

Safety first for maximum benefit

A flash fire resulting in a serious injury to an employee was the catalyst for an exhaustive risk assessment programme, taking in both the hot-melt manufacturing process and the raw materials involved

Since time began, fire has been of great benefit when suitably controlled, but if uncontrolled it can cause great damage. Fire is the result of fuel and oxygen coming together in the right ratios with a source of heat. The three factors that must be present for a flash fire to take place – fuel (a flammable or combustible material), oxygen and an ignition source capable of igniting the fuel – are present in making a hot-melt adhesive.

This article will discuss the methods employed to determine how best to safely handle hot-melt raw materials and the key findings of the testing of commonly used raw materials.

Many hot-melt raw materials are hydrocarbon-based and can act as the fuel source for a fire. Under certain processing conditions during the manufacturing of hot-melt adhesives, a vapour phase can develop from any volatile component of the hydrocarbon materials. This situation can have serious consequences if the process is not properly controlled. This type of situation occurred at a National Starch & Chemical (NSC) Company hot-melt plant, resulting in a flash fire that caused one of our colleagues to be seriously injured. To prevent this type of incident from recurring, an exhaustive risk assessment of the raw materials and the manufacturing process was conducted.

The focus of the raw materials analysis was to assess the flash points, auto-ignition temperatures and the upper and lower flammability ranges of

TABLE 1 FLASH POINT VALUES FOR RAW MATERIALS

Name	MSDS Flash Point°C	Pensky-Martens Flash Point°C
EVA	N/A	155
EVA	343	155
EVA	260	155
G9	218	>288
Styrene	232	171
G5	>152	166
Rosin Ester 40°C	>93	188
Rosin Ester 105°C	>93	249
Rosin Ester 10°C	>93	204

each. When the Material Safety Data Sheets (MSDS) were reviewed, NSC learned that there was no clear answer as to why this situation occurred.

The initial focus was on the Flash Point (FP) values for the raw materials used in the formulation that was being made when the fire occurred. This is because the FP of a liquid is the minimum temperature at which it gives off sufficient vapour to form an ignitable mixture with air near the surface of the liquid or within the vessel used. FP is a critical property relative to fire and explosion hazards but it can be confused with ignition temperature. It was quickly determined that the data available was not specific enough to be helpful in understanding the root cause of the problem and providing guidance on an effective corrective action.

One reason that NSC had a difficult time assessing the risk of each raw material involved in the fire was that the conditions used to determine FP varied by supplier. For example, FP can be measured by ASTM methods

D56, D92, D93, D1310 or D3278². Two of the most common are Cleveland open cup and Pensky-Martens closed cup. As can be seen in Table 1, this can make a significant difference in the results and this was why NSC felt it could not make the necessary judgments. Data commonly available from MSDS documents not only had different methods but were also run at different temperatures.

MIXTURES

Hot-melts are mixtures of many organic compounds, and most raw materials themselves are a range of compounds. Fuel concentrations vary almost continually over the course of a batch as the constituent raw materials are added. Each raw material can have its own range of upper and lower flammability level, dependent upon pressure, temperature of the batch, and percentage of volatile components present.

An alternative method of estimating the degree of volatility was needed. Several were reviewed and Minimum Oxygen

Content (MOC, also known as Limiting Oxygen Concentration [LOC]) was selected. Below this point there is not enough oxygen to sustain combustion when fuel and an ignition source are present. The lower the MOC, the greater the risk that the raw material in vapour form can be ignited. The MOC also provides a value of oxygen content to be achieved when inerting the vessel to ensure that the conditions are outside the flammable range during manufacturing conditions³.

MOC was chosen because it addressed the requirement of providing a method to prevent combustion. It was judged to be a robust method in terms of effectiveness and reliability and took into account the fact that mixtures were involved. This test is particularly suited to predicting hazards in a closed vessel.

MOC is not a parameter that suppliers commonly list on the MSDS, as it is dependent on the processing temperature. NSC took the step of requiring all suppliers to provide the MOC for their materials at 400°F (205°C) and to also provide the FP by closed cup and vapour pressure at the same temperature. The reason for selecting these conditions was to best simulate the most severe conditions that could occur under standard processing conditions.

This article will focus on MOC and how this has provided guidance for NSC when assessing hazards of raw materials and designing process conditions to ensure the safety of our plant personnel. One of the early tests considered was an estimation of volatility by measuring weight loss using thermogravimetric analysis (TGA). A sample of a raw material with a known quantity is heated and its weight loss is measured over a fixed period of time. The greater the percentage weight loss, the more fuel is present in the vapour phase of the mixing vessel under standard processing conditions.

