INITIATION OF SMOLDERING COMBUSTION IN
FLEXIBLE POLYURETHANE FOAMS

by

AUDIE Y. K. MAK

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Signature Redacted

Signature of Author

Department of Mechanical Engineering
March 14, 1980

Signature Redacted

Certified by

T. Y. Toong
Thesis Supervisor

Signature Redacted

Accepted by

W. M. Rohsenow
Chairman, Department Graduate Committee

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Submitted to the Department of Mechanical Engineering on March 14, 1980 in partial fulfillment of the requirements for the Degree of Mechanical Engineer

ABSTRACT

This work presents the experimental investigation carried out to study the initiation of smoldering combustion in uncovered flexible polyurethane foams when exposed to a given heat source. The investigation disclosed some of the criteria necessary to attain self-sustained smoldering and the major factors governing the initiation process. The experimental procedure also served to provide a rational test method for evaluating the relative smoldering tendency of different foam systems.

Results showed that most available foams by themselves are unlikely to sustain smoldering. For a type of polyurethane foam (PU18) that exhibited high smoldering potential, it is established that an additional well-defined size and geometrical orientation are necessary in order that self-sustained smoldering may prevail after being initiated. Moreover with this well-defined foam system, experimental results indicate that a minimum and a maximum initiation heating rate exists, below and above which, steady self-sustained smoldering may not be initiated. Within this range of maximum and minimum heating rates, additional minimum heating durations are required. These threshold heating durations decrease with increasing heating rates. As a result, a minimum thermal energy density is established capable of initiating self-sustained smoldering in uncovered flexible polyurethane foams.

For a foam that exhibited less potential to sustain smoldering, it is observed that it favored in forming volatiles and tars upon heating. Char formation was insignificant. Moreover, the minimum heating rate needed to initiate any char formation is higher and the range between
minimum and maximum heating rate is greatly reduced.

For comparable polyurethane foams with and without flame retardant, there were indications that char formation occurred at lower heating rates in the presence of flame retardant. These results may indicate that the addition of flame retardant in flexible polyurethane foams does not necessarily decrease the potential hazard from accidental initiation of smoldering combustion.
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I wish to dedicate this work to my parents.

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I. INTRODUCTION

Available data\(^1\) indicated that in the five-year period, 1968 through 1972, there were approximately five million accidental fires in buildings with an estimated loss of ten billion dollars. Fire deaths, most of them in home fires, during the same period were estimated at 60,000 and 1.5 million injuries. The National Commission on Fire Prevention and Control predicted an annual home fire loss by 1980 of 1 billion dollars a year unless positive action is taken\(^2\). Thus, the problem of accidental fires has been recognized. Research to understand fires and reduce their potential hazards are well underway.

One factor in fire hazard is the possibility of transition to flaming and subsequent fire spreading from a situation in which smoldering combustion is initiated at the initial stage\(^3\). Previous experiments showed that, depending on the fuel and environmental characteristics, once being initiated, smoldering may self-sustain and propagate steadily or it may be a transient phenomenon, leading either to extinguishment or to flaming\(^4\). The role of smoldering as early behavior of fire in many industrial and home materials is thus self-evident. Hence, investigations to understand the smoldering phenomenon has become an essential part in fire research.

Smoldering is generally observed to occur in solid fuels such as wood, paper, etc. It can be defined as a flameless mode of combustion. The phenomenon involves interactions between exothermic chemical reaction and heat transport. During the process, it is usually accompanied by
the evolution of smoke, heat and light (usually referred to as glow).
It is postulated that, by exposing certain solid fuels to heat, they may decompose to form volatiles, chars and/or tars. In cases where chars are formed, the chars react with oxygen, diffusing from the surroundings, to provide the heat needed for pyrolysis in the neighboring unreacted material. Smoldering may be interpreted as a cyclic process involving pyrolysis char formation, char oxidation and heat transfer. Propagation of a smoldering wave may be maintained only with successfully-balanced interactions in each mode of the cyclic process, otherwise, transition to extinguishment or flaming is expected.

In the past, the problem of smoldering fires in several common materials has been considered. Cohen and Luft studied the propagation of smoldering in still air for a range of dusts including magnesium, coal, cocoa, hynecodium, wood, sawdust and Pyrites. Sir Alfred Edgerton and K. Gugan investigated the smoldering of cigarettes under the conditions of alternating natural and forced convection fields as would occur during smoking. Kinbara studied smoldering in rolled paper, incense sticks and strips of cardboard. A coordinated theoretical and experimental investigation of the mechanism of smoldering in cellulosic materials has been conducted by Moussa.

The hazards of smoldering fires also include for example home insulation, bedding and upholstery furniture. Many of these items are made from flexible polyurethane foams that are now having a major and increasing share of cushioning market. Attention and experimentation has been focused mainly on the flame-supporting tendencies of the
foams$^{10,11}$. Retardant additives for foams have been designed exclusively to inhibit flaming combustion$^{12}$. However, it is also believed that a great life-saving incentive may well exist in reducing the propensity to smolder in polyurethane foams.

