A Synopsis of Explosion Hazards During the Transfer of Powders into Flammable Solvents and Explosion Preventative Measures

by Martin Glor

Introduction

Explosion prevention must be a primary objective of employers wherever the process of transferring powders into flammable solvents is utilized, regardless of the industry and existing practices. In Europe, the ATEX directives and Directive 1999/92/EC provide guidance for manufacturers of equipment and manufacturers of good sound explosion prevention and protection. In the US, this topic is addressed within the NFPA standards 69 and 77.

The addition of powders such as catalysts, pigments, and other reactants into a reactor, hopper or large container is a common operation within the process industry. Frequently, the vessel into which the powder is being added will already be charged with flammable solvents. These solvents can create an explosion environment both within the vessel and in the surrounding atmosphere. This potential hazard is dependent on the flashpoint of the solvent, the temperature of the solvent and the ambient temperature of the surrounding atmosphere.

Equally significant is the nature of the powder and the act of transferring it. The combustibility of the powder, combined with the characteristics of the powder in addition to the transfer process, increases the potential for formation of an explosive dust/air mixture both in the container and in the immediate surroundings. The amalgamation of flammable solvent vapors and explosive dust/air mixtures can form a volatile hybrid mixture.

The presence of such types of explosive atmospheres corroborates the fact that this type of operation is clearly one of the most hazardous within the process industry if exclusion of effective ignition sources is the only basis of safety. If all those effective ignition sources generally considered common and insignificant, including those ignition sources related to electrical equipment, mechanical load, open flames, cutting, welding and smoking etc., have been excluded through the introduction of precautionary measures, the hazard of electrostatic ignition inherent in the powder transfer remains a viable possibility for causing an explosion.

Considering the facts above, the probability of an explosion occurring during the transfer process is high because the probability of a coincidence in space and time of an explosive atmosphere and the activation of an effective ignition source, such as static electricity, is high. Furthermore, the severity of such an explosion could be disastrous, especially when taken into consideration the number of operators that would be directly exposed to the initial blast wave and
subsequent fireball. Serious if not life threatening burns are likely, especially in the presence of a dust cloud or hybrid mixture explosion.

Therefore, it is an employer’s responsibility to ensure the appropriate organizational, operational, and technical preventative measures are in place. Organizational, at a minimum, this can be addressed by assigning hazardous areas and issuing fire permits, combined with the adequate training of operators. Operational and technical measures are addressed through standardized, documented, and approved operating instructions, earthing, dissipative shoes, an adequate and appropriate repair and maintenance program, in addition to appropriate ventilation, temperature control, nitrogen blanketing, and in the case of an emergency, adequate and appropriate explosion suppression systems.

Procedures relating to the process and the materials of use are implemented utilizing the following basic principles given in the relevant standards and codes of practice:

- Prevent the formation of explosive atmospheres.
- Where prevention due to the nature of the process and materials is precluded, then:
  - Ignition sources must be avoided.
  - Mitigation of the detrimental effects of an explosion must be a priority to ensure the health and safety of operators.

According to the author’s experience, most pharmaceutical companies are well aware of the explosion hazards and make appropriate efforts to minimize the explosion risk (explosion probability as well as explosion severity). However, experience also shows that management of changes is not always dealt with in a prospective way in the field of explosion prevention. The cumulative effect of small single changes of the process, operation, or product may lead to a substantial increase of the explosion hazard. In addition, increasing turnover of personnel may lead to a lack of knowledge, which can only be compensated with increased training.

Even with the characteristics of explosions well known and comprehensively investigated in the past, explosion issues have not gone away, even with modern techniques. This was recently demonstrated by the sugar dust explosion on 8 February 2008 in Georgia, USA.\(^5\)

**Formation of Explosive Atmospheres: The Probability and Causes of Explosions**

Determining the risk of an explosion is important in assessing how a process should be carried out and if adequate safety measures are in place. Explosion risk is defined as the product of the explosion severity multiplied by the explosion probability. The explosion severity has to be classified high since fatalities can hardly be ruled out in manual transfer operations. In order to assess the explosion probability associated with charging powder into a reactor already containing flammable solvents, the following two main criteria need to be established:

1. the ignition sensitivity of the atmosphere which is categorized by the Minimum Ignition Energy (MIE)
2. the probability of an explosion occurring at different locations

Once these criteria have been established, the hazard of a specific ignition source, e.g., static electricity creating an explosion also can be determined.

For most commonly used solvents, the relationship between their vapor pressure curve, explosive range of their vapor, and their flashpoints are well recognized - Figure 1. The majority of universal solvents, including white spirit, toluene, acetone, ethyl acetate, ethanol, methanol, isopropanol etc., have flashpoints below room temperature. Explosive range of solvents tends also to increase with increasing temperature.