The results of a few of the raw

TABLE 2 THERMOGRAVIMETRIC ANALYSIS OF RAW MATERIALS

Type	TGA % Weight Loss	Flash Point°C
Oil	16	227
Terpene tackifier	17	199
Tyrene-based tackifier	9	171
APAO	<1	193

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materials tested are seen in Table 2. This illustrates the difficulty we had meeting our objectives by use of just the TGA weight loss method. The TGA results did not correlate with the FP results and in some cases would have caused us to assume we were dealing with raw materials that were less dangerous in our process conditions than they actually were. The results of the APAO and styrene-based tackifier show that a low FP can be found in a material that has a low percentage weight loss by TGA.

This is an example of the work that led us to choose MOC as the method for assessing the flammability hazard of the hot-melt raw materials used by NSC. As stated previously, MOC is the point below which there is not enough oxygen to sustain combustion when fuel and an ignition source are present. If the oxygen concentration of a combustible mixture is low enough, flames will not propagate. This is critical because there are many possible sources for ignition in a plant environment, including electrostatic discharge, open flames, metal to metal contact sparks and auto-ignition.

Auto-ignition temperature (AIT) is the lowest temperature at which spontaneous combustion can take place, using only energy generated by the heat of the mixer walls. MSDS will often – but not always – list an AIT obtained using a standard test method. The AIT in a mixer depends on the composition of the flammable vapour, the size of the mixer and the operating temperatures and the ratio of fuel to oxygen present in the atmosphere. The lower flammability limits in air are decreased by 8% when the temperature is increased by 100°C; pressure has only a slight effect of the lower flammability limits^{1,4,5}.

As stated previously, hot-melt formulations are often composed of mixtures, Le Chatelier's rule can be used to calculate the lower flammability limit of mixtures by the formula⁶.

LE CHATELIER'S FORMULA

$$LFL (mixture) = \frac{100\%}{c1/L1+c2/L2+...cn/Ln}$$

where:
c1,c2...cn =percentage of

volume of total combustibles L1,L2...Ln =lower flammability limit of each combustible.

This rule can be helpful in understanding when mixtures are flammable, even if the concentration of each component is below its lower flammability limit, but exceptions do occur and it should not be applied for chemically dissimilar components.

UNDERSTANDING MOC

By understanding the MOC for each raw material used, NSC has found the use of MOC a predictive tool to work towards the goal of preventing fires, no matter what the concentration of the combustible material and no matter what the mixture is. Table 3 shows some data on commonly used hot-melt raw materials.

- If raw materials A and E are compared, the FPs and MOC value are very different even though the softening points of the materials are the same.
- Samples A and B have very different softening points but the same MOC and a similar FP.
- Sample J has the highest FP but the lowest MOC.
- Raw materials E and F are similar in FP but different in MOC, as are samples C and D.
- The highest softening point resin, sample G has an MOC value similar to paraffinic oil, sample F.
- Raw material I has a very high FP, is a higher molecular weight than many of the others, but has a lower MOC value than the 10°C softening point rosin ester (sample E).
- Samples H and F show that the chances for problems are very similar once vapours are present for wax and oil.

TABLE 3. DATA ON COMMONLY USED HOT-MELT RAW MATERIALS

Name	Pensky-Martens Flash Point	MOC
A – 10°C soft. pt hydrocarbon	330°F	9-10%
B – 85°C soft. pt. styrene-based tackifier	340°F	9-10%
C – 40°C soft. pt. rosin tackifier	370°F	10-11%
D – APAO	380°F	21%
E – 10°C soft. pt. rosin tackifier	400°F	21%
F – Paraffinic Oil	410°F	10-13%
G – 140°C soft. pt. terpene phenolic	420°F	12-13%
H – Paraffinic Wax	450°F	11-12%
I – EVA (28/400)	525°F	18-19%
J – UV stabiliser	545°F	8-9%