The smoldering behavior of various types of flexible polyurethane foam has been studied. There were indications$^{13}$ that some foams, by themselves, are relatively impervious to smoldering and often serve as a protective barrier to the inception of smoldering. However, there are foams that may exhibit self-sustained smolder which are judged exceptionally hazardous. Moreover, when the foams are combined or in contact with other materials with smoldering tendencies, interactions usually occur to promote combustion and the situation becomes complicated. Questions have risen regarding the manufacture of foams to meet fire safety requirements.

A detailed analysis$^{14}$ of 130 upholstered furniture ignition incidents in the National Bureau of Standard's Flammable Fabrics Accident Case and Testing System (FFACTS) in April 1972, indicated that, cigarettes were the major ignition sources in accidental fires in which upholstered furniture was the first product ignited. In addition, a study$^{15}$ conducted by the National Fire Protection Association indicated that smoking on upholstered furniture was responsible for over 16 percent of single fatality non-clothing fires studied, for which the causes of ignition were known and stated. Therefore, cigarettes would appear to be a significant combustion/ignition hazard when associated with upholstered furniture. Experiments on cigarette induced smoldering of uncovered
Flexible polyurethane foams have also been conducted\textsuperscript{16}, the report showed that flexible polyurethane foams may be hazardous when the surface is exposed to smoldering cigarettes. Furthermore, there were indications that smoldering tendencies were enhanced when smoldering cigarettes were embedded between foams. It is therefore, recognized that accidental exposure of some flexible polyurethane foams to certain heat sources (e.g., careless disposals of cigarette remains) can initiate smoldering and, subsequently, lead to serious damages and/or fires. Research to understand the criteria and mechanisms in the initiation of smoldering is thus needed in order to provide a basis for improved materials and diminished hazard.

The present study surveyed a random collection of different foam compositions. A type of foam (PU18) that formed significant amount of char upon heating was chosen for detailed study. As a result, criteria leading to self-sustained smoldering in the foam is disclosed and established. This foam system was then used to investigate factors governing the successes and failures in the initiation process. The same experimental procedure was then repeated on a lighter foam with and without flame retardant (GM23 and GM21, respectively). Differences in the smoldering characteristics were observed and the results suggested a method for identifying and ranking the relative smoldering tendencies in different foams. Details are discussed in subsequent chapters.
II. QUALITATIVE DESCRIPTION OF THE SMOLDERING PHENOMENON

1. The Postulated Model

Smoldering is basically defined as a non-flaming mode of combustion normally observed in solid fuels such as wood, coal, paper and fabric etc. The sustained smoldering process mainly involves interactions between chemical reactions and heat transport. It is characterized by pyrolysis, charring of virgin material, evolution of volatiles and sometimes emission of glow (light).

The main features of smoldering are illustrated in Figure 2.1 as a cyclic process involving pyrolysis, charring, char-oxidation and heat transport. A solid fuel decomposes when subjected to heating. Depending on the fuel composition and the heating rate, the fuel material may simply degrade (physically indicated by discoloring) and extinguish or it may continue to react and spread through its neighboring material. In general, the initiated reactions in a fuel that smolders may involve evolution of volatiles (vapor phase) and formation of chars (solid phase), of which the ratio of the amount, again, depends on the fuel composition and heating rate. In cases where the fuel materials are plastics (including some flexible polyurethane foams), the formation of tars (liquid phase) are also involved. With the formation of char that more or less remained at its original location, the char reacts with oxygen (char-oxidation reaction) diffused from the fuel surroundings to provide heat to sustain smoldering. That is why, char-formation and the presence of oxygen are necessary elements needed
for sustaining smoldering.

Smoldering, once being initiated, may be steady and self-sustained, or it may be a transient phenomenon leading to extinguishment or flaming.\(^4\) Propagation of a steady smoldering wave may prevail only under critically balanced reactions and interaction in each mode of the above mentioned cyclic process.

2. Initiation of Smoldering

The initiation of smoldering may primarily be thought as equivalent to the initiation of char-formation, since char-oxidation is the major process in sustaining smoldering. However, this does not imply that sustained smoldering may prevail after being initiated, it may still be unsteady leading to flaming or extinguishment due to several factors.

The initiation of steady self-sustained smoldering is defined such that smoldering, after being initiated, may self-sustain and propagate throughout a test sample. In addition to the fuel and environmental restrictions, the initiation requirements are also restricted in order to establish steady self-sustained smoldering. This shall be discussed in later chapters.

A heat source (e.g., a smoldering cigarette) is required in order to initiate smoldering in a fuel that smolders. The thermal responses of a given fuel material may vary according to the intensity of the heat source. Presumably, at very low heating intensity, none or only a small amount of thermal degradation reaction may occur with none or a negligible amount of char formed. On the other hand, at very high heating
intensity, ignition to flaming is expected. It is expected that smoldering may be initiated only within certain range of intermediate heating intensities. This is verified in the experimental studies discussed in later chapters.

The main features in the initial transient development of smoldering may be illustrated as shown in the temporal development of the temperature profile in Figure 2.2. At early time near the heat source, in general, none or insignificant exothermic reactions may be noticed during which, only small amount of thermal degradation reaction may occur. At sufficient heating intensity and heating time, the temperature profile may continue to develop. The onset of significant exothermic reactions (char-oxidation reactions) may be indicated by the change in shape of the temperature profile. Under favorable conditions and heating intensities, a steady state profile may be established and continue to propagate steadily away from the heat source; otherwise, transient smoldering leading to extinguishment are represented by dotted lines in Figure 2.2. The governing factors that determine the success and failure in establishing steady self-sustained smoldering are discussed in subsequent chapters.

