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Spontaneous Ignition

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Please note

This publication is a part of a discontinued series and is archived here as an historical reference. Readers should consult design and regulatory experts for guidance on the applicability of the information to current construction practice.

Spontaneous ignition is a possible cause of unwanted fire. It is a complex phenomenon of combustible material ignited by its own heat of reaction without external heat or other source of ignition. The purpose of this Digest is to outline the factors responsible for spontaneous heating and ignition and the laboratory methods available for studying the problem. A list of materials with a tendency towards spontaneous ignition is included.

One of the best known examples of spontaneous ignition is that of a drying oil such as linseed oil absorbed in cotton waste. Linseed oil slowly takes oxygen from the air to form a skin of solid material, a process caused by an oxidation reaction that produces heat. When linseed oil is spread on a solid surface such as wood, the heat of oxidation is dissipated quickly. If, however, the same amount of oil is absorbed in cotton waste, the heat cannot escape so rapidly and the temperature of the waste increases. This accelerates the rate of oxygen absorption and results in further temperature increase. If this process continues, the temperature of the oil-soaked waste may gradually rise until ignition occurs spontaneously. The process usually takes several hours or even days. As the rate of the oxidation reaction is greater at high temperature, spontaneous ignition is more likely to occur during the hot summer season or in a warm area in a building during cold weather. If the oily mass is placed near a source of heat such as a heating system, the danger of ignition is much greater.

Heat Generating Reactions

Two basic factors contribute to spontaneous heating and ignition: heat generation and heat dissipation. If heat generates faster than it dissipates, it accumulates, i.e., temperature increases. Of the many kinds of heat-generating reactions, oxidation is the most common. Practically all organic substances and some inorganic ones will oxidize if exposed to the atmosphere and produce heat. Usually the rate of oxidation is very slow. Only materials that are self-heating have a significant rate.

A biological reaction is a common cause of self-heating of agricultural products. This is usually oxidation assisted by microorganisms in the presence of moisture. For hay to self-heat to ignition it has been reported that a moisture content as high as 33 per cent must be present. Self-heating of fish meal starts with the decomposition of proteins by the action of bacteria; and self-heating of wood chips at paper mills is initiated by the respiration of living cells and a

bacterial growth on or within the wood. These also require the proper amount of moisture. As bacteria or fungi cannot survive at temperatures much above 70 to 80°C, continued heating to ignition temperature is due to oxidation, which is chemical in nature.

Some unstable chemical compounds decompose from various causes such as light, mechanical action, biological action, or impurities and in the process they produce heat. Examples of such compounds are cellulose nitrate and organic peroxides. Decomposition reactions are usually slow at normal temperatures but accelerated at higher temperatures, often leading to spontaneous ignition or explosion.

Other chemical compounds, mainly inorganic, react with water to produce heat. Although this is not a self-heating reaction, it can cause spontaneous ignition. Materials that react with water are not combustible themselves, but they produce sufficient heat to ignite nearby combustibles or flammable gases produced by the reaction. The temperature of the material is not an important factor in this case because the reaction is sufficiently fast even at room temperature.

Reactions that cause spontaneous ignition include polymerization reactions and those between two highly reactive materials. Examples are given later in this Digest. In general, the actual mechanism of self-heating is not simple because two or more reactions often occur, either simultaneously or consecutively.

Water plays a number of important roles in self-heating reactions. As a reactant in certain exothermic chemical reactions and an influence in the growth of microorganisms in biological reactions its action has already been mentioned. Water may also suppress self-heating reactions of a chemical nature by absorbing heat by vaporization and by assisting heat dissipation.

Physical Factors for Spontaneous Ignition

Sawdust and wood chips self-heat much more readily than solid wood; in general, fibrous and finely divided materials are more susceptible to spontaneous ignition. One reason is that a material in a finely divided state has a lower thermal conductivity than one in the solid state so that heat is accumulated more easily. Another is that any decrease in particle size results in increased surface area. An oxidation reaction takes place on the surface exposed to the air. Powdered metals such as aluminum and magnesium powders are much more easily ignited than solid metals.

A few pieces of coal or some wood chips do not self-heat, but when they form a huge pile, as in a coal mine or paper mill, self-heating is a common problem. The larger the pile, the easier it is for self-heating and ignition to occur. This is because heat generation is proportional to the volume of the pile and this, in turn, is proportional to the third power of the radius; the heat loss, however, is proportional to the surface area of the pile, and this is proportional to the second power of the radius. The critical size, above which spontaneous ignition can occur and below which spontaneous ignition does not occur, is called the "critical radius" or "critical diameter."

The effect of ambient temperature is twofold. High surrounding temperatures provide the conditions not only for self-heating reactions to take place but also for heat loss to be restricted. In this case too, there is a critical temperature level above which spontaneous ignition can occur and below which spontaneous ignition does not occur. It is called the "critical ambient temperature" or "critical surface temperature."

