# SOLVENTS IN POWDER

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The presence of solvents in powders and dusts can lead to a variety of hazards. The combined presence of flammable vapours and dispersed dusts can result in hybrid atmospheres[1]. Additional problems for solids containing solvents are, that burning properties may become enhanced, and the material could exhibit a flash point below 60.5°C, both of which could affect transport classification.

For flammable gases it is relatively straightforward to assess the vapour phase contribution to a hybrid atmosphere. For flammable solvents, however, this is less obvious since the fuel availability, predicted by vapour pressure, is a function of temperature and interactions with the solid.

The literature contains some guidance as to 'safe' solvent levels within a powder, yet, these suggested levels are not consistent with one another, nor do some of them explain the basis upon which they have been set. Some rules are weight based, ranging from 0.2 to 1.0% wt[2–6] solvent on powder. Other criteria are based on the Lower Flammable Limit (LFL) of the vapour, ranging from 10% or less is acceptable, to above 20–50% can be problematic[3,7,8]. Other approaches require case-by-case assessment.

The criteria based on solvent weight are easiest to apply, however, appear to be rules of thumb, which may be generally acceptable, but are only applicable under certain conditions and durations. The LFL based criteria are harder to apply, but will tend to give more general and conservative answers. This paper will discuss the problem of providing acceptable guidelines on 'safe' levels of solvent in powders. Some robust, and necessarily conservative, LFL based criteria will also be presented. These use flash points to simplify their application.

## BACKGROUND

Powder handling involving the charging, discharging and transport of containers and vessels is common within the chemical and associated industries, with many raw materials, products and intermediates coming in solid form. After operations such as isolation (filtration/crystallisation), washing and drying, residual solvent may still be held up in the powder.

That the presence of a flammable vapour with a dispersed dust can lead to hybrid atmospheres is well established[1]. Compared to pure dust in air, hybrid atmospheres can demonstrate increased sensitivity to ignition, increased explosion violence and increased flammable range, over the pure components[8–10]. Pure dust or solvent systems are easier to quantify in terms of relevant safety measurements, and necessary hazard precautions. It has become apparent that the guidance for dealing with solvents in powders varies throughout the industry, and is applied from a variety of sources

varying with company, geography, professional bodies and competent authorities. The guidance used has different emphasis, which can lead to different interpretation.

The concern is that with the rise of trans-global operations, more intermediates are being moved between sites that are spread around the globe. This leads to the question of whether we have been fortuitously safe in the past because much of the industry has been located in benign climates in northern latitudes.


## DISCUSSION OF CRITERIA APPLIED

The various criteria we have come across in our work and research into the issue are:

1. 1% and below can be consider not solvent wet[6].
2. 0.5% wt is acceptable[3], will not affect venting[4] and is acceptable if not stored for a prolonged period[5].
3. 0.2% wt and above are solvent wet and should considered for flammable/combustible liquid provisions[2].
4. 10% of LFL in vapour space is no additional hazard over pure dust[7]. 20 and 50% LFL do not necessarily affect the Minimum Ignition Energy (MIE) sufficient to change hazard precautions that should be applied.
5. Not acceptable — it must be assessed on a case-by-case basis and the safety case proved vs the possible hazards to be encountered. Measure vapour pressure if necessary.
6. Not safe — avoid if possible. In preference water wash or isolate. Measure MIEs and other parameters with representative samples.

The problems with the above criteria are:

- Consistency. A quick inspection reveals that they are not consistent
- Loss of provisos. When used by humans the limitations and restrictions tend to be dropped. The weight-based criteria may be normally acceptable under a limited set of conditions. For example, Jaeger and Siwek[5] suggest that up to 0.5% is acceptable provided that material will not undergo size reduction, nor will it be stored not for a long period.
- Undefined time period in provisos. Unacceptable storage duration is defined as a long period[5] without any indications of scale, whether long is minutes, hours, days or weeks, all of which can be normal storage durations depending on the product.
- Misapplication: The authors have seen examples where the 0.5% criteria has been applied separately to more than 1 solvent.
- Material seen for laboratory testing historically has had solvent levels far below 0.2–1%, although the material specification may nominally allow these levels. Any statistically significant deviation from normal levels due to mal-operation might be dangerous, yet still within specification limits, and hence no action would be taken.
- Rules based on weight are easy to apply, but lead to the problem of not thinking about the operation, and assessing the hazard present. People can be lulled into a false sense

of security because they have applied a rule[11]. Rules of thumb in design work are acceptable for setting the expected magnitude of an answer, but safety work rules must catch all hazardous situations, being very conservative for general and non-expert users. Expert assessment can always provide some leeway.