3. Steady Self-Sustained Smoldering

Depending on the fuel compositions, configurations and ambient condition, a steady state smoldering structure may be established after being successfully initiated. Consider that smoldering has certain
similar features as a flame other than the formation of char one may expect a steady smoldering wave to propagate at a characteristic speed that is proportional to the square root of thermal diffusivity and the chemical reaction rate of the fuel material, viz.  

\[ V_s \sim \left( \frac{\lambda}{\rho C_p} \cdot \frac{1}{\bar{T}_{\text{chem}}} \right)^{\frac{1}{2}} \]

where \( V_s \) is the steady propagation speed, \( \lambda \) is the effective thermal conductivity of the fuel, \( \rho \) is the fuel density, \( C_p \) the specific heat and \( \bar{T} \) is the average fuel chemical characteristic time.

Essentially, three separate regions may be distinguished in a smoldering structure (Figure 2.3):

Pyrolysis zone - The preheat region. At lower temperature wherein the virgin material decomposes indicated by discoloring and emission of small amount of volatiles.

Char-oxidation zone - Characterized by charring of the degraded materials. The char reacts with oxygen (diffused from the fuel surrounding) to provide heat flux necessary to sustain smoldering.

Char residue - Upon completion of char-oxidation reaction, non-reacting residue is left behind as part of combustion product.

In a steady self-sustained smoldering wave, all three zones propagate at the same characteristic speed \( V_s \). The size of the char-oxidation zone may be estimated as
\[ \delta_s \sim v_s \overline{t}_{chem} = \left( \frac{\lambda}{\rho C_p} \cdot \overline{t}_{chem} \right)^\frac{1}{2} \]

where \( \delta_s \) is the characteristic length scale representing the size of the char-oxidation zone.
III. EXPERIMENTAL STUDIES, RESULTS AND DISCUSSIONS

1. Preliminary Remarks

This chapter presents the experiments carried out to examine the various responses of foams of varying compositions and geometrical configurations when exposed to a given heat source at various heating intensities. The primary objective of the experiments was to investigate the principal factors that determine whether a foam of given composition and geometrical configuration may self-sustain smoldering and, to establish criteria required to initiate self-sustained smoldering in uncovered flexible polyurethane foams. Moreover, it is intended to provide means of identifying the relative smoldering tendency of different foam systems.

Different foam samples were examined, each exhibited a different degree of smoldering tendencies. Differences in thermal responses and smoldering features are evaluated. The effects of foam size and geometrical orientation are examined. The heating criteria necessary for successful initiation of self-sustained smoldering are determined. An examination of the temporal development of the temperature profiles and the quantitative and qualitative comparison of the char structures (formed as part of combustion products) served to suggest some of the features and mechanisms that prevail for the initiation of self-sustained smoldering and for the failure to sustain the smoldering. It is suggested that the test method used in the experiment may serve for evaluating the relative smoldering tendency of flexible polyurethane foams of varying
configuration and composition.
2. Experimental Apparatus and Procedure

The experiments were carried out in a pressure vessel as illustrated in Figure 3.1. The vessel is 3' (0.91 m) diameter and $4\frac{1}{2}'$ (1.4 m) long, prefabricated from $\frac{1}{2}''$-thick (1.27 cm) steel, with dome-shaped ends and a swinging door. The vessel door may be bolted to the vessel with a number of bolts and nuts. Two 6'' (15 cm) diameter windows are installed for visual observation. A number of valve connections are available for monitoring the environmental condition inside the vessel. An exhaust blower and suction fan installed above the vessel serve to regulate the vessel environmental condition through a $3\frac{1}{2}''$ (3.9 cm) diameter valve. A number of circuit boards are available for connecting electrical equipment from the outside to the inside of the pressure vessel. The vessel is also implemented with a wire frame to support the polyurethane foam samples with minimum quenching during experiments.

Flexible polyurethane foams of different size and orientation were tested. A nickel-chrome heating coil (0.39 cm dia x 9 cm long with 10.5 $\Omega$ at room temperature) was used as the heat source. Inside the heating coil was implemented with a chromel-alumel thermocouple (0.13 cm dia) to measure the approximate temperature at the heating coil. Since heating was provided by means of electric current supplied to the heating coil, the thermocouple and the heating coil were separated by sleeving a thin-wall glass tube between them, as shown in Figure 3.2. Heating was controlled by maintaining various electric power supplied across the heating coil for different durations. A schematic of the
electric circuit providing power to the heating coil is shown in Figure 3.3. Power supply was controlled by turning the electric variac and by noting the readings on the bolt-meter and the amp-meter. A switch was available for monitoring heating durations.