There is a theoretical relation between critical ambient temperature and critical radius of material shown for some materials in Figure 1. The higher the ambient temperature, the smaller the critical radius and vice versa. If the ambient temperature is just slightly lower than the critical temperature, the material self-heats but does not ignite. When it is slightly higher, spontaneous ignition can occur after a long period. The time period to ignition is sometimes called the "induction period"; the higher the ambient temperature above the critical temperature, the shorter the period.

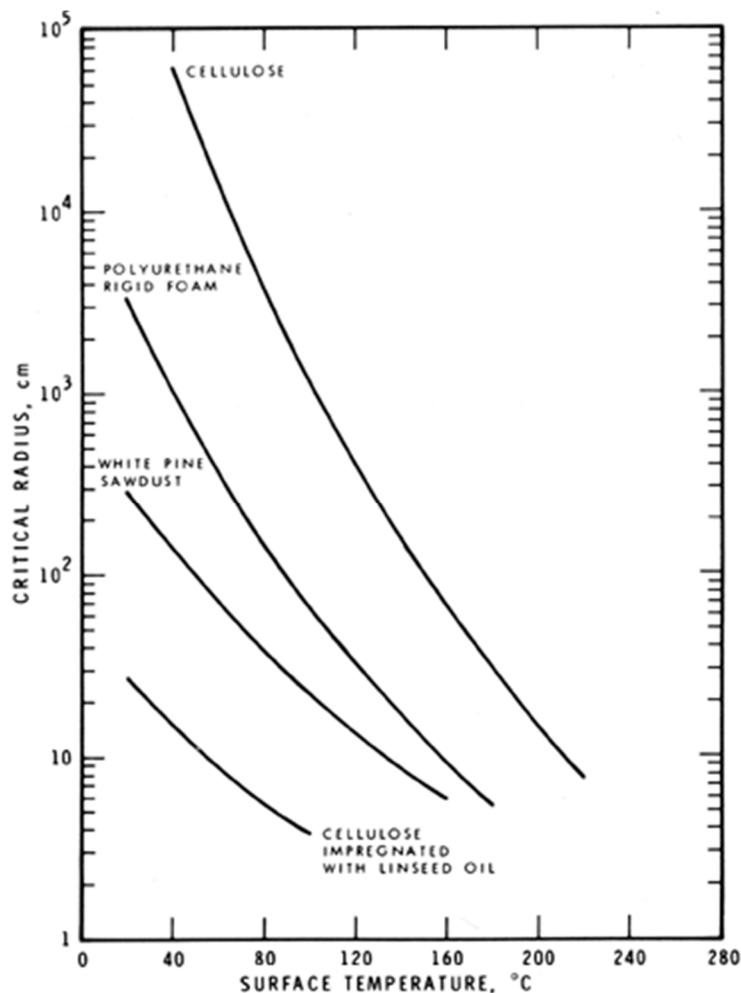


Figure 1. Surface temperature vs critical radius in spontaneous ignition

Testing and Prediction

It is often difficult in investigating the scene of a fire to establish whether the cause was spontaneous ignition. Laboratory studies of materials suspected of having ignited spontaneously often reveal whether this was likely. DBR/NRC is equipped for such studies and is capable of determining the tendency towards spontaneous ignition.

The Mackey tester, originally developed for oils, is one method of testing the tendency of materials to heat spontaneously. The oil is absorbed in cotton wool, the cotton placed in the tester and heated indirectly with hot water. The ensuing temperature in the specimen indicates the tendency of material to heat spontaneously. With a hazardous oil, the temperature rises fairly quickly. In 1 to 2 hours it may exceed 200°C and start smoking. The temperature increase of less dangerous materials is much slower, or no temperature increase may be detected. The Mackey tester is a relatively insensitive device because the sample size is small and the heating temperature of 100°C is relatively low for inducing self-heating reactions. Very dangerous materials can, however, be identified by this means.

The adiabatic furnace method is technically and theoretically more advanced than the Mackey tester for examining materials susceptible to spontaneous ignition. It can determine the relation between critical ambient temperature and critical radius. In the furnace available at DBR/NRC about 100 cm³ of sample is positioned in the tester and the specimen heated to a pre-selected temperature. The furnace is then switched to the adiabatic mode, which allows the specimen to self-heat by its heat of reaction. During the adiabatic heating period the

temperature surrounding the specimen is so controlled that there is no temperature difference between the centre and the surface of the specimen. The temperature of the specimen is recorded continuously until ignition occurs. If the increase under adiabatic mode is too slow or too fast the experiment is repeated after the pre-selected temperature has been adjusted. A wide range of materials can be tested with this method and from the time-temperature relation kinetic constants of the self-heating reaction can be obtained. Using the values of the kinetic constants and physical properties of the material, predictions can be made of the tendency towards spontaneous ignition of the material for various ambient temperatures and sizes of piles.

