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PROBABILISTIC ANALYSIS OF ACCIDENTS INVOLVING PYROPHORIC PARTICLE ACCUMULATION IN A CLOSED SYSTEM CONTAINING HIGH EXPLOSIVES

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ABSTRACT

This paper describes a probabilistic analysis of an unusual safety concern encountered during safety analysis of a closed system containing high explosive (HE). In this application, a pyrophoric material could be generated inside the system by corrosion of system components. This pyrophore may form extremely small particles that could be transported through a complex path to a high explosive component, where they could collect on exposed surfaces as a result of routine handling operations. A potentially serious accident could be initiated if the system is opened for maintenance and oxygen reaches the pyrophoric particles that are resting on the surface of the high explosive. The pyrophoric particles react vigorously in the presence of oxygen and will ignite the high explosive if there is a sufficient concentration of the particles in a localized area. This paper reports on models for estimating the probability of achieving hazardous concentrations of pyrophoric particles on the explosive surface. These probability estimates are based on occupancy likelihood and geometric models. The probability models provide a means for exploring the effects of material behavior, heat transfer, and material transport on the likelihood of achieving unwanted concentrations of pyrophoric particles on the explosive surface.

INTRODUCTION

The potential for the ignition of high explosives (HE) resulting from reactions of small, highly reactive particles on the surface of the HE is a potential safety concern for certain systems with closed internal environments. In these systems, pyrophoric particles can be generated by corrosion of susceptible materials within the assembly. These corrosion products could collect on bare HE surfaces within the system. When the system is opened for maintenance, the energetic reaction of the pyrophoric particles with the oxygen in the in-leaking air could generate sufficient energy to ignite the HE.

In the system of interest in this study, pyrophoric particles might be generated if it is assembled under conditions of high relative humidity. Under these conditions, an abnormally high amount of moisture could be trapped inside the system when it is sealed at the end of the assembly process. This can lead to the formation of pyrophoric particles from corrosion of internal components. Such pyrophoric particles normally oxidize essentially as fast as they are formed and hence do not exist in sufficient quantities to pose a hazard. However, in a closed system, the amount of free oxygen is limited, and when all the available oxygen is consumed, such particles may accumulate. Although the pyrophore generation region is spatially separated from the HE, there is a continuous path between the two volumes in the system. Thus, pyrophores in the form of extremely small particles might be transported to the HE by vibration or changes in orientation of the system as it is handled as part of normal operations. Occasionally, the system is opened for maintenance or inspection. Opening the assembly to the outside atmosphere would initiate the reaction of any pyrophoric particles that exists in the interior when air enters the system. If the particles have accumulated in sufficient quantities on the bare surfaces of the HE, ignition could result with potentially serious consequences.

The work reported in this paper is part of a larger program to evaluate the pyrophoric hazard in a specific system. The complete study included an analysis of pyrophore generation, particle transport, and heat transfer in the system formed by the reacting particles and the HE. The effort began with predictions of the potential mass and the form pyrophores might have inside the system. This analysis determined that the pyrophoric mass would be quite small but that it might exist as a large number of very small individual particles. This form of the pyrophore could easily disperse throughout the system and represents the only significant likelihood for depositing reactive particles on the HE surface. The heat transfer to the HE resulting from oxidation of aggregates of small pyrophoric particles on the HE surface was

examined. These studies defined the geometric configuration that required the minimum accumulation of small particles that could result in HE ignition.

The estimates of pyrophore mass, particle size, and minimum particle accumulation for ignition all included considerable uncertainty. Therefore, probabilistic models were developed for estimating the likelihood of achieving hazardous concentrations of pyrophores on the HE surface as a function of the material, transport, and heat-transfer properties of the hydride. These probabilistic analyses are the focus of this paper.

PYROPHORIC FORM, QUANTITY, AND TRANSPORT

A short description of some system characteristics is presented to help the reader visualize the accident sequence discussed in this paper. The actual system involved in this study is quite complex, but the simplified diagram in Fig. 1 captures the information required for the analysis reported here. The system is nominally airtight, a feature that allows pyrophoric material to exist without reacting when all of the available oxygen is consumed. Pyrophores can be generated in the "Particle Generation Region" indicated in the figure. From there, the pyrophoric material in the form of small particles could move through gaps between system components and down a narrow, complex pathway that provides access to the exposed HE surfaces identified as the HE gap in the figure. In this analysis, we assume that the system is oriented as shown in the figure when it is opened, so the particles will rest on the lower surface of the HE gap. When the system is opened for maintenance, air enters a valve shown as the "Introduction Point for Air" at the top of the diagram. This air diffuses to the HE gap, where it can react with any exposed pyrophoric particles that have deposited there.

