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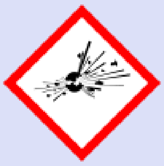
Safety Services Guidance



Guidance on the Recognition, Handling and Storing of Energetic and Explosophoric Chemicals

Key word(s) : Chemicals, Explosive, DSEAR, Autoxidation, Azides, Peroxides, Chromates, Dichromates, Nitrates, Oxidising, Storage

Target audience : Postgraduate and Postdoctoral Research workers, Laboratory staff

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Introduction

1. In recent years there have been a number of high profile incidents in Higher Education involving energetic and explosophoric chemicals. These incidents have resulted in personal injury, damage to premises and facilities and caused significant amounts of disruption not only to the business of the Institution involved but also the wider community.

2. The aim of this document is to help researchers and other laboratory staff to identify explosive chemicals and specific reactive chemical groups, and to provide guidance for the safe use and storage of these substances.

3. Before any work is done involving chemicals, a chemical risk assessment must be carried out. This should involve considerations of risk and control measures in line with both the Control of Substances Hazardous to Health (COSHH) Regulations and the Dangerous Substance and Explosive Atmospheres Regulations (DSEAR).

4. This guidance is not intended for chemicals that exhibit physical hazards other than being explosive (e.g. extremely flammable, highly flammability, compressed gas etc.) though these factors would need to form part of the overall chemical risk assessment process.

5. An explosion occurs when there is a chemical reaction or a change of state which occurs over an exceedingly short space of time with the generation of significant heat and gas.

6. According to the Classification, Labelling and Packing for supply regulation, (CLP), an explosive is a solid or liquid substance (or a mixture of substances) which is itself capable by chemical reaction of producing gas (often by decomposition) at such a temperature and pressure and at such a speed as to provide damage to the surroundings. Pyrotechnic substances are included in this definition even when they do not involve gases.

7. A pyrotechnic substance (or mixture) is a substance or mixture of substances designed to produce an effect by heat, light, sound, gas or smoke (or a combination of these) as the result of non-detonative self-sustaining exothermic (gives out heat) chemical reactions.

8. A common feature of many (not all) explosives is that they contain nitrogen or oxygen groups attached to a small constricted carbon skeleton. As these molecules are often chronically strained, the amount of energy required to split them is very low. The high velocity of the energy that is released when the molecule dissociates creates a blast pressure.

Different Types of Explosive Materials

9. Explosives can be categorised according to chemical composition (heterogeneous or homogeneous), stability and performance.

10. Mixtures of material with separate chemicals providing the fuel and oxygen are known as heterogeneous explosives, and the rate of reaction is determined by the time it takes for the components to mix. An example of a heterogeneous explosive is gunpowder (a mixture of charcoal, potassium nitrate and sulphur), or grain dust and air.

11. Homogeneous explosives contain the fuel and the oxidising elements in the same molecule, and the rate of reaction of these compounds is not dependent on a rate of mixing, e.g. trinitrotoluene, (TNT).

12. Explosives can also be classified as low or high explosives. This classification is made on the basis of the rate of decomposition of the material.

13. Low explosives decompose at or lower than the speed of sound, 340 ms^{-1}, e.g. gunpowder.

14. High explosives decompose much more rapidly than the speed of sound, 340 ms^{-1} e.g. triacetone peroxide, TATP. The faster the speed of detonation, the greater the shattering effect of the blast (brisance).

15. Classification according to performance gives three types of explosives

    a) Primary explosives rapidly transition from burning to detonation and these chemicals have the ability to transmit detonation via shock waves to less sensitive explosives. They detonate when exposed to heat, shock, friction, electric sparks etc. e.g. lead azide ($Pb(N_3)_2$).

    b) Secondary explosives are more stable and cannot be detonated by heat or direct shock. However, when they do detonate (usually from the shock wave produced by a primary explosive), they are more powerful and the shock wave has a great shattering effect, known as brisance, which occurs before the pressure wave. Plastic explosives, e.g. cyclotrimethylenetrinitramine (RDX) fall into this category.

    c) Propellants are combustible materials that contain all the oxygen within the molecule that is required for combustion. These chemicals burn rather than explode, however, the burning may be violent, e.g. nitrates, perchlorates.

Recognition of Explosive Chemicals and Explosophoric Functional Groups

16. Chemicals and mixtures that have been obtained from a third party (e.g. commercial supplier, business partner or other institution etc.) must be accompanied by a safety data sheet and have appropriate warning symbols on the packaging. The first method of identifying explosive substances is therefore to look at the warning pictogram on the packaging. Explosive materials have the following physical hazard pictogram and the signal word ‘Danger’ for the most hazardous classes of material, and ‘Warning’ for the least hazardous.

17. Physical hazard information provided on the safety data sheet for various types of explosive materials have the format H2xx or EUHxxx, as shown in Table 1:

Table 1 Hazard information pertinent to explosive materials

Hazard Number	Hazard Statement
H200	Unstable Explosive
H201	Explosive; mass explosion hazard
H202	Explosive; severe projection hazard
H203	Explosive; fire, blast or projection hazard
H205	May mass explode in fire
H230	May react explosively even in the absence of air
H231	May react explosively even in the absence of air at elevated pressure and or temperature
H240	Heating may cause an explosion
H241	Heating may cause a fire or explosion
H271	May cause fire or explosion; strong oxidiser (the explosive pictogram would also be accompanied by the Oxidiser pictogram in this instance 
EUH001	Explosive when dry
EUH006	Explosive with or without contact with air
EUH018	In use may form flammable/explosive vapour-air mixture

Hazard Number	Hazard Statement
EUH019	May form explosive peroxides
EUH044	Risk of explosion if heated under confinement

18. Strong oxidising agents, compounds containing fuel (carbon) and the oxidising agent in the same molecule or mixture, and compounds containing elements with many oxidation states may be very energetic (see homogeneous explosives, above).

