a Sample
 - Press “Tare” on Cone.
 - Fill in all preliminary data on PC.
 - Load plaque onto holder.
 - Press 1 on Cone Remote Control.
 - Open the cone door.
 - Press 2 when plaque ignites.
 - Press 4 when burning ceases.

Vitae

Alexander G. Zestos was born in Bloomington, Indiana, on December 7, 1984. At the age of eight, he moved to Virginia with his family. He was the York High School Class of 2003 Valedictorian. In August of 2003, he entered the College of William and Mary as a James Monroe Scholar. He was active in recreational sports, the Hellenic Society, the Chemistry Club, Phi Eta Sigma, Alpha Lambda Delta, and the National Society of Collegiate Scholars. He subsequently became a Chemistry major and joined the Starnes research group in 2005. In May of 2007, he was graduated with a B. S. Degree in Chemistry with Honors. Upon receiving the M. S. degree, he aspires to attend medical school.