

Fire & Explosion Investigation
Essay Assignment

Spontaneous Combustion of Drying Oils as a Fire Cause

Due Date:- 1/5/00
Kelly Rampling

Spontaneous Combustion of Drying Oils as a Fire Cause

Abstract:-

Spontaneous combustion occurs when the temperature of a material increases, without drawing heat from the surroundings, until the ignition temperature of that material is reached. Materials which are susceptible to this process, under the right conditions include sawdust, oily materials (including drying oils), hay, waste paper, coal and charcoal, pyrophoric metals and incompatible chemicals. Due to the nature of the drying oils employed in paint manufacture all paints and oil varnishes, which contain drying oils, are capable of self-heating to the point of ignition when they are in contact with cellulosic materials and fibres. The majority of spontaneous combustion is due to an oxidation process. Many materials can undergo an oxidation process which results in the generation of heat. However, most substances which are susceptible to oxidation will not spontaneously combust if this process is slow and any heat generated is so small that an increase in temperature of that material is unmeasurable. An example of this is the rusting of iron. Under normal temperatures, this oxidation process will not result in spontaneous combustion. There are three conditions which are important in the spontaneous ignition process. These are: (i.) rate of heat generation, (ii.) air supply and (iii.) insulation properties of the immediate surroundings. A loosely packed pile of drying oil soaked cloths may spontaneously combust whereas a tightly packed pile or a single cloth on a clothes line will not. In the case of a single cloth on a clothes line, although there is sufficient air supply to accommodate oxidation, any heat generated will be carried off quicker than it is formed. Drying oils are commonly found in paints and varnishes due to their drying effects and they are the non-saturated oils found in vegetable and animal products. Some examples include linseed oil, soya bean oil and tung oil. Saturated hydrocarbon oils such as those found in petroleum products are not susceptible to spontaneous heating at normal temperatures. Fats and oils are not likely to oxidise sufficiently fast in bulk liquid form. Ignition most commonly occurs when these oils are spread out in the form of a thin layer, such as on a rag or cloth. This is because the surface area of the oil is maximised and thus exposure to oxygen is also maximised and the reaction occurs faster.

Investigation of a spontaneous combustion fire is very difficult due to the fact that there are no significant fire residues left by this process. Thus, when flaming ignition occurs the chemical detection of residues of the preliminary material may be impossible. In the investigation of a suspected spontaneous combustion fire there are a number of diagnostic signs to look for. The major one being the presence of more fire damage to the middle of a material mass than around the edges. In spontaneous ignition the most severe fire damage will most often be in the centre of the fuel mass and in very large masses there may also be several separate pockets of smouldering which may lead to several points of origin. Other signs of spontaneous ignition include a brown discolouration of the fuel mass and an acrid odour. The brown discolouration, it has been suggested, is not just a result of charring but may be the product of reactions between amino acids and reducing sugars. The acrid odours are a result of aldehydes being present in the smoke later in the ignition process. The smoke is produced when the heat resulting from the oxidation process evaporates any moisture present from the surrounding fuel. Another indicator of whether or not a fire was caused by spontaneous combustion may be its behaviour when suppression of the fire is attempted. Initial attempts may only result in momentary suppression of the flames followed by re-ignition.

The prevention of spontaneous combustion in drying oils has until recently been a difficult process. Addition of flame retardants to drying oils may lead to changes in oil's physical properties. Some retardants may make the oil brittle, tacky or stiff, whilst others may have effects on the colouration, transparency, appearance, resistance to light or heat and its durability. As these properties are very important in the use of drying oils it is essential that flame retardants are selected in such a way as not to affect the materials to the extent that they are then unsuitable for use. These problems can be overcome by the addition of flame retardant halogenated compounds, followed by further addition of phosphorous compounds, to the drying oil formulation. Hence, the added compounds create a combustion resistant formulation which function is not adversely affected.