● Indications are that some of the rules may be risk assessment based, but without the basis of the original assessment, and with the push to bigger pack sizes, new packaging material and operations in warmer climates, the chances that the assessments have been violated are high.

## SAFETY ISSUES ASSOCIATED WITH SOLVENTS IN POWDER

Safety issues can be associated with the dispersed dust, or the bulk powder. For the dust dispersed in air a hybrid atmosphere may be formed. Hybrid atmospheres exhibit lower MIE values compared to the pure dust, decreasing as more vapour is added (see Figure 1). The flammable range can increase (even to concentrations where neither component is flammable on its own), the violence of the dust explosion can be increased ($K_{ST}$) with increases in both $P_{max}$ and $dP/dt$[8−10]. The optimum dust concentration may also be reduced. It has even been suggested that such effects are synergistic and not just
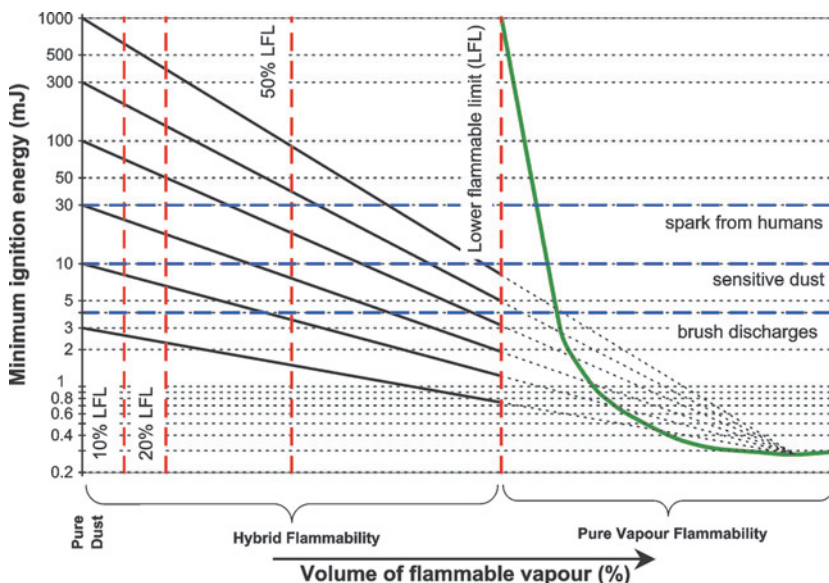


**Figure 1.** Variation of hybrid minimum ignition energy with vapour concentration. Sloping lines show decrease in MIE with increased volume of flammable vapour. Lines have been generated using methodology of britton[8,12]

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additive[13]. The Limiting oxygen concentration (LOC) may be reduced to that of the component with the lower value. Other issues are that the powder may exhibit a flash point, and that the burning properties of the bulk may be enhanced.

## EXPERIMENTAL EVIDENCE

Within our laboratories experiments have been conducted with 2 powders and 3 different solvents (with sub-ambient flash points). Powder was added to jars with a very large ullage, such that the powder occupied approximately 10% of the jar. 0.5% wt solvent (was added to the powder and it was left mixing over night to equilibrate. All of the jars exhibited a flash when a flame was introduced.

Some of the same powder was also tested for MIE with the solvent present, and was found to have reduced MIE compared to the pure dust.

These two tests prove that the 0.5% criteria at least is not universally safe.

## THEORETICAL ANALYSIS

Britton[7] has suggested that 10% of the LFL is taken as the criterion to ignore the presence of vapour. Certainly at 20% of LFL the effect of vapour can been seen on the explosion violence[8], which is consistent with results from our own laboratory. Sometimes this criterion is interpreted as 0.2% vapour in air[14], which is consistent with hydrocarbons having an LFL of approximately 1%. This criterion would appear to be reasonable, but not straightforward to apply since it requires vapour pressures.