Fig. 1. Simplified System Diagram

The generation and transport of particles within the system was analyzed by material scientists familiar with such systems. These experts estimated ranges for the amount and dimensions of pyrophoric particles that might be generated. They also evaluated the behavior of such particles in the system based on their experience in laboratory and process settings. Given the expected conditions inside the system, they believed that disc-shaped pyrophoric particles in a very specific size range could be present in considerable numbers within the system interior. Particles of this size could freely migrate around the internal volume, easily passing through even the complex path that leads to the HE surfaces. Several known mechanisms for concentrating particles were examined. Some of these, such as electrostatic attraction, inertial clumping, and thermal convection, do not appear to be important for the pyrophoric particles based on experience with similar systems. Because no mechanisms were identified for concentrating the pyrophoric particles in the HE gap, we assumed that the particles will distribute uniformly throughout the open volume inside the system in a fairly short period of time.

Using the mid-point of the predicted particle size range as a nominal size, we performed heat-transfer calculations to determine the minimum quantity and most favorable geometry for aggregates that could result in HE ignition if they react with oxygen at a specified rate. The reaction of individual pyrophores releases far too little energy to ignite the HE. Only when the particles are concentrated into aggregates of sufficient mass can they pose an ignition hazard. In Fig. 2, an idealized model of a small pyrophoric disc resting on a flat HE surface is shown to illustrate the heat-transfer model for a single particle. Based on calculations with a simplified version of this model, a minimum aggregation of about 400 pyrophoric particles of nominal size was required for HE ignition.

LIKELIHOOD MODELS FOR PYROPHORIC PARTICLE CONCENTRATIONS

Based on the above discussion, there is some potential for an HE ignition accident during maintenance on the system of interest as a result of pyrophoric particles resting on the HE surfaces. A probabilistic model was developed to estimate the likelihood of this accident for

Fig. 2. Model of Reacting Pyrophore on HE Surface

nominal particle conditions and to evaluate the dependence of this likelihood on the values of pyrophore parameters.

No concentrating mechanisms were identified inside the HE gap that would tend to attract particles to a particular region on the HE surface. However, geometric concentration and random variations in density can still lead to accumulations of pyrophores locally because of the roughness of the HE surface on the size scale of the particles and because of random variations from uniformity in the particle distribution. Given that geometric and random concentration can occur, the probabilities of achieving the minimum particle concentration that can result in an ignition spot was calculated approximately using probabilistic models.

Probability Modeling for Random Particle Concentration

The probabilistic model for concentrations of particles arising from random variation in particle distribution is based on an idealized conception of the particle behavior in the HE gap. First, it is assumed that the introduction of new pyrophores into the gap is very slow compared with the time scale of suspension and settling of the particles. It is further assumed that sufficient time has elapsed to result in a uniform distribution of the pyrophoric particles throughout the system, including the HE gap volume. If the system has been quiescent in the orientation shown in Fig. 1 for some time, it is assumed that there will be a large number of pyrophores resting on the lower horizontal HE surface in a random distribution and that any disturbance such as a jolt to the system will suspend these particles in the HE gap. It is assumed that the suspended particles will quickly settle on the lower HE surface in a random manner. If clumps or concentrations of particles occur on the HE surface during the settling process, then the pyrophores may create local ignition spots on the HE surface if they are oxidized. The probability of realizing one or more such ignition spots is approximated as an occupancy problem and may be addressed using a ball-and-cell model (von Mises, 1964). An interesting alternative approach that yields similar results is a random-clumping model (Roach, 1968).