Introduction:-

Spontaneous combustion is defined as occurring when the temperature of certain materials increases, without drawing heat from the surroundings, until the ignition temperature of the material is reached and hence ignition occurs. The majority of spontaneous combustion occurs when the material undergoes oxidation with the air resulting in the evolution of heat. However, most substances which are susceptible to oxidation will not spontaneously combust if this process is slow and any heat generated is so small that an increase in temperature of that material is unmeasurable. An example of this is the rusting of iron. Under normal temperatures, this oxidation process will not result in spontaneous combustion.

Spontaneous combustion is commonly associated with accidental fires but it does not rule out arson. The necessary conditions for spontaneous combustion to occur may be set up by an arsonist.

There are three conditions which are important in the determination of whether an oxidation reaction will result in the dangerous heating of a material and subsequent spontaneous ignition. These conditions are:-

- Rate of heat generation
- Air supply
- Insulation properties of the immediate surroundings

The air supply is important in that there must be enough oxygen present to permit the oxidation process but not so much that any heat produced by the reaction is carried away by convection as rapidly as it is formed. Hence, a loosely packed pile of oily rags may undergo spontaneous combustion whereas a tightly packed pile or a single oily rag hung on a clothes line will not. During the oxidation process materials subject to the reaction will first form products of partial oxidation which may then act as catalysts for further oxidation. An example of this is that olive oil which has been exposed to air, and become rancid, will have a higher rate of oxidation than that of pure, fresh and previously unexposed olive oil.

Additional heat may also initiate spontaneous ignition of some combustible materials which would not be subject to this process at normal temperatures. In these cases, the increase in the temperature of the surroundings leads to an increase in the rate of oxidation so much so that the heat is being produced more rapidly than it can be lost. Examples of this are foam rubber and cotton cloths which have been heated in a dryer.

Materials which may be subject to spontaneous combustion, under the right conditions, include:-

- Sawdust
- Oily materials (including drying oils)
- Hay
- Waste paper
- Coal and charcoal
- Pyrophoric metals
- Incompatible chemicals
- Oxidising agents etc

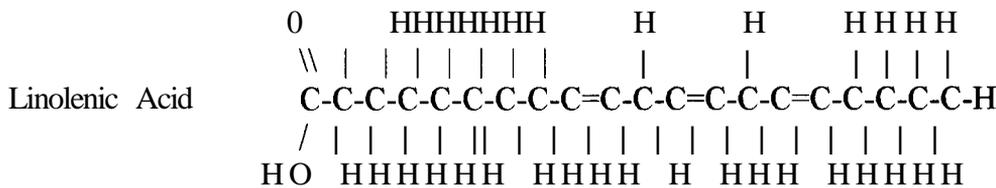
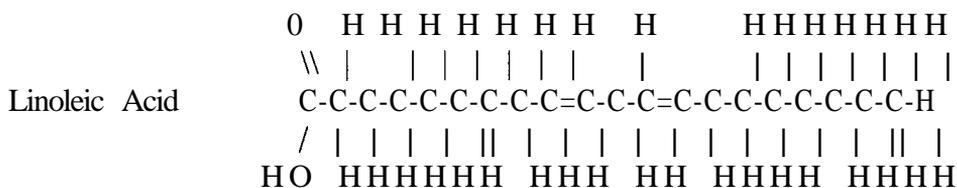
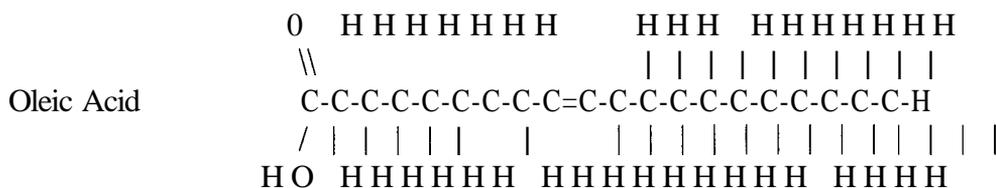
Fatty oils are a more common cause of fires caused by spontaneous combustion and can be as being either drying, semi-drying or non-drying oils. Drying oils are commonly found in paints and varnishes due to their drying effects and they are the non-saturated oils found in vegetable and animal products. Some examples include linseed oil, soya bean oil and tung oil. Saturated hydrocarbon oils such as those found in petroleum products are not susceptible to spontaneous heating at normal temperatures.