During experiment, the heating coil and other additional chromel-alumel thermocouples (0.013 cm dia) were embedded 1 cm apart and along the mid-plane of the thickness of the foam sample. The thermocouples were used to record the temperature responses of the foam upon heating. The sample foam was then mounted to the wire frame with the heating coil terminals connected to the power supply circuit and the thermocouple terminals connected to recorders outside the vessel during experiment. Electric power supply and measurements were monitored from outside the vessel. All experiments were carried out under normal atmospheric conditions.
3. Effects of Foam Geometrical Orientation and Size in Self-Sustained Smoldering

Several preliminary experiments were carried out on various types of foams (chosen randomly in the market) in order to establish experimental procedure and to identify the various smoldering features and smoldering tendencies in different foam systems. In these exploratory experiments, large foam samples were heated at 0.18 cal/sec cm$^2$ by the heating coil embedded inside the foam. It is observed that most flexible foams tend to form volatiles upon heating, the amount of char-formation was often negligible or surrounded with large irregular cavities that led to subsequent extinguishment. These preliminary tests suggested that, with few exceptions, most available flexible polyurethane foams by themselves are not likely to self-sustain smoldering under normal ambient condition. They frequently behave unsteadily, leading to extinguishment even after smolderings were initiated.

A type of polyurethane foam (denoted as PU18) that formed significantly more char was observed to smolder more readily than all other foam samples being tested. Experiments were carried out to examine whether there exists a situation in which the foam may prevail self-sustained smoldering after being initiated. Results showed that certain well-defined size and gravitation orientation are required to self-sustain smoldering. These experimental results and discussions of their implication and importance contributed to the determination of the relative tendencies are presented in the following sections.
3.1 Horizontal Smoldering

Flexible polyurethane foam PU18 (4\(\frac{1}{2}\) x 9 sq cm in cross-sectional area and 22 cm long) was tested horizontally as shown in the schematic in Figure 3.3.1. The objective was to determine whether this foam system may sustain horizontal smoldering propagation. The heating coil was embedded 5 cm from one end and in the mid-plane of the thickness of the foam sample. A heating rate of 0.17 cal/sec cm\(^2\) at the heating coil was maintained throughout the experiment. The thermal responses were recorded by thermocouples embedded at 1 cm apart and along the length of the test sample. Figure 3.3.1 illustrates the temporal development of the temperature profile in the horizontal foam sample upon heating. The result shows that exothermic reaction was not initiated until after 400 sec. Initiation of exothermic reaction near the heating coil was noted at 500 sec and is indicated by the change of temperature distribution to an s-shaped profile. Volatiles were emitted. Char formation was observed to have extended to the exposed surface and continued to propagate away from the heating coil. The temperature profile continued to develop both in magnitude and width indicating the growth and propagation of smoldering along the length of the foam sample. However, at 1000 sec, cooling was initiated at some distance behind the propagating smoldering front. The development of the temperature profile indicates that, as the smoldering front continues to propagate, the effect of cooling spread simultaneously from behind, subsequently overtook and weakened the exothermic reaction in the precursor smoldering wave. The cooling effect then became more pronounced. Further smoldering propagation was prohibited
and went to extinguishment. As a result of the initiated reactions, char was formed and left behind as combustion residue. It is noticed that, as a consequence of the foam sample orientation, the char formed on the upper portion of the foam sample was relatively more porous than the lower part, presumably caused by the flow of volatiles through the reacting char. It is postulated that the formation of porous char in this orientation enhanced the convective heat losses from the reaction zone and reduced the heat flux available to sustain pyrolysis, thus leading to extinguishment. It is suggested that the effect of orientation and size would cause a different heat flux and heat loss mechanism, while at the same time may result in the formation of various char structures. Other configurations being investigated are discussed in subsequent sections.

3.2 Vertically Upward Smoldering

The same type of polyurethane foam PU18 with the same size ($4\frac{1}{2} \times 9 \times 22$ cu cm) was examined again, this time, orientated vertically with the heating coil embedded $5$ cm from the bottom and in the mid-plane of the thickness of the foam sample (as shown in the schematic in Figure 3.3.2). A heating rate of $0.17 \text{ cal/sec cm}^2$ was maintained at the heating coil throughout the experiment. The thermal response is reflected in the temporal development of the temperature profile shown in Figure 3.3.2. The overall feature of this temperature development appears essentially similar to that discussed in Section 3.1 on horizontal smoldering behavior that resulted in subsequent extinguishment. Nevertheless, differences appeared in the char structure that formed as a result of the initiated reactions in foam samples of different
orientation. In the case of vertically upward smoldering, a significantly large cavity was formed between the char residue and the virgin material. This cavity seemed to have been created by the volatiles that rose from the reaction zone. It is postulated that, the formation of this cavity diminished the amount of char and thereby the exothermic char-oxidation reaction and could also have behaved as a thermal insulator. Hence, the heat flux towards the virgin material was greatly reduced. As a result, smoldering behaved unsteady and went to extinguishment soon after being initiated. Therefore, it is determined that, due to the above observed phenomenon, uncovered flexible polyurethane foams are not likely to self-sustain steady smoldering in the vertically upward direction.

3.3 Vertically Downward Smoldering and the Effect of Size

Smoldering in the downward direction was tested with the heating coil embedded at the top of the 4½ x 9 x 22 cm foam sample as shown in the schematic in Figure 3.3.3. Heating rate was maintained at 0.15 cal/sec cm² throughout the experiment. In this experiment, smoldering was initiated and self-sustained throughout the test sample as illustrated in Figure 3.3.3. Char-oxidation was initiated after 500 sec. Smoldering then continued to propagate downwards while volatiles issued from the top and sides of the foam sample. Finally, a steady-state temperature profile was achieved and propagated throughout the sample at approximately 0.55 cm/min with a maximum temperature of 480°C. As a result of the successful initiation and self-sustained smoldering,
uniform char was formed throughout the test sample without any cavities. It is postulated that the formation of uniform char without cavities may contribute significantly to the success in the development of steady self-sustained smoldering.