Figure 1 shows the impact on the dust ignition sensitivity. This chart is generated using the method outlined by Britton[2,12] for generating lines of hybrid MIE. Britton's method is based on work published by Bartknecht[8]. Another equation for the lines of hybrid MIE based on the same data has also been published[15]. Such a chart can be used with various flammable vapours to examine the ignition hazard. These flammable vapours can originate from added gases, solvents or decomposition products, although most research on hybrid atmospheres has been with added 'pure' gases.

Analysing Figure 1 shows that at 50% of LFL only dusts that are already classified as sensitive might become susceptible to ignition by to brush discharges. 50% of the LFL could also make a dust with an MIE of 100 mJ sensitive to ignition by the discharge from a human. 20% of the LFL does not change the MIE sufficiently to change precautions that should be taken. Of course sufficient safety factor should be taken to allow for the uncertainty in vapour fuel content.

This approach though good still lacks ease of application, since for flammable solvents fuel availability, predicted by vapour pressure, is a function of temperature and interactions with the solid.

## IS THERE A SAFE WEIGHT LIMIT?

It is interesting to ask whether a weight fraction criterion can be generated which is universally safe. Calculations have been made to see how much fuel is required in the vapour
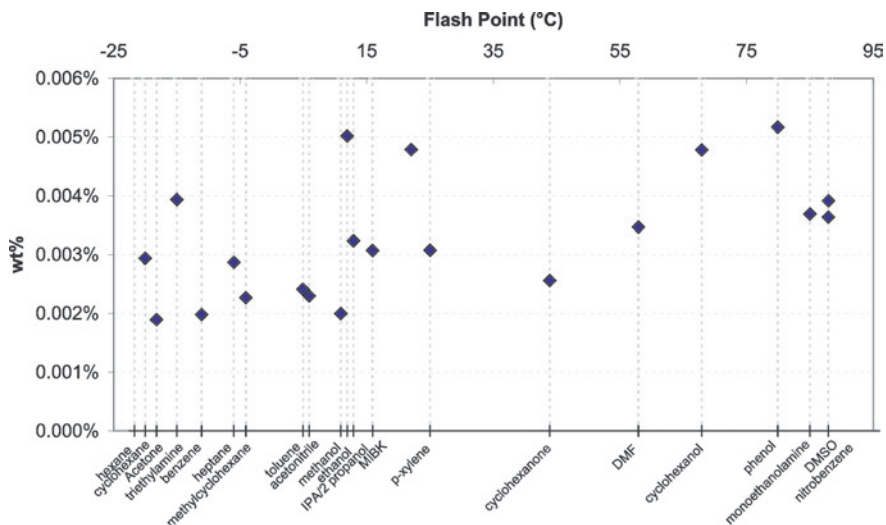
**Figure 2.** Amount of solvent required to provide sufficient fuel for flammable atmosphere (in a drum). Amount is plotted as weight fraction on the total solid. Assumes 50% of drum filled with solid is voidage

phase to form a flammable atmosphere in a drum. These values have been plotted for a variety of solvents (Figure 2), as the weight fraction on solid. The calculations assumed perfect gas behaviour, a total drum voidage of 50% and bulk density for the powder of $500 \, kg/m^3$. The figures calculated are 2 orders of magnitude below the 0.5% rule. This is obviously not an acceptable rule.

## CONSIDERATION OF VAPOUR PRESSURE REDUCTION

The vapour pressure of a solvent on a solid will not necessarily be the full pure liquid vapour pressure. There are various mechanisms that can affect the solvent activity.

1. Capillary effects. Solvent held in the pores of a solid or between particles can form hydrogen bonds with the surface and form a convex meniscus, which can lead to the capillary climbing effect. The bonding also reduces the effective vapour pressure. To predict the magnitude of this effect it is necessary to know the wall contact angles, which are material specific, and the pore sizes. This could be particularly difficult in the case of a formulated product.
2. Adsorption. This is a surface area, and surface chemistry effect. Carbon is a material for which this effect is deliberately utilised, not all materials are so effective. Isotherms could be measured to indicate what the capacity for adsorption is and how

it varies with temperature. However, there is no general *a priori* prediction of such effects. Desorption is a time and temperature related effect.

3. Solvation. In some cases the solvent will be chemically linked to the solid material, however, for the purposes of assessment the quantity of solvated material should be well understood. The material can revert to other crystal forms with time and temperature variation, which can result in the release of solvent.