Explosive dust clouds formed during the transfer of powders can be located within the reactor or at the point of entry into the reactor, i.e., the manhole and its surrounding area. Particle size and distribution, moisture content, concentration, and explosibility of the powder in its tumultuous state when being charged to the reactor, make up the powder characteristics which can then be expressed in terms of the Lower Explosion Limit (LEL), Minimum Ignition Energy (MIE), and Minimum Ignition Temperature (MIT), etc.

When a dust cloud mixes with flammable solvent vapors, either within the reactor or at the manhole, a hybrid mixture is formed. The explosion hazards of hybrid mixtures have been extensively reported; however, the most relevant points regarding their characteristics are listed below:\(^6\)

![Figure 2. Vapor pressure curve for different solvents at concentrations below the lower explosion limit.](image-url)
• A solvent’s MIE is generally much lower than that of a pure powder. Therefore, when a hybrid mixture is formed, its MIE will be somewhere between the two and tends to veer toward the lower range, even if the flashpoint of the solvent is above ambient temperature.
• Regardless of whether the concentrations of the dust cloud and solvent vapor are below their own LELs, a hybrid mixture is an entirely separate entity that may well be within the explosion range.

There are exceptions regarding the explosive properties of a hybrid mixture, specifically the MIE. If the vapor concentration is below 20% of the LEL of the solvent, the MIE of the pure powder would then be representative of the explosion hazard for the hybrid mixture. The vapor pressure, temperature, LEL, and flashpoint of solvents are used in conjunction with each other to determine the probability of a hybrid mixture forming under specific environmental conditions. The “30 to 40 K” rule applies to this calculation, i.e., the vapor pressure reaches a concentration of 20% of the LEL at temperatures 30 to 40 K below the flashpoint of most commonly used solvents - Figure 2.

Vapor atmospheres also can be created by charging powder where solvents or solvent residue and therefore vapors are not already present in the reactor, as the powder itself may contain solvent residue capable of creating a vapor atmosphere. If solvent residue in a powder is present at less than 0.5% (by weight), the probability of a hybrid mixture being formed can be negated as a rule, the exception being when the powder is ground up allowing the desorption of vapors creating a vapor atmosphere.

In the case of toluene or methanol, which are solvents with flashpoints only slightly below ambient temperature, the entire gas phase within the reactor, i.e., from the liquid surface to the point of entry (manhole), can be filled with an explosive atmosphere. In their gas phase, solvents are at their most ignition sensitive concentration; this is especially the case for toluene.

Conversely, if a solvent has a low flashpoint (high vapor pressure at room temperature), the environment within the reactor will tend to be saturated. In this instance, the most explosive range will occur around the manhole. However, if large amounts of powder are conveyed into a reactor containing a solvent with a low flashpoint, the entrainment of air associated with the operation also may cause the atmosphere within the reactor to become explosive.

### Potential Process Induced Ignition Sources

#### Static Electricity

The occurrence of static electrical discharges at different locations and during distinct phases of the process of powder transfer are dependent on the methods used for transferring the powder into the reactor. Electrostatic ignition associated with packaging, equipment, and operators can in theory be removed with the use of conductive materials, reliable earthing, and other such measures. Discharges associated with the products remain. Substantial changes to the product properties would be required in order to remove the electrostatic ignition sources within specific products. Details regarding the incendiary properties of the electrostatic discharges related to gases, vapors, dusts, and hybrid mixtures are given in the literature.

Typical potential discharges when transferring powders are listed below:

- spark from any conductive, but not earthed bag, bin, drum, container, etc.
- brush discharges from any non-conductive bag, bin, drum, container, etc.
- spark discharges from any conductive, but not earthed auxiliary device used in the transfer procedure, e.g., shovel, funnel, chute, pipe, etc.
- spark discharges from the operator if he is not reliably earthed
- brush discharges from any non-conductive auxiliary devices, e.g., shovel, funnel, chute, pipe, etc.
- brush discharge from the dust cloud formed within the reactor during transfer of the powder

- spark discharges from any conductive, but not earthed fixtures and fittings within the reactor
- brush discharges from the charged solvent, suspension, or emulsion preloaded in the reactor
- brush discharges from the powder heap formed on top of the liquid phase within the reactor
- cone discharges from the powder heap formed on top of the liquid phase

#### Mechanical Sparks and Hot Surfaces

During the transfer of powders into a liquid, an agitator is normally running in the reactor. The rotating mechanical seal on the agitators shaft is a potential ignition source that cannot be ruled out because the hot surfaces potentially present on the shaft can induce a reaction. Additionally, mechanical faults of the agitator, such as mechanical sparks caused by the operation of the agitator, are also potential ignition sources.

The addition of the powder prior to the solvent, in an effort to reduce risk, is commonly not possible due to the formation of lumps and problems with the homogeneity of the mixture.