The above experiments thus illustrate the various features and the effects of gravitational orientation on the smoldering tendencies in foam systems. In addition to the effects of gravitational orientation, the effect of size (thickness) in self-sustained smoldering were also investigated. PU18 polyurethane foams, 9 cm wide by 22 cm long, each with a different thickness were tested vertically with the heating coil embedded 5 cm from the top of the foam sample as shown in Figure 3.3.4. The results are shown and discussed in the following.

A relatively thinner PU18 foam sample (3 cm thick x 9 cm x 22 cm) was tested to examine whether it may self-sustain vertically downward smoldering propagation. A heating rate of 0.17 cal/sec cm$^2$ was maintained at the heating coil throughout the experiment. The result shown in Figure 3.3.5 indicates that, for this foam size, no significant char-oxidation reaction was initiated at this heating rate. As a result of this experiment, only a small amount of thermal degradation reaction occurred. A small amount of volatiles was emitted. Char formation was negligible and smoldering was not initiated. In order to initiate smoldering in this foam system, the heating rate was raised to 0.26 cal/sec cm$^2$ at the heating coil. At this heating rate, the result in Figure 3.3.6 shows that even though smoldering was initiated, yet, self-sustained smoldering was not achieved. Unsteady smoldering behavior was noticed
after being initiated and eventually went to extinguishment in spite of the significant amount of well structured char being formed. It is postulated that a thin foam sample may allow excessive convective heat losses through the exposed surfaces, thus reducing the heat flux below what is required to sustain smoldering. As a result, smoldering was not sustained. This experiment thus suggested that, a minimum size (thickness) of the foam must be exceeded in order that self-sustained smoldering may prevail after being initiated.

A thicker foam sample (6 x 9 x 22 cm) placed vertically was also tested in the same fashion with the heating rate maintained at 0.17 cal/sec cm² throughout the experiment. Different from the previous experiment in the thinner foam sample, at this heating rate, smoldering was initiated. Moreover, as shown in Figure 3.3.7, smoldering continued to develop and sustained for a longer period. Nevertheless, steady self-sustained smoldering was not achieved. At approximately 1200 sec, some unsteadiness in the temperature profile is noted to have initiated at some distance behind the propagating smoldering front. The onset of the temperature fluctuations led to a further drop in temperature in the reaction region. These features continued to spread and thus weakened the smoldering wave. Further smoldering propagation was then prohibited and went to extinguishment. As a result of the initiated reactions in this thick foam system, significant amount of volatiles were emitted, char was formed surrounded by large irregular cavities. In this case, it is postulated that the formation of these cavities resulted in a reduction in char oxidation reactions and at the same
time enhanced the convective heat losses that led to eventual extinguishment.

From the above experiments, it has thus been illustrated that a well-defined size for an uncovered foam is required in addition to the gravitational orientation to self-sustain steady smoldering.
4. Heating Criteria for the Initiation of Self-Sustained Smoldering

The previous section established the additional size and gravitational orientation restrictions in PU18 foam under which self-sustained smoldering may prevail after being initiated. Steady self-sustained smoldering in PU18 was observed to have propagated only in samples of 4½ x 9 sq cm cross-section area and only in the vertically downward direction after being successfully initiated under normal ambient condition.

Questions had also been raised regarding the cause of smoldering and its possible development to either transient or steady smoldering. As an effort to answer part of this question, this section presents the experiments carried out to determine the necessary criteria in the initiation process and to examine the major factors governing the success and failure in the development of steady self-sustained smoldering.

In the initiation experiments, PU18 polyurethane foams of 4½ x 9 sq cm cross-sectional area by 22 cm long placed vertically, were tested under normal ambient conditions. The heating coil was embedded 5 cm from the top and at the mid-plane of the thickness of the foam sample (Figure 3.4.1). The heating rates were controlled and monitored. The thermal responses were recorded.

Two major types of experiments were carried out in the initiation studies:

(1) Effects of Heating Rates - A different heating rate was maintained throughout each experiment. Various thermal responses were noted.
(2) Threshold Heating Rate and Heating Duration - For each heating rate, heating was terminated at a different time. Various thermal responses were also noted.

Experimental results are discussed in the following sections.

4.1 Effects of Heating Rates

Experiments on PU18 were carried out to examine the various thermal responses to a given heat source. A specific heating rate was maintained throughout each experiment. The thermal responses were recorded and the char residues left as combustion products were examined.

At a heating rate of 0.14 cal/sec cm$^2$, the result shown in Figure 3.4.2 indicates that the PU18 foam sample ($4\frac{1}{2} \times 9 \times 22$ cm$^3$, placed vertically) responded almost as one without reaction. The temporal development of the temperature profiles near the heating coil shows negligible exothermic reaction and remains steady after 400 sec. A small amount of volatiles were emitted. Char formation was negligible. Only a small amount of thermal degradation occurred (indicated by change in color) near the heating coil. As a result, smoldering was not initiated.