In developing an occupancy approximation to random particle concentration, we made a number of specific assumptions. First, we assumed that the system orientation is as shown in Fig. 1 so that all particles will settle on the lower HE surface after suspension. We further assumed that all the pyrophoric particles in the HE gap are suspended as a result of each system disturbance and that each particle can settle anywhere on the lower HE surface. These assumptions are consistent with observations of similar pyrophoric powders. We also assumed that the probability density of settling is equal over the entire allowable HE surface, so any particle in the HE gap can settle anywhere on the lower HE surface with equal probability. This assumption is conservative because it increases the number of potential particles that can settle on any one surface region. In actuality, the particles will tend to settle quickly after being suspended and most will not be transported a great distance parallel to the HE surface. Thus, only those suspended particles that are immediately above a given surface region will actually be very likely to settle there. We finally assumed that there are no force fields on the HE surface that tend to attract particles as they settle.

With these assumptions, the settling problem can be viewed as the probability of random concentrations of particles in a cell, which is one of the classical occupancy problems. In our case, we are interested in the probability that m or more particles from a total of k available

particles will concentrate in any one or more of N equal areas on a surface. To use this approach, we first divided the HE surface into a grid of N equal area cells, each of which is the minimum area into which k particles must be concentrated to get HE ignition. A particle whose center of mass falls within that cell is counted as an occupant. Thus, our physical problem is approximated by random assignment of k indistinguishable items to N cells.

Although many occupancy problems are found in the literature, we were unable to find a solution to our specific problem. Thus, we will outline our derivation using the theory of arbitrarily linked events. Arbitrarily linked events can be visualized as sets of points A_i . The probability of occurrence of A_i is p_i . We define the probability of the occurrence of the intersection of sets A_i and A_j as p_{ij} . Using this notation, a general formula for the probability of the occurrence of at least one of N arbitrarily linked events, is derived from Poincaré (Roach, 1968):

$$P_N^m(\geq 1) = \sum_{r=1}^N (-1)^{r+1} S_r \quad (1)$$

In this equation, S_1 is the sum of the probabilities, p_i (in our case one occurrence of m or greater occupancy among N cells), S_2 is the sum of the probabilities p_{ij} of two occurrences of m or greater occupancy, and so on. In general, the value of S_1 is the expected number of occurrences. Higher order terms such as S_2 and S_3 are important when the overlap between events is large, but usually the higher order terms rapidly decrease in importance when the probabilities of the different events are small.

The probability of interest in this study is that of one or more occurrences of m or more particles in any cell. This probability may be calculated by counting the number of assignment vectors with 1 or more occurrences of m or greater occupancy. The occurrence of a cell with m or greater occupancy may be calculated by starting with assignment vectors of the type

$$A_i = \langle 1, 1, \dots, 1, i, j, \dots, k \rangle \quad (2)$$

where each element in the assignment vector is the cell into which one of the k particles is assigned, so this assignment vector represents the first m particles in the trial being assigned to the first cell with the next $k-m$ assigned to any cell. The probability of occurrence for this assignment vector is the number of ways it can occur divided by the total number of assignment vectors that could occur. The first m places are specified in this vector, but the next $k-m$ may occur in any way or in N^{k-m} ways. There are N^k assignment vectors total, so the probability for this vector is

$$p_1 = \frac{N^{k-m}}{N^k} \quad (3)$$

By moving the positions of the 1's around in Eq. (2), we generate $k!/m!(k-m)!$ other assignment vectors with m or greater occupancy of cell 1, and by considering all the possible $N-1$ cells besides the one labeled as "1", we generate N times as many different assignment

vectors. Thus, the sum S_1 is

$$S_1 = \frac{Nk!}{N^k m!(k-m)!} \quad (4)$$

In an analogous manner, the assignment vectors for 2, 3, or more occurrences of m or greater occupancy may be generated in general by sums for r occurrences of m or greater occupancy

$$S_r = \binom{N}{r} \frac{k!}{(m!)^r (k-rm)!} \frac{(N)^{k-rm}}{N^k} \quad (5)$$

Using these sums in Eq. (1), we get

$$P_N^m(\geq 1) = \sum_{r=1}^k (-1)^{r+1} \binom{N}{r} \frac{k!}{(m!)^r (k-rm)!} \frac{(N)^{k-rm}}{N^k} \quad (6)$$

The value of N is large for our computations because the critical area for accumulation of pyrophoric particles is very small compared with the total exposed HE surface area. The value of k is also very large because there are many particles in the HE gap. Even the value m is quite a large number because many particles must accumulate to produce HE ignition when the system is opened to the atmosphere. For relatively low ratios of k to N , meaning sparse particle density, only the term S_1 is important because the probability of getting more than one cell with high occupancy is so small. This is a generalization of the rare-event approximation commonly encountered in risk assessment.