### Practices, Techniques, and Equipment: Avoidance of the Creation of Explosive Atmospheres

If an explosion occurs, it is likely to cause significant damage to equipment and the infrastructure of the plant. More importantly, jeopardizing personnel and exposing them to possible injury or even death is unacceptable. Therefore, it is clear that operations where the transfer of powder into reactors containing flammable solvents or even where very sensitive powders with MIE’s below a few Millijoules are being transferred into solvent free vessels, the transfer should not be carried out using open methods.

As previous sections have outlined, it is nigh on impossible to prevent the formation of explosive atmospheres. Additionally, the exclusion of effective ignition sources from a process is not simple and can in no way be a guaranteed measure against explosion risks.
is necessary for employers to utilize every possible precaution to prevent explosions from happening and protect both their personnel and their plant.

In order to attain the required level of safety for such transfer operations, powders must be conveyed under inert conditions, especially when the recipient vessel is preloaded with flammable solvents. Inert conditions exist where the oxygen content of the reactor is at a level below the Limiting Oxygen Concentration (LOC), where explosions are no longer possible.6

Reducing the oxygen content of a vessel is achieved with the addition of carbon dioxide, nitrogen, or any other inert gas.11 However, as illustrated in Figure 3, the opening of any access port and the addition of the powder itself will cause the previously inerted reactor atmosphere to be lost. The opening of the manhole allows the inert atmosphere within the reactor to diffuse into the surrounding environment, thus increasing the level of oxygen. The addition of powder also increases the oxygen level within the reactor due to the entrains of oxygen within the powder resulting from the turbulence created by the powder swirling around in the oxygen rich atmosphere outside and at the manhole of the reactor. The LOC within the reactor is compromised and the hazard of explosion is again present. Modern technology provides the solution to these problems; using any type of lock to transfer the powder into an inerted or reduced oxygen containing reactor is a method of choice.

Figure 4 illustrates some of the more common lock systems available today demonstrating the different methods of powder transfer into a reactor. Table A compares some of the existing lock systems against criteria for prevention of an explosive atmosphere. Notably, oxygen enrichment within the reactor is a fundamental problem associated with all the lock systems, with the exception of the PTS system, as more powder is transferred into the reactor. Oxygen enrichment is increasingly highlighted when low bulk density products (apparent density as opposed to skeletal density) and/or large volumes of powders are being transferred. Figure 5 illustrates the effect of oxygen enrichment in the reactor due to the oxygen entrained within the powder.

Explosion Protection and Containment: The Practicalities Examined

Consideration of the safety aspects
associated with the transfer of powders into flammable atmospheres must incorporate measures taking into account the toxicity and the reactivity of the powder being transferred. This is especially true within the pharmaceutical industry. These factors, in addition to the evermore stringent quality control and production standards, make containment inevitable and also should make manual handling obsolete.

The addition of powders into reactors through open manholes is still practiced in the process industry. The introduction of alternatives to this method (Figure 6) tend to be more focused on the containment aspect and do not incorporate the added need for improving the safety of the process with regard to explosion hazards.

Most contemporary methods for contained transfer of powders use gravity as the impetus to charge the powder into a reactor. This requires multi-story facilities to be built. The powder is delivered to a higher floor and falls through a chute directly into the production equipment. The problem of containment around the loading zone is addressed by incorporating a laminar flow booth, for example, into the area and a drum lifting system within it to eliminate manual handling. In these instances, operators must still wear personal protective equipment, including full body suits, masks, and depending on the toxicity of the powder, external respiratory apparatus.

Alternatively, containers may be equipped with automatic connecting valves (active and/or passive) or Flexible Intermediate Bulk Containers (FIBC – Figure 7) fitted with docking devices that enable a receiver to be connected or disconnected...
in an *almost* airtight manner. These systems enable large quantities of powder to be transferred, in excess of 100 kg, and reduce the requirement for manual handling. This method also would be suitable for processes where intermediate products are used in a process that requires storage or isolation between phases.

A product with high toxicity will require more containment. Glove boxes offer one of the only solutions and protect the operator, product, and environment - Figure 8. However, the cost of this solution can often be prohibitive in that most glove boxes are rigidly designed for a specific use, require a large dedicated area within the plant and are not ergonomically designed, causing operators’ discomfort.

The chutes used for charging the powder into the reactors can get clogged and bridging may occur, especially if the powder has poor flow characteristics or high moisture content. Cleaning and validation is an inherent problem and increases proportionately with the length of the chute.