Actual Incidents

Two incidents investigated by DBR/NRC illustrate the sometimes unusual nature of spontaneous ignition. Both involved imitation sheepskin pads made of fluffy polyester with a backing of synthetic material. Such pads were used on hospital beds to add to the comfort of patients. In the first incident the fire department was called to investigate smoke in a hospital. They found the source of the smoke to be a sterilizer in which an imitation sheepskin pad was smouldering.

The second incident occurred in a government laundry where a number of pads had been washed, sent through a dryer and placed in a wire basket at the end of a working day. By the following morning they were completely burned. Laboratory studies showed that the imitation sheepskin was much more susceptible to spontaneous ignition than cotton or viscose rayon.

Materials Subject to Spontaneous Ignition

Examples of materials that have a tendency to ignite spontaneously are listed below. Additional examples may be found in the literature^{1,2}.

Rags that are contaminated with vegetable or animal oil are susceptible.

Coal, especially soft coal in dust form, is liable to ignite spontaneously. The principal conditions believed to affect susceptibility are fineness of particles, absorptivity for oxygen, moisture, presence of pyrites, height of pile and temperature of the environment.

Charcoal made from hardwood appears to be susceptible. Spontaneous heating occurs very readily in fresh charcoal, and the more finely divided it is, the greater the hazard.

Carbon black is formed by incomplete combustion of natural gas or liquid hydrocarbons. Lamp black is formed by burning low-grade heavy oils with insufficient air. Both are fine carbon particles susceptible to spontaneous heating, especially if they are freshly prepared.

Wood subjected to prolonged periods of heating and cooling cycles may ignite spontaneously. The alternate heating and cooling processes may chemically decompose the wood to produce pyrophoric carbon, which oxidizes rapidly. Many incidents of spontaneous ignition have occurred with wood in contact with hot surfaces such as hot water and steam pipes.

Wood chips in huge piles, as at paper mills, are known to ignite spontaneously.

Hay, clover, grains and other agricultural products are subject to self-heating. The first stage of heating is caused by biological action, which requires moisture. Wet or improperly cured hay is very likely to heat in barn lofts.

Alfalfa meal that has been exposed to rain and then stored in bins or piles is susceptible to spontaneous heating.

White phosphorus is readily oxidized and ignites when exposed to the atmosphere. For this reason, it is usually kept in water.

Metals in the form of fine powder are oxidized in the atmosphere and self-heat. Fresh turnings of iron are an example.

Calcium oxide or quicklime is a well-known example of a material that produces heat by reacting with water. In former days quicklime was made from seashells. Transportation of the

product was often by boat and fires were sometimes caused by accidental wetting. Quicklime itself does not burn, but it produces sufficient heat to ignite nearby combustibles.

Alkali metals react violently with water and produce heat and hydrogen gas that flames easily.

Sulphuric acid and other concentrated inorganic acids in contact with water produce a great deal of heat. When sulphuric acid is in contact with an organic substance, the acid decomposes the substance and ignition may result.

Cellulose nitrate used in celluloid and gunpowder decomposes with aging. The accumulation of decomposition products and heat accelerates further decomposition so that ignition can occur. The decomposition reaction does not require oxygen. Celluloid has now largely been replaced by various plastics, but some of the old products may still remain.

Organic peroxides are a group of chemicals in wide use, for example as polymerization initiators, in the plastics industry and as bleaching agents. They can decompose with heat, shock or light and then ignite or explode. They are often diluted with another liquid or solid, or wetted with water to reduce the hazard.

Monomers of plastics such as styrene, methyl methacrylate, vinyl acetate and ethylene oxide start polymerization with heat, light, shock or by the addition of a catalyst. This reaction is exothermic and can go out of control, resulting in fire or explosion. Inhibitors are usually added to prevent the onset of spontaneous polymerization.

Polyurethane foam is made by the polymerization of an isocyanate and polyether or polyester. The reaction is exothermic. Fresh products, when piled up, may cause spontaneous heating.

Concluding Statement

Better understanding of spontaneous ignition could prevent many fires. The important factors regarding this phenomenon and a number of examples of materials known to ignite spontaneously have been presented. Readers are also asked to keep in mind that DBR/NRC can assist with investigations of materials suspected of being subject to spontaneous ignition.

References

1. Materials Subject to Spontaneous Heating, Fire Protection Handbook NFPA, Boston, Mass., Jan. 1976.
2. Kayser, E.G., and C. Boyars, Spontaneously Combustible Solids, U.S. Dept. of Commerce, National Technical Information Service, PB244046, May 1975.