The approach followed here has similarities to statistical mechanics calculations for Boltzmann statistics. Any significant deviations from the most probable state are exceedingly unlikely. In our case, this means that if the particle density on the surface is such that particles only cover some small fraction of the surface area, the probability of concentrating a significant number in a closely packed array or pile is vanishingly small. Only when the particle density is high enough to cover a significant fraction of the area (~ 0.3 or more) will such concentrations be at all likely.

With an expression for the probability of achieving hazardous accumulations of particles as a function of system and pyrophore parameters, we are ready to examine the effect of parameter variations on the ignition probabilities. This is important because the uncertainty in pyrophore parameters such as number and size are large. Using the experts' nominal estimates for pyrophoric mass and particle size, about 1×10^{11} particles would spread uniformly throughout the communicating volume, leading to approximately 1×10^8 particles within the HE gap. The probability of randomly concentrating enough particles into a potential ignition spot has an infinitesimally low probability of occurring under these conditions because the expected number of particles in this area is less than 1, so a tremendous concentration is required.

The pyrophore mass is quite uncertain because it is based on a substantial extrapolation of past experience. Thus, the effect of variations in mass on the probability is of interest. As the mass increases, the number of available particles increases. For masses up to 100 times the nominal case discussed above, the probabilities are still infinitesimal. If the mass is approximately 140 times the nominal case, the calculated probability of an ignition spot is about 1×10^{-6} . For further increases in mass, the probability of an ignition spot increases rapidly. A

probability of 1×10^{-3} is reached at 150 times nominal pyrophoric mass and increases rapidly thereafter with small changes in mass.

Pyrophoric particle size is also a parameter of interest, both because there is undoubtedly some distribution in particle size and because the actual range of likely sizes is somewhat uncertain. In our model, we have assumed a uniform particle size. When the size of the particles is reduced but the mass of pyrophore and the mass required for an ignition spot are held constant, the probabilities of achieving ignition spots are reduced because the particle number, k , and the ignition spot occupancy number, m , both increase as the inverse cube of the change in particle radius. As the particle radius increases, m , the number of particles required for an ignition spot, decreases, so the probability of getting the required ignition spot occupancy in one of the N cells increases. However, this will only become significant at high pyrophore masses.

The number of particles required for ignition is also a very important parameter in determining the probability of ignition. A smaller accumulation requirement for ignition translates into a smaller m in the equations for the probability, meaning that fewer particles are required in a given cell. This has a large effect on the calculated probabilities. For example, if only 10 particles are required for an ignition spot, the probability for the nominal pyrophoric mass is about 2×10^{-6} . On the other hand, increasing the number of particles required for an ignition spot rapidly reduces the probability of achieving the result for a given set of conditions.

Another effect of interest is agglomeration in which many particles come together to form larger particles. This has a great effect on the probabilities of achieving an ignition spot because the number of required particles, m , is reduced proportionally to the number of particles, k , whereas the number of sites stays the same. An agglomeration factor of 10 changes the probability for the nominal case by many orders of magnitude, but the probability of an ignition spot is still very small.

Based on this idealized model of ignition-spot probability, the relative efficacy of different effects that could increase the probability of ignition can be compared. Agglomeration is less effective in increasing probabilities than is decreasing the ignition spot particle number, m , but it is more effective than increasing mass. In general, this calculation indicates that for nominal pyrophore mass and for a fairly large ignition spot mass requirement (in the order of many 10's to 100's of particles), the probability of an ignition spot occurring after any jolt is infinitesimal. Only when there are relatively large masses of pyrophore will the probability become significant.

Probability Modeling for Geometric Particle Concentration

In addition to the purely random concentrations discussed previously, the geometry of the HE surface will have features that could tend to concentrate small particles. An example of this is a fissure in the HE surface with a wide mouth that narrows like a funnel. Such a geometry will collect particles that settle onto a wide area of the HE surface and concentrate them at the bottom of the fissure into a much smaller area. The probability of achieving such concentrations can be estimated if the number of such sites and the collecting area are estimated.