Although the mechanisms explain how the vapour pressure may be reduced compared to that of the pure solvent, they do not allow us to generalise about what the reduction will be. Measurement is the only reliable method.

## OTHER CONSIDERATIONS

The odour threshold for solvents is usually at levels far below the flammable range. Toxicity and hygiene issues also generally occur below this level.

As well as temperature and time in storage leading to solvent release, size reduction operations can also lead to solvent release.

Powders can be notoriously difficult to get representative samples, and this can make reliable determination of actual solvent content very hard.
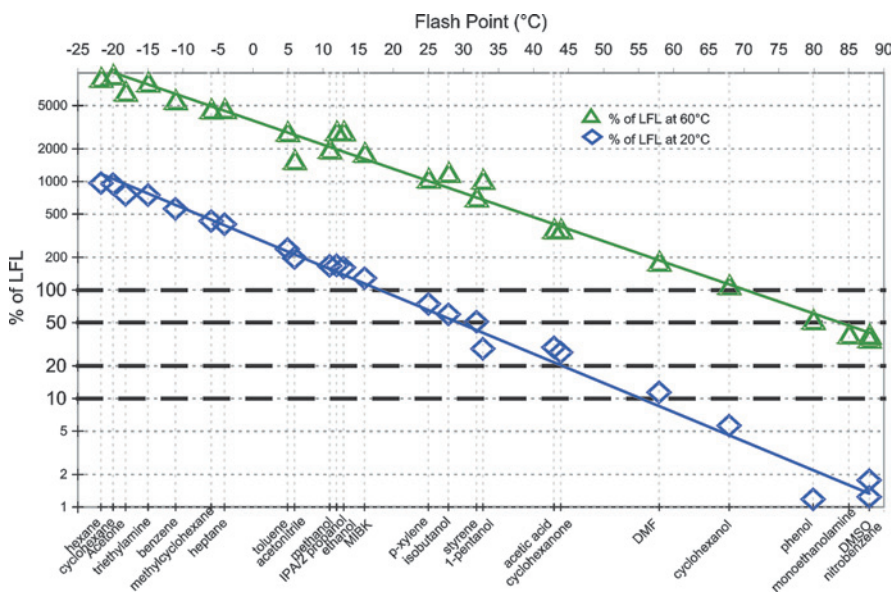


**Figure 3.** Flash point temperature vs the percentage of the lower flammable limit achieved by the equilibrium vapour concentration for a variety of solvents at 20 & 60°C

## GENERATION OF NEW WORKING CRITERIA AND GUIDELINES

Figure 3 shows the results of equilibrium vapour pressure calculations for various solvents at temperatures of 20°C (nominal ambient) and 60°C (transport classification temperature) plotted as fractions of their respective LFLs. Vapour pressures were calculated using Antoine correlation data from SMSwin[16]. This chart shows how high the solvent flash point must be to eliminate the possibility of hybrid atmosphere formation, if no interactions with the solid can be assumed.

The calculations can be looked at again from a different perspective (see Figure 4). This figure plots the vapour pressure as a fraction of LFL again, but at flash point temperature minus a safety factor. The more usual safety factors of 5 K and 10 K, are shown, but also shown are 20, 30 and 40 K below the flash point. Flash point minus 10 K can be seen to be approximately 50–60% of LFL. Flash point minus 40 K and flash point minus 30 K are seen to reasonably correspond to 10 and 20% of LFL respectively. Since flash point data is more readily available than vapour pressure data (with sources such as NFPA[17]), this enables us to develop easily applicable and robust guidelines for analysing hybrid atmospheres using the LFL criteria suggested by Britton[8] but without vapour pressure data or correlations.
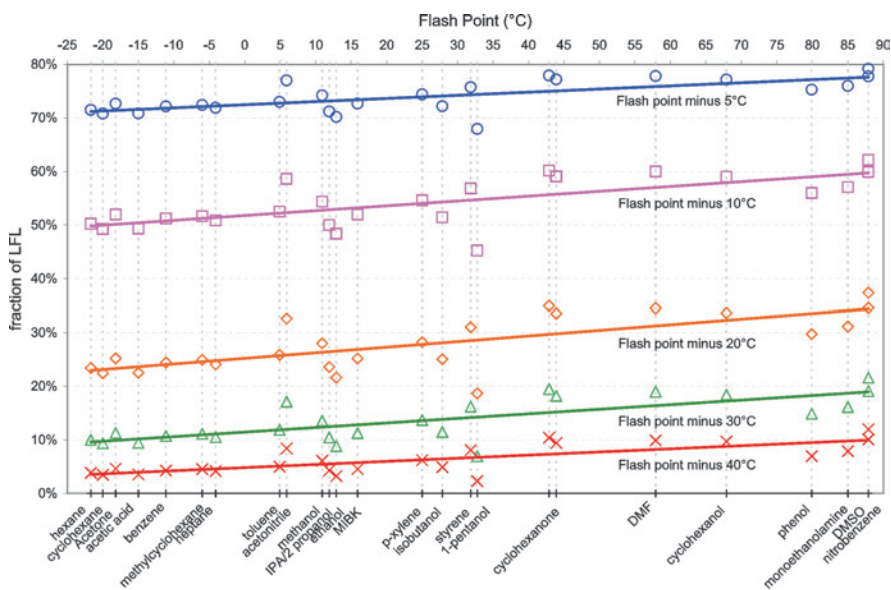