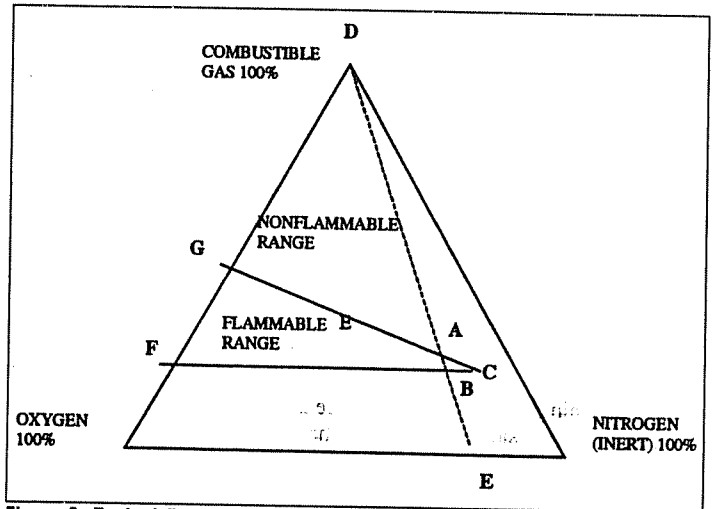


Figure 1. Typical flammability diagram

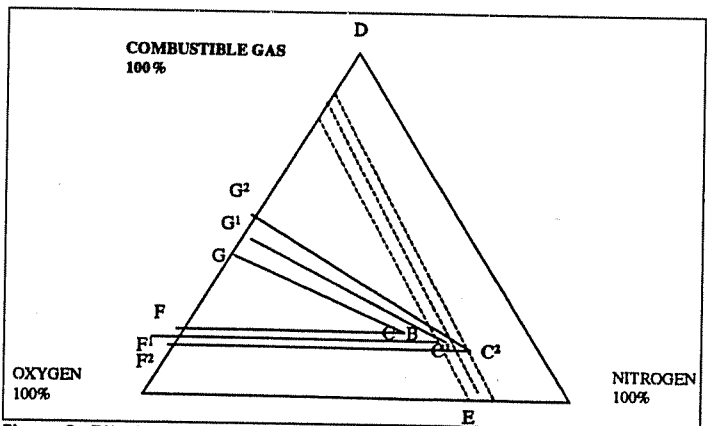


Figure 2. Effect of pressure/temperature on flammability diagram

With this information, NSC has looked at various ways to effectively control the oxygen content in the mixer to stay below the MOC. One of these is inerting the vessel.

The theory of inerting is based upon the amount of oxygen is available. Purging a mixing vessel with an inert gas such as nitrogen or carbon dioxide will not ensure that the oxygen level

is reduced enough to prevent a fire. The critical step in the process was determined to be when raw materials were to be added manually to the mixing vessel. Air is a mixture of 79% nitrogen and 21% oxygen. A mixture of air and combustible gas can be represented in a typical flammability diagram by line DABE in Figure 1³.

A given mixture of air and combustible gas is represented on this line. Point A indicates the upper flammability limit of this typical mixture. Point B represents its lower flammability limit. Any point within the line FBCAG is in the flammable range and can be ignited. Any point outside represents a mixture that can not be ignited. Point C is the MOC to prevent ignition.

As can be seen in Figure 2, pressure and temperature can have an effect on the flammability diagram. An increase in temperature or pressure results in an increase in the upper flammability limit (G2) but a decrease in the MOC to

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prevent ignition (C2). It is critical to measure the MOC at the temperature that the combustible mixture will be exposed to during mixing. The temperature at which a vapour/air mixture can ignite is both a fundamental physical property of the chemical and a function of the system variables (temperature, pressure, oxygen content, etc).

TEMPERATURE

If the temperature of a closed mixer containing a mixture of fuel and oxygen is slowly increased then slow oxidation will consume enough oxygen to render the vessel inert, but a sudden influx of air at high temperature can lead to ignition after short delay. Oxidation reactions are exothermic and when the fuel is spread in a thin layer on a hot surface (like on the wall of a mixing vessel), rapid oxidation can occur and the temperature can increase locally.

As can be seen in Figure 3, a study by TJ Snee⁷ shows an experiment with the manufacture of a glycerol ester of gum rosin. Temperature and gas concentrations were measured as a function of time during the process. The initial part of the process involved heating the raw materials to 200°C. Figure 3 shows the drop in concentration of oxygen due to a slow vapour phase oxidation. At 200°C, the percentage of oxygen is below a level that could support a flame.

When the vessel is opened to add additional raw materials, the oxygen concentration rises rapidly to 21%. When the vessel was closed, the oxygen concentration fell more steeply than at the beginning of the experiment. The concentration of fuel in the vessel's vapour phase

was measured as a percentage of the Lower Explosive Limit (LEL). It was found to be 47% LEL at 150°C and 417% at 200°C. The manual addition of some raw materials during the process is a normal step in some hot-melt manufacturing. As can be seen, if an ignition source is also present at this time, a recipe for disaster is present.