Fats and oils are not likely to oxidise sufficiently fast in bulk liquid form. Ignition most commonly occurs when these oils are spread out in the form of a thin layer, such as on a rag or cloth. This is because the surface area of the oil is maximised and thus exposure to oxygen is also maximised and the reaction occurs faster. Even in very small amounts, such as grams or ounces, these oils have been documented in laboratory experiments to result in the spontaneous ignition of their support materials. In these tests the support materials had a large surface area and were reduced to small volumes by being placed in a pile rather than being spread out.

Linseed oil is prepared by crushing the seeds of the flax plant and is primarily a mixture of the three fatty acids oleic, linoleic and linolenic acids, The linoleic and linolenic acids will rapidly auto-oxidise in air. When linseed oils is spread onto a support material and exposed to air the oil polymerises and hardens. The hardening process involves both polymerisation and oxidation and this process is directly related to the concentration of linolenic acid in the oil. This concentration may vary from batch to batch. The potential for linseed oil to self-heat is quantified by the iodine number, which increases with an increasing concentration of linolenic acid. The iodine number is a measure of the amount of iodine that is taken up in the reaction with the C=C unsaturated bonds to form C-I-C and iodide. The iodine number is related to the oils ability to absorb oxygen and thus it's drying ability. The average iodine values of some drying oils are listed below:-

. Perilla oil	194
• Linseed	188
• Tung	162
• Hempseed	153

The structure of linolenic acid shows a potentially dangerous arrangement of unsaturated bonds. In linolenic acid the double bonds are much closer together than in linoleic acid. The closeness of these unsaturated bonds makes it easier to oxidise the long chain fatty acid. This is because the heat from one oxidised bond warms up the next one and so on. The structures of the three fatty acids found in linseed oils are:-



Studies by Howitt, Zhang and Sanders on the self-heated of linseed oil confirm that it is the linoleic acid and particularly linolenic acid which undergo oxidation more rapidly at room temperature. It was discovered that it is linolenic acid which is principally responsible for the oxidation and polymerisation. The drying ability of the oil may be accelerated by boiling and separating out the denser components of the oil. In modern paints and varnishes the linseed oil is modified by the addition of chemical drying agents or catalysts. These components can accelerate the drying process by much more than just boiling. Thus, these formulations which contain modified linseed oil can polymerise and self-heat at a fast rate with an increased likeliness of ignition.

It was reported that a single rag the size of a handkerchief, which had been dampened with one of these drying agents containing modified linseed oil, can burst into flames within 6-8 hours after exposure to the air. Also the fire can continue to burn for an hour or more after ignition.

Another mechanism of spontaneous combustion is most commonly associated with commercial laundry facilities or in hospital laundries. In this mechanism, hot laundry is removed from a dryer and placed in a pile. Some time later the pile of laundry may spontaneously ignite. It has been suggested that, because clean cotton does not readily self-heat, this form of spontaneous combustion may be due to oil residues present on the fabrics. Also the lower water temperature and less aggressive detergents used in the washing process may contribute to higher concentrations of oils left in fabrics after the laundry process.

Investigation of Suspected Spontaneous Combustion Fires:-

As with all fire investigations the first step is the determination of the origin of the fire. This must always be achieved before a great deal of time and effort is taken in considering the mechanism of spontaneous ignition. Eyewitness reports, information from fire fighters and officers, as well as careful interpretation of burn patterns, charring depths, calcination and other indicators are used in the determination of the origin. Following the determination of the origin the investigation will then focus on the presence of residues.