As would be expected, the probability of creating an ignition spot by geometric concentration depends on the concentrating power of the geometric features and the number of geometric features on the HE

surface. In addition, some particles may not be resuspended by successive vibrations, for example, if the geometric feature is a reentrant pit or a crack so that there is a long-term buildup of particles in a localized region. Thus, under worst-case conditions, a geometric feature could collect particles over a relatively wide area and concentrate them in a roughly spherical geometry.*

When the particles are resuspended by a jolt, they may accumulate in a depression or crack by geometric concentration, which occurs when a relatively large area funnels the particles that strike it into a smaller region. For an average particle size, a mass, M , will correspond to a number of particles, m . There will be some mass accumulation at which the pyrophores will have the potential to create a spot sufficient to ignite the HE. Thus, a model of the probability of an accumulation of particles in a given area was developed. The probability of accumulating exactly m particles in an area, A , when k particles are randomly spread over an area, S , is given by (Pipes and Harvill, 1970)

$$P_m = \left(\frac{Ak}{S}\right)^m \frac{e^{-Ak/S}}{m!} \quad (7)$$

The probability of one or more of such aggregates occurring on a given suspension may be found by making assumptions about the number of sites in the entire HE surface and using the binomial distribution with the above probability as the parameter.

First, we find the probability that any one concentrating area will have m or greater particles by finding the probability of m or more occupancy for an area. The individual events of m or $m+1$, etc. are all mutually exclusive so that no sums higher than S_1 exist in the generalization of Eq. (7) to m or more out of Q events. Thus, the probability of m_x or more particles in area A_x is

$$P_{>m_x}^x = \sum_{r=m_x}^{k/A_x} \left(\frac{A_x k}{S}\right)^r \frac{e^{-A_x k/S}}{r!} \quad (8)$$

We again use the Poincaré formula [Eq. (1)] to find the probability of one or more of the areas being at ignition spot occupancy, with the probabilities from Eq. (8) in the sums

$$P_{>1}^Q = \sum_{x=1}^Q (-1)^{x+1} P_{>m_x}^x \quad (9)$$

where Q is the number of concentrating sites on the HE surface, each with area A_x . The probabilities calculated in Eq. (8) are independent and, in general, small so that the products of the probabilities that form the terms in higher order sums are very much smaller than the probabilities themselves. Thus, the rare-event approximation, which is always conservative, can be used.

As an example, assume the nominal mass of pyrophoric particles uniformly distributed throughout the volume. If one geometric feature with a concentrating factor of 100 is assumed, the calculated probability of collecting 100 particles in this feature is about 4×10^{-8} per suspension event assuming no between-event retention in the feature. Comparing this result with a similar calculation for random variations demonstrates that geometric concentration is far more effective at

particle concentration than random variations. Thus, the probability of achieving particle concentration is highly dependent on the number and geometry of potential concentrating features on the HE surface.

CONCLUSIONS

The formation of pyrophoric "ignition spots" on the HE surface that could ignite the HE under various conditions has been explored. Experience with similar systems indicates if pyrophores do exist, very small particles may be present. The amount of pyrophoric material that will be present is believed to be small. Heat-transfer calculations indicate that an aggregation of a considerable number of small particles is required to cause ignition if an oxidation reaction occurs. This aggregation of mass requires a concentration of particles in a localized area on the HE surface.

No concentrating mechanisms other than geometric and random variation are expected on the HE surface. Approximate formulae for calculating the probability of achieving random or geometric concentrations of particles have been developed. These formulae provide a means for exploring the effect of uncertainties or variations in pyrophore mass, particle size, and the number of particles required to achieve HE ignition. Calculations of the probability of creating ignition spot concentrations by random variation with nominal parameters indicate that these mechanisms are extremely unlikely to aggregate the masses of pyrophores sufficient for HE ignition given the expected conditions within the system. Similar calculations using geometric concentrating mechanisms indicate that this mechanism has much more potential for causing hazardous buildups of particles on the HE surface. In this case, the number and geometry of collecting features determines the probability of achieving a hazardous collection of particles.

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*The presence of such features in other parts of the system would act to reduce the average volumetric particle concentration.

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