Figure 3.4.3 (same as Figure 3.3.3) shows the result in which the heating rate was maintained at 0.15 cal/sec cm$^2$. In this case, smoldering was successfully initiated and self-sustained throughout the foam sample. The temporal development of the temperature profile indicates that no exothermic reaction was noticed before 400 sec. However, at 500 sec,
significant exothermic reactions were initiated. The onset of exothermic reaction is indicated by the change in temperature distribution to an s-shaped profile. The reactions continued (indicated by further development and propagation of the s-shaped temperature profile), at the same time emitted significant amount of volatiles. Char formation was observed to have extended to the exposed surface and continued to propagate along the length of the foam sample. Subsequently, a steady state temperature profile was arrived at 1000 sec and at approximately 7 cm from the heating coil with a maximum smoldering temperature of 480°C. This steady state temperature profile is noted to propagate steadily at approximately 0.55 cm/min. Steady self-sustained smoldering was thus successfully initiated and propagated throughout the foam sample. As a result of steady smoldering, char was formed throughout the foam sample and was noticed to be relatively dense and well structured without large irregular cavities. It is postulated that the formation of dense char without accompanying large cavities may contribute to the success in sustaining smoldering and thus, may be used as an indication of the potential smoldering hazard of the foam system.

When the heating rate was raised to 0.51 cal/sec cm² however, only transient smoldering was initiated that led to subsequent extinguishment. Figure 3.4.4 shows the thermal responses at this high heating rate. At this high heating rate, exothermic reactions were quickly initiated and continued to develop rapidly. Large amounts of volatiles were emitted. Formation of char that extended to the exposed surface was visible. However, at approximately 600 sec, some fluctuations in the temperature
profile are noticed to have initiated at some distance behind the propagating smoldering front. These unstable temperature fluctuations continued to grow and spread in the reaction zone. Exothermic reactions in the smoldering wave were then weakened. Temperature dropped everywhere and subsequently went to extinguishment. As a result of this high heating rate, insignificant amounts of chars were formed, however, they were surrounded with large irregular cavities. It is postulated that, as a result of high heating rate, heat flux from the heating coil continued to transport to the reacting char during and after char oxidation, the char thus continued to react or degrade forming more volatiles and hence created large irregular cavities. The formation of these cavities at high heating rate resulted in a reduction in exothermic char oxidation and simultaneously enhanced the convective heat losses through the pores and the outer surfaces. Therefore, smoldering became unsteady and went to extinguishment following the formation of cavities caused by high heating rates.

These experimental results suggest that, for each given foam system, there may exist a minimum and a maximum heating rate below and above which steady self-sustained smoldering may not be initiated. Below the minimum heating rate, only a small amount of thermal degradation may occur or the char formed is insufficient to sustain further smoldering. On the other hand, above the maximum heating rate, only transient smoldering may be initiated with char formation followed by the formation of large irregular cavities that may cause convective heat losses and lead to subsequent extinguishment. It is only within the range between
maximum and minimum heating rates that steady self-sustained smoldering may be initiated with the formation of well-structured char without large irregular cavities.
4.2 Threshold Heating Rate and Heating Duration

This section presents the results from experiments carried out to examine the effects of different heating time in the initiation of smoldering in PU18. In these experiments, within the range of maximum and minimum heating rates, external heating was terminated at a different time after being started. Various thermal responses were noted.

Figure 3.4.5 shows the experimental result whereby, within the maximum and minimum heating rates, external heating was terminated as soon as char was observed to have formed and extended to the visible surface (external heating was maintained throughout the experiment in the experiments discussed in previous sections). Smoldering was initiated and the response that followed was continued to be recorded. This figure shows the result in which a heating rate of 0.15 cal/sec cm$^2$ was maintained for 600 sec. At 600 sec when significant amount of char formation was observed, the power supplied to the heating coil was terminated. Corresponding temperature distribution for this case showed a gradual drop in temperature beyond 600 sec, leading eventually to extinguishment. Although significant amount of char was formed without large irregular cavities, steady self-sustained smoldering was not initiated, presumably due to insufficient amount of char formation. Further experimental results showed that for the same heating rate (0.15 cal/sec cm$^2$), a minimum heating duration of 700 sec is necessary in order to initiate self-sustained smoldering. Thus, one finds a corresponding minimum heating duration in addition to the restricted heating rates to define the initiation requirements.
Figure 3.4.6 shows the initiation requirements in terms of the heating rate and heating duration. The X represents regimes where no steady smoldering was initiated. The 0 represents regions where initiations were successful. The results of the initiation experiments shown in this figure thus indicates that, for a given foam system, there exists a minimum and a maximum heating rate below and above which steady self-sustained smoldering may not be initiated. Within the range of difference, a minimum heating duration is required. Moreover, for each heating rate within this range, a corresponding threshold heating duration exists. These threshold heating durations decrease with increasing heating rates. By taking the product of heating rates and the corresponding threshold heating durations from the results in Figure 3.4.6, Figure 3.4.7 is plotted. As a result, it is found that a minimum thermal energy density (cal/cm²) may be established that is capable of initiating steady self-sustained smoldering.
5. Initiation Requirements in GM Foam and the Effects of Flame Retardant

In order to identify the major differences in the initiation requirements in different foams and the major features contributing to these differences, similar experiments have been carried out on a different foam sample supplied by the Products Research Committee (denoted as GM21). The experimental method, procedure and test sample configurations were the same as those presented in previous sections on PU18.