Results also reported by TJ Snee show that ignition temperatures in a 20-litre vessel could be as much as 20°C lower than the minimum ignition temperature in a 200ml vessel. In addition, ignition delays of up to 22 minutes were recorded. Snee's work also showed that complex chemical compositions, such as rosin oil, behave differently from reported values for AIT and time for ignition to occur in different size vessels.

Ignition temperatures observed under one set of conditions can change significantly under different conditions. Ignition temperatures should be viewed as guidelines and not absolute temperatures. A minimum ignition temperature in a commercial-sized mixer is likely to be lower than values determined by laboratory scale testing and the ignition delay will increase as vessel size increases.

VARIABLES

Other variables in selecting process controls depend not only on the product's chemical composition, the temperature and design (ie open or closed) of the vessel, and vented or nitrogen blanket/inerting, but also the heating method (electric band, steam, hot oil), potential hot spots in tank, dead air spots/areas for potential 'fuel' collection, and the mechanism of

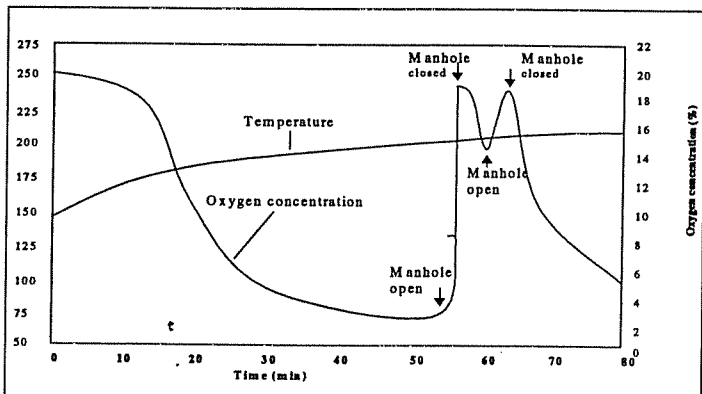


Figure 3. Changes in oxygen levels during heating of raw materials to 200°C

TABLE 4. EXAMPLES OF MOC LEVELS AT NSC PLANT

Name	Pensky-Martens MOC		Manufact. MOC
	Flash Point	MOC	
10°C soft. pt. hydrocarbon	330°F	10%	6%
85°C soft. pt. styrene-based tackifier	340°F	10%	96%
40°C soft. pt. rosin tackifier	370°F	10%	6%
APAO	380°F	21%	12%
10°C soft. pt. rosin tackifier	400°F	21%	12%
Paraffinic oil	410°F	12%	7%
140°C soft. pt. terpene phenolic	420°F	12%	7%
Paraffinic wax	450°F	11%	6%
EVA (28/400)	525°F	18%	10%
UV stabiliser	545°F	8%	5%

feeding raw materials to ensure proper grounding. Process safeguards are aimed at removing one or more conditions in the fire triangle⁸.

Pre-ignition oxidation can be seen if the oxygen concentration is monitored. A drop in oxygen and increase in carbon dioxide concentration manifest this. NSC determined that to effectively reach and maintain the MOC the process had to be monitored to ensure that the levels were maintained in the desired region. 'Flooding' a vessel opening with an inert gas when adding raw materials was not an effective way to stay below the MOC.

As a further step to ensure safeguards were in place, the MOC level that is typically being practiced in our plants is 60% of the test results. Table 4 shows examples of this based on the results from Table 3.

Hot-melt mixing conditions can pose the risk of flash fires or explosions. A risk assessment of the process has resulted in alternative techniques to reduce the chance of a flash fire. The risk assessment should include fuel sources by listing the FP, MOC and the AIT for each of the raw materials. These should be compared with the process conditions and temperatures that the interior of the mixing vessel can reach and also the temperatures of the walls of the vessel. It is suggested that a review of the temperatures necessary for adequate mixing and ventilation systems is conducted and also to ensure proper training of plant personnel is conducted on a regular basis. Possible ignition

sources should be reviewed by measuring current grounding systems and reviewing and correcting potential dust and electrical discharge sources. This type of risk assessment should be done on each individual mixing vessel. As has been shown, the size and the temperatures reached are key factors in understanding the hazards of a flash fire. It is critical that reducing one hazard does not cause another. In this case, we have added oxygen monitoring to ensure that we have a safe working environment for our employees.

This information is being shared with the industry to communicate the best practices for the safe manufacture of hot-melt adhesives, to help ensure that we are all meeting our commitment to employee safety.

MOC can be effectively used as a tool to conduct risk assessments of raw materials and to help set process parameters to ensure that at least one of the three components necessary for fire is not present during the manufacture of hot-melt adhesives.

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