**Figure 4.** Flash point safety factors and the percentage of lower flammable limit (based on vapour pressure) to which these correspond

## GUIDELINES

The guidelines accept that 10% of LFL is an acceptable criteria for ignoring hybrid effects. 20% does not significantly change MIEs and is only a problem if venting needs to be considered. For low MIE dusts expert advice should be sought anyway.

The guidelines are summarised in Tables 1 and 2. Table 1 is more general and Table 2 is for transport.

These guidelines are very conservative (and deliberately so), as an alternative detailed expert measurements and assessment can be used to show that a material is acceptably safe.

Assessments can be based on the measured vapour pressure of equilibrated material. Possible alternatives are flash point measurement or MIE measurement, however, these latter two may prove more difficult to generate reliable data. If adsorption isotherms or drying data are available these could also be referred to as evidence. If the chemistry of bound solvates is understood, then these could form the basis of an assessment.

The authors advocate thinking about what materials are present then assessing carefully what operation is actually going to be carried out and the hazards of that operation, rather than blind application of a rule that says it will be acceptable.

## CONCLUSIONS

Weight based safety criteria for solvents in powder are not robust, and are easily misused. Hence such criteria are not acceptable.

Criteria based on the vapour lower flammable limit are more reliable. These criteria have been developed to make them more easily applicable using readily available flash point data.

**Table 1.** Robust and conservative, practical guidelines for the handling of solvents in powder, assuming that solvent is free, and unbound

| Criteria | Comments | Exceptions |
|---|---|---|
| FP ≥ (Max ambient temp + 40)°C | Can ignore presence of solvent for dust handling. No hybrid atmosphere is formed. | |
| FP ≥ (Max ambient temp + 30)°C | Can ignore presence of solvent for dust handling. | Venting or other times where $K_{ST}$ and explosion parameters are important. MIE in range of 3–10 mJ or less. |

Testing may prove that solvent is adequately bound into the crystal structure such as not to present a problem. Drying and or adsorption isotherm data may also be available which will allow assessment.

**Table 2.** Practical guidelines for handling powders containing solvent for transport

| Criteria | Comments | Exceptions | Work arounds |
|---|---|---|---|
| FP ≥ 90.5°C | Can ignore all solvent effects upon hybrid atmosphere for transport and/or handling | None at ambient temperatures (anywhere) | |
| FP ≥ 80.5°C | Ignore effects of solvent for transport or handling | Explosion venting. MIE in range of 3–10 mJ or less | Testing may be necessary to demonstrate safety for certain operations. |
| FP ≥ 60.5°C | Not treated as flammable liquid for transport. However, testing needed. | May have enhanced burning properties, affect MIE and explosion properties | Testing will be needed for properties possibly affected by solvent presence. |
| FP ≤ 60.5°C | Treat as a flammable solvent | | Testing will be necessary if treatment as a flammable solvent is too restrictive. |

It is recognised that the approach of using guidelines for non-experts necessitates large safety factors, which has cost implications.

Measurement and interpretation by experts may be more costly in the short term, but can be cheaper in the long term due to less stringent safety requirements. Such assessment is in line with the Dangerous Substances and Explosive Atmospheres Regulations 2002 (DSEAR).

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