Figure 3.5.1 shows the thermal response of GM21 being heated throughout the experiment at 0.24 cal/sec cm². The result shows that, even at this high heating rate, no significant exothermic char-oxidation reaction was initiated. It is noticed that only a small amount of thermal degradation reaction occurred, after which, the temperature distribution remained steady without any indication of further reaction. A small amount of volatiles were emitted. Char formation was almost negligible. As a result, smoldering was not initiated.

When the heating rate was slightly raised, at 0.30 cal/sec cm², transient smoldering was initiated with char-oxidation reactions and simultaneous emission of significant amount of volatiles. At this heating rate Figure 3.5.2 shows that exothermic reactions were initiated and prevailed for 500 sec. However, this was followed by abrupt drop in temperature everywhere in the reaction zone. Smoldering thus behaved unsteady and went to extinguishment soon after being initiated. As a result of the initiated reaction, porous char was formed surrounded by irregular cavities. Hence, smoldering went to extinguishment, in a
manner somewhat similar to that in PU18 at high heating rate (cf. Figure 3.4.4). The experimental result and observations thus suggested that GM21 by itself is not likely to sustain smoldering under normal ambient condition due to the formation of char that is accompanied with cavities.

A comparison of experimental results on PU18 and GM21 shows that, the minimum heating rate required to initiate char-oxidation reaction in GM21 is higher than that required in PU18. Moreover, for GM21, the range of difference between minimum and maximum heating rate required to initiate char oxidation without cavities is greatly reduced. A comparison of these differences suggest a means of evaluating the relative smoldering tendencies in foams of different compositions. Thus, GM21 is determined as being less likely to be initiated to sustained smoldering.

GM21 impregnated with flame retardant (denoted as GM23) was also tested in the similar fashion in order to determine the effectiveness of flame retardant in suppressing smoldering in polyurethane foams. Experimental results on GM23 display in Figure 3.5.3 shows that, at 0.15 cal/sec cm$^2$, only small amount of thermal degradation reaction occurred. Char formation was almost negligible and hence smoldering was not initiated. However, at a heating rate of 0.24 cal/sec cm$^2$ (Figure 3.5.3), transient smoldering was initiated and developed for 600 sec, after which, was followed by abrupt drop in temperature everywhere in the reaction zone. The char formed was surrounded with irregular cavities. As a result, the initiated smoldering became unsteady and went to extinguishment in a similar fashion as in GM21 when being heated at 0.30 cal/sec cm$^2$. Because of the similar smoldering
behaviors in GM21 and GM23, it appears that the addition of flame retardant does not effectively suppress smoldering in uncovered flexible polyurethane foam. On the other hand, the fact that the addition of flame retardant to GM21 lowered the heating rate required to initiate char-oxidation does imply that, the addition of flame retardant may enhance smoldering tendency in uncovered flexible polyurethane foams.
6. Ranking of Smoldering Tendencies

The method used in the initiation experiments may also serve as a suitable test procedure to identify the relative smoldering tendencies in different foams. Via the experimental method, the relative smoldering tendencies of different foam systems can be ranked by comparing the various thermal responses to different heating rates and by examining the differences in the char formations.

Table 3.6.1 illustrates results from the initiation experiments. It displays the possible range of heating rates within which char formation of excessive cavities. Based on the results and the observed differences in char formation conclusions are drawn as follows:

For a type of polyurethane foam possessing high smoldering tendency (e.g., PU18), char-oxidation reactions in the foam when subjected to external heating, may be initiated at a relatively lower heating rate. The range of difference between the maximum and minimum heating rate that may initiate the formation of char without large irregular cavities is expected to be larger according to the results from the experiments. Moreover, upon successful initiation of char-oxidation reactions, the chars formed as part of combustion products are denser and well structured. It is also noticed that, even for the same type of foam composition under the same ambient condition, the degree of smoldering hazard may vary, depending on the geometrical orientation and size of the foam that determine the various heat transport mechanisms. According to the experimental results, smoldering appeared to be most stable while propagating vertically downwards. Other unsteady features in different
orientations were also discussed previously.

For foam compositions that are less likely to be initiated and sustain the smoldering (e.g., GM21 and GM23), more volatiles may form upon heating while char formations are often insignificant. Even in cases where char may form, they would be porous, less dense and surrounded with cavities. Char oxidation reactions are expected to be initiated at higher heating rates and the range of difference between maximum and minimum heating rate that may initiate significant char-oxidation reactions without excessive cavities may be greatly reduced.
IV. SUMMARY AND CONCLUSIONS