Investigation of a spontaneous combustion fire is very difficult due to the fact that there are no significant fire residues left by this process. This is because there are no additional elements of fuel for ignition necessary other than the material itself. There is also usually a lack of unreacted material after a fire has occurred as the reacting material will be located at or near the origin of the fire. Thus, when flaming ignition occurs the chemical detection of residues of the preliminary material may be impossible. Experiments carried out by the Centre of Forensic Sciences showed that following ignition of linseed oil on cotton cloths extraction of the unburnt cloth yielded virtually no unreacted linseed oil. Thus it is impossible to chemically identify the mechanism responsible for the fire. The lack of residue is due to the temperature throughout the reacting material, over time, increasing to the point where all the reactant has become involved. Any fire which results will destroy any significant chemical residues. As there is a slight chance of detecting any unreacted materials debris samples should always be collected and placed in a sealed can or glass jar. The investigator should also search the area for similar containers or equipment, found at the origin, both in the general area of the fire and elsewhere. These containers may contain the same materials as that which caused the fire and thus should be examined. The investigator should also be aware that there may be a residue present which is not that of the unreacted starting material but of the final products of the oxidation reaction.

There are numerous diagnostic signs of spontaneous ignition the major one being the presence of more fire damage to the middle of a material mass than around the edges. This suggests that the fire began at the centre of the material, as with spontaneous combustion, and did not start externally. It is common to see that, in normal fires, the exposed outside of the fuel mass will result in more damage to these outside layers. This is caused by low heat conductivity of the fuel which is usually cellulosic, such as rags or cloths. In spontaneous ignition the most severe fire damage will most often be in the centre of the fuel mass and in very large masses there may also be several separate pockets of smouldering which may lead to several points of origin.

It should be noted that a fire found in a fuel mass which has caused more damage to the interior of the mass may be the result of a very hot ember, or similar item, dropping externally into the middle of a loosely packed mass of material. This may be the result of welding sparks, industrial processes, overheated bearings or a cigarette which may fall into a pile of material and be buried deeply in the centre of the mass. In these cases the charring induced by these objects can take hours or even days to move through to the surface of the mass, and thus be detected. Detection of the presence of these external hot materials may be achieved by careful sifting of the ashes of the fire to find any particles which are present. Of course in these fires, other diagnostic signs of spontaneous combustion will be absent,

Other signs of spontaneous ignition include a brown discolouration of the fuel mass and an acrid odour. These signs are often present in fires in haystacks, masses of cotton fabric and other similar cellulosic materials. The brown discolouration, it has been suggested, is not just a result of charring but may be the product of reactions between amino acids and reducing sugars. These reactions are called “Maillard” reactions and they produce dark brown pigments. Investigators classify these acrid odours and discolouration properties as being acidic and are mostly associated with drying oils on cotton cloth, haystack and feedstock spontaneous combustion fires.

The heat produced by the oxidation process of materials susceptible to spontaneous ignition evaporates any moisture present from the surrounding fuel. This may be seen as smoke which may be present for an hour or more before flaming ignition of the mass. Later in the ignition process the smoke may contain aldehydes, such as pentanal and hexanal, as well as acrolein and other chemicals which have distinctive acrid odours. Thus, anyone near the material will be able to detect the odours before the actual fire begins. Tests carried out by the Center of Forensic Sciences and the Ontario Fire Marshal’s Office confirmed this. They placed boiled linseed oil on cotton rags and placed them in large waste containers at a temperature of 16-18°C. Smoke and acrid odours were produced within one hour of the start of the test with flaming ignition produced 4-5 hours later. As well as the acrid odours, some lachrymatory side effects were detected, such as watering eyes. Hence, people who discover the fire and encounter watering eyes may be an indicator of a continuing chemical process.