Gravity charging as a process itself can be a safety issue. The process cannot be rendered completely inert and the problems associated with increasing the oxygen concentration within the reactor is, as previously discussed, a significant issue. The use of inert gases to reduce the oxygen content introduced to the reactor via the powder is costly as large volumes of such gases, i.e., Nitrogen is required with this system. To counterbalance these inadequacies, solutions are required, convoluted instrumentation may need to be incorporated to monitor oxygen levels, etc. These in turn increase the cost, affect the reliability of the process by requiring calibration, maintenance, and other repairs that necessitate down time. Or the system itself may have to be modified, e.g., charging the powder into an empty reactor; this may address most of the safety issues, but the efficiency of the process will be compromised. The following points listed below illustrate the detrimental effects of charging powder into a reactor in the absence of solvents:

- production of static electricity as powder is introduced under dry conditions
- damage to the reactor lining due to abrasion or corrosion
- damage of agitator seal or the agitator itself by the large amounts of solids at the bottom of the reactor
- increased mixing cycle and problematic product homogenization due to the formation of agglomerates

ATEX standards determine the delineation of zones within a process environment. The choice of equipment, its configuration, and the methodology employed within a plant can directly impact the determination of zones. Therefore, certain zones may be downgraded, for example, where the plant would then benefit from operational advantages and associated economic benefits.

Common to the majority of powder handling systems is the lack of a physical barrier between the reactor and other production equipment, thus rendering them neither pressure nor explosion proof. The operating pressure of the recipient vessel, temperature, and presence of flammable atmosphere are serious hazard risks, especially when charging powder and even more so when powder is charged in an open way by gravity. The powder loading area must be classified as a hazardous area where explosive dust and/or solvent vapor atmospheres may be formed.
Economic constraints within the process industry create a diversity of challenges. From the conception and implementation of a flexible production unit which complies with current quality control and safety legislation, also capable of adapting to changing demands in the marketplace and future changes in policies, to maintaining the lowest possible overheads. Existing process systems which may need updating to comply with legislation and increase productivity face even tougher fiscal dilemmas as the nature of such systems do not lend themselves to modification and often entirely new systems are required.

Having established that gravity charging systems are fundamentally unsafe, manufacturers face the predicament of a loss of productivity versus significant costs associated with addressing the inherent operative hazards. The solution for manufacturers is to use a system capable of isolating process equipment during the filling stage and transfers powder in a contained way.

The patented Powder Transfer System (PTS) - Figure 9, is a technology which provides a total solution to the problems faced by manufacturers including safety, containment, and productivity. The concept of the PTS is to actively convey a powder of any characteristic without using gravity, effectively in the same way liquids can be handled. Vacuum and pressure are combined to allow the transfer of powder from any receptacle (container, drum, big bag, silo, process equipment, etc.) over long distances (horizontally and vertically). The problems of designing new plants or processes are solved.

The simple, yet effective operation of the PTS works as the product is sucked into the main body/chamber by vacuum. A filtration membrane fitted inside the PTS at the top of the chamber acts to ensure no powder escapes or enters the vacuum line. Once the chamber is full, the vacuum remains on to eliminate excess oxygen that has been entrained in the powder during its transfer and then the cycle is reversed. The powder is discharged into the recipient vessel under pressure by using compressed gas (i.e., nitrogen), the compressed gas also is used to clean the internal membrane and prevents it from clogging up before the whole operation is repeated.

The PTS installed directly onto the reactor (or other process equipment) is designed to operate under pressure and when in use, isolates the two systems from each other. The technology not only acts to reduce the oxygen content of the powder before it is discharged into the reactor, but also keeps the atmosphere within the reactor inert while powder is being charged into it by using nitrogen or other inert gas to pressurize and empty the PTS chamber. This equipment allows powder to be safely charged in to a reactor, even one that contains solvents or operates under pressure without the hazard of explosions or gas leaks.

Conclusions

Historically, operations where powders are transferred into reactors have resulted most conspicuously in fires and explosions. This risk is increased significantly where flammable solvents are present within the process. A large proportion of such operations are still carried out manually, thus exposing personnel to safety hazards. Either in the presence or absence of flammable gases or vapors, the MIE of the powder and the method of transfer affect the probability of occurrence of an explosion. In order to assure the safety of these processes, the transfer of powders should be carried out:

- in closed systems
- utilizing every precaution during and after the transfer to maintain the lowest possible oxygen concentration within the reactor
- separated by a physical barrier

Most gravity based transfer systems offer overall poor levels of safety and explosion hazards are further compounded by the nature of the material being transferred and the process conditions. An operation that is considered safe under one set of parameters can be de-stabilized by changing one small aspect of the system. Systems which do not use gravity, like the PTS system, provide the features listed below:

- eliminate oxygen from the powder
- have a physical barrier between the powder and the reactor during loading
- provide a safe solution for powder transfer regardless of the characteristics of the powder and the process parameters

The importance of process optimization in conjunction with ever changing safety and quality criteria means that in order
for manufacturers to effectively function in a competitive marketplace, the process technology they choose must be flexible and guarantee full safety of their personnel, product, and equipment regardless of the process parameters and powder characteristics.

References

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