Results from the present experimental investigation showed that most uncovered foam systems tested in the experiments exhibited transient smoldering that led to extinguishment. Only a type of polyurethane foam (PU18) that formed significant amounts of char upon heating demonstrated self-sustained smoldering possibility under normal ambient condition. According to the experimental results, this foam seemed to possess high tendency in sustaining smoldering. In addition to the foam composition, a well-defined size and orientation were needed in order that smoldering may be self-sustained and propagate steadily after being successfully initiated. Otherwise, change in the foam geometry caused changes in heat loss mechanism that resulted in transient smoldering. Below the minimum heating rate, the foam responded with little or no exothermic reactions with negligible char formation, smoldering was not initiated. On the other hand, heating above the maximum heating rate, significant reactions were rapidly initiated and accompanied by the emission of large amount of volatiles and formation of large cavities around the char. As a result, smoldering became unsteady followed by subsequent extinguishment. It was only within a certain range of intermediate heating rate that sufficient amount of well-structured char was formed (without the formation of large cavities) that led to successful initiation and propagation of steady self-sustained smoldering. Within the range of maximum and minimum heating rates, corresponding minimum heating duration was required. These threshold heating durations
decreased with increasing heating rates. As a result, it is established that a certain minimum energy density (cal/cm$^2$) may exist capable of successfully initiating self-sustained smoldering in flexible polyurethane foam.

For a type of polyurethane foam that is determined to possess less tendency to sustain smoldering (GM21), it is observed that it favored in the formation of tar and volatiles, thus diminishing the possibility in char formation. Even at intermediate heating rates when char was formed, the quantity was relatively insignificant and was often surrounded with cavities. The minimum heating rate needed to initiate char formation was found to be higher. Moreover, the range between the minimum and maximum heating rate needed to initiate char formation without too many cavities is greatly reduced.

For comparable foam system treated with flame retardant, the minimum heating rate needed to initiate char formation was lowered. This indicates that the addition of flame retardant does not necessarily diminish the tendency in the accidental initiation of smoldering in uncovered flexible polyurethane foams.

The procedure used in the initiation experiments thus provides a method for ranking the relative smoldering tendencies in different foam systems. It is concluded that foams with high smoldering tendency may form denser char with less cavities. Smoldering may be initiated at lower heating rates. Moreover, the range of difference between maximum and minimum heating rate that can initiate significant char formation without excessive large cavities is relatively larger.
REFERENCES


10. G. H. Damant: "Flammability Aspects of Flexible Polyurethane


Figure 2.1 The Postulated Model
Figure 2.2 Temporal Development of Smoldering
Figure 2.3 Steady Self-Sustained Smoldering Structure
Figure 3.1 Schematic Diagram of Pressure Vessel
Figure 3.2 The Heating Source
Figure 3.3 Schematic of Electric Power Supply
Continued Heating

Figure 3.3.1 Temperature Profiles
PU18

$4\frac{1}{2} \times 9 \text{ cm}^2$ Vertically Upwards

0.17 cal/sec-cm$^2$

Continued Heating

Figure 3.3.2 Temperature Profiles
Figure 3.3.3 Temperature Profiles
Figure 3.3.4 Foam Sample
PU18

3 x 9 cm² Vertically Downwards
0.17 cal/sec-cm²

Continued Heating

Figure 3.3.5 Temperature Profiles
3 x 9 cm² Vertically Downwards
0.26 cal/sec-cm²
Continued Heating

Figure 3.3.6 Temperature Profiles
FU18

6 x 9 cm² Vertically Downwards

0.17 cal/sec·cm²

Continued Heating

Figure 3.3.7 Temperature Profiles
Figure 3.4.1 Sample Configuration
$4\frac{3}{4} \times 9 \text{ cm}^2$ Vertically Downwards

0.13 cal/sec-cm$^2$

Continued Heating

Figure 3.4.2 Temperature Profiles
PU18

4 ½ x 9 cm² Vertically Downwards

0.15 cal/sec-cm²

Continued Heating

Figure 3.4.3 Temperature Profiles
PU18

4½ x 9 cm² Vertically Downwards

0.51 cal/sec-cm²

Continued Heating

Figure 3.4.4 Temperature Profiles
4.18

4\frac{1}{2} \times 9 \text{ cm}^2 \text{ Vertically Downwards}

0.15 \text{ cal/sec-cm}^2

Heated for 600 sec

Figure 3.4.5 Temperature Profiles
Figure 3.4.6 Threshold Heating and Duration

0 Successful Initiation
X Unsuccessful Initiation
Figure 3.4.7 Illustration of the Existence of Minimum Energy Density
GM21
4.5 x 9 cm² Vertically Downwards
0.24 cal/sec-cm²
Continued Heating

Figure 3.5.1 Temperature Profiles
GM21
4 1/2 x 9 cm² Vertically Downwards
0.30 cal/sec-cm²
Continued Heating

Figure 3.5.2 Temperature Profiles
GM23

$4\frac{1}{2} \times 9 \text{ cm}^2$ Vertically Downwards

0.15 cal/sec-cm$^2$

Continued Heating

Figure 3.5.3 Temperature Profiles
GM23

4½ x 9 cm² Vertically Downwards

0.24 cal/sec-cm²

Continued Heating

Figure 3.5.4 Temperature Profiles
<table>
<thead>
<tr>
<th>Material</th>
<th>Heating Rate (cal/sec-cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU18</td>
<td>0.15 0.50</td>
</tr>
<tr>
<td>GM23</td>
<td>0.15 0.24</td>
</tr>
<tr>
<td>GM21</td>
<td>0.24 0.30</td>
</tr>
</tbody>
</table>

Table 3.6.1 Ranges of Possible Heating Initiation to Smoldering