Another indicator of whether or not a fire was caused by spontaneous combustion may be its behaviour when suppression of the fire is attempted. Initial attempts, such as application of water, carbon dioxide or solid chemical fire extinguisher to the flames, may only result in momentary suppression of the flames followed by re-ignition. This is because the reacting material is located deep within the middle of the mass. In very large masses of material attempts to suppress the flames may result in exposure of the reacting material to the air and thus a flash or flame. For these reasons it is important to interview the first fire fighters on the scene.

If spontaneous combustion is believed to be the cause of a fire it is necessary for the investigator to determine if this is possible. Firstly, it should be determined whether or not the materials involved in the fire are susceptible to spontaneous combustion. This may not only require investigation of the material itself but also the conditions present at the time of the fire. For example vegetable and animal oils are susceptible to spontaneous heating, if found on a rag or cloth, however petroleum oils are not. It should be noted that petroleum oils will spontaneously combust if in the presence of a stronger oxidiser such as chlorine. For this reason it is necessary to not only note the materials present in the fire but also other substances which may be present in and around the origin of the fire.

The configuration of the reacting mass is also important in determining whether sufficient heat could build up to the point of ignition. As discussed earlier, a tightly packed pile oil soaked cloths is unlikely to undergo spontaneous ignition whereas a loosely packed pile will. If the configuration of the material does not allow heat buildup to the point of ignition temperature of the material than spontaneous combustion is impossible. Often the determination of the configuration of the reacting material is difficult as the fire may have destroyed all of the original material, Interviewing any person or persons who may have knowledge of the area and material prior to the fire can help in these cases.

Another important factor in the determination of fire cause is the time frames involved and the size of the mass as they are interlinked with the type of material suspected in the fire. Typically, the larger the mass of reacting material the longer the time required for spontaneous ignition to occur. Pre-heated materials, such as hot laundry, involved in spontaneous combustion fires require large masses, for a large enough heat build-up, but also result in flaming ignition in short periods of time. This is because the preheating skips the material past the early stages of fire development. Materials such as drying oils, that will react in small masses, will also result in combustion in small amounts of time, particularly at high ambient temperatures.

Prevention of Spontaneous Combustion in Drying Oils:-

A study carried out by C.J. Abraham produced a solution to spontaneous combustion of linseed oil by the addition of specific flame retardants. The study found a way to dissolve flame retardants in linseed oil formulations, to prevent spontaneous combustion, without degrading the oil's properties or making it unsuitable for use as a drying agent. The addition of flame retardants to any material, particularly drying oils, may lead to changes in that material's physical properties. Some retardants may make the oil brittle, tacky or stiff, whilst others may have effects on the colouration, transparency, appearance, resistance to light or heat and its durability. As these properties are very important in the use of drying oils it is essential that flame retardants are selected in such a way as not to affect the materials to the extent that they are then unsuitable for use.

The study focused on linseed oil formulations, however, the method is applicable to other unsaturated drying oils which contain glycerides of unsaturated acids. Liquid flame retardants added to a coating which contained linseed oil made the coating become tacky whilst solid retardants which are not soluble in the formulation resulted in an opaque finish. Reactive retardants affected the drying properties of the oil and materials with poor light stability may degrade on exposure to sunlight. Thus, to prevent spontaneous combustion, flame retardants which are additive in nature and soluble in linseed oil or soluble in a low boiling point solvent which is compatible with the oil. They must form clear films which do not affect the transparency of the drying oil formulation.

These problems were overcome by the addition of flame retardant halogenated compounds, followed by further addition of phosphorous compounds, to the linseed oil formulation. The halogenated compounds make the formulation combustion resistant and the phosphorous compounds enhance the flame retardant properties of the halogenated compounds whilst preserving the physical properties of the drying oil formulation. Hence, the added compounds create a combustion resistant formulation which function is not adversely affected.

References:-

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