19. When there is no documented safety information available, for instance the chemical of potential concern has been synthesised in situ, as a general guide chemicals with the functional groups shown in Table 2 are known to be energetic

Table 2 Chemicals and functional groups that are known to be energetic.

Functional Group (R is aliphatic and/or aromatic or inorganic)	**Compound type**
$R\text{-}O\text{-}NO_2$, R-NO2, R-O-N-O	Nitro compounds nitrates or nitrites
$R_2\text{-}N\text{-}NO_2$	Nitramines
$R\text{-}N{=}N^{+}{=}N^{-}$	Azides, organic and metallic
$R\text{-}NCl_2$	Chloramines
Tetrazoles, Tetrazines	Nitrogen rich heterocyclic compounds
N=O	Nitroso (Esters and salts)
N-O	Nitrogen oxides
$\text{-}C{\equiv}N^{+}\text{-}O^{-}$	Fulminates (salts of oxidoazaniumylidynemethane)
$(NO_3)^-$, $(ClO_4)^-$, $(ClO_3)^-$, $(CrO_4)^-$	Organic and inorganic salts, coordination compounds of oxidising acids, nitrates, chlorates, perchlorates, chromates etc.
R-O-O-H, R-O-O-R	Peroxides and ozonides
$\text{-}C{\equiv}C\text{-}$	Acetylene and metal acetylides
M-C-	Metal carbon bonds in some organometallic compounds

20. In the University sector, the majority of accidents involving explosions have been attributed to azides, nitrates, perchlorates, chlorates and peroxides.

21. Unintentional explosive risks may occur in some solvents with labile hydrogen atoms when they are oxidised with atmospheric oxygen to form hydroperoxides. These are very sensitive materials and can explode spontaneously if they are allowed to build up.

22. Chemicals prone to autoxidation as described above are ethers, tetrahydrofuran, aldehydes, alkenes etc.

23. Peroxides that are formed in a solvent are less volatile than the original solvent. Therefore they become concentrated in the original vessel when pure solvent is removed, e.g. by vacuum distillation or rotary evaporation.

24. Processes that have high heats of reaction, e.g. nitration and hydrogenation, can be energetic and thermal runaway is possible which can cause an explosion.

Chemical Hazards in Mixtures

25. There are mixtures of chemicals that are known to be dangerous, and should never be inadvertently mixed, e.g. solvent and mineral acid wastes, hydrogen peroxide with acetone, methyl ethyl ketone or ethers. If the intention is to make an explosive material, appropriate controls must be in place to prevent harm to individuals and property.

26. Publication of a reaction/method in the literature does not necessarily mean it is safe, especially when generic conditions are being used to make new compounds.

27. Published methods may require the mixing of reagents known to be incompatible in order to obtain the desired product, e.g. acetic anhydride and nitric acid oxidations; oxidations using organic solvents. If there are no alternative methods to carry out these reactions, they should be carried out with caution under carefully controlled conditions.

28. When consideration is being given to altering a process, extreme care needs to be taken to avoid adverse events, for example prevention of thermal runaway in scale-up, see guidance http://documents.manchester.ac.uk/display.aspx?DocID=12105 which may mean that the method of heat exchange – generally cooling – or solvent system need further contemplation.

Safety Measures to be taken when working with explosive and energetic materials.

29. Literature surveys on similar compounds should be researched along with, structure / sensitivity relationships, the presence of reactive groups - as above - and also metallic coordination compounds with oxidisable ligands, oxygen balance (see separate note), nitrogen content, structural relationships of any oxygen molecules (e.g. stable in an ester, unstable in a peroxide), heats of formation, chemical compatibilities, sensitivity to impact, friction, sparks and static electricity etc. before any work is carried out.

30. Work should be carried out on a small scale, and if the product is expected to be explosive, techniques such as Differential Scanning Calorimetry (DSC) should be used to check the thermal stability of compounds before they are subject to heat. Less than a gram of an explosive has been known to cause significant injuries and damage to premises.

When using materials known to be energetic, suitable precautions should be taken, e.g. handling of materials with long tongs behind appropriate blast screens and suitable Personal Protective Equipment, for example Kevlar gloves, aprons etc. should be worn http://www.hse.gov.uk/pubns/indg174.pdf,
http://www.hse.gov.uk/foi/internalops/oms/2009/03/

31. The location of work involving energetic materials needs careful consideration, and in particular, whether a special facility is required. If work is to be carried out in the usual laboratory, the number of people in the laboratory for its' duration should be reduced to a minimum without creating a lone working scenario.

32. The dilution of explosive materials with an inert diluent should be maintained wherever and whenever possible.

33. The isolation of energetic intermediates should be avoided whenever possible. If energetic intermediates are to be used in further work it is good practice to synthesise only as much as is immediately needed, as these substances can be unsafe to store.

34. Solvents that are prone to autoxidation should be regularly checked for peroxide levels. http://www.sigmaaldrich.com/chemistry/solvents/learning-center/peroxide-formation.html It is good practice to do this at least every 6 months after solvents with added inhibitors have been opened. Solvents without added inhibitors should be checked on opening and at least every 3 months (or more frequently as per the risk assessment) once opened. Where such solvents are being used in vacuum distillation or evaporation, peroxide levels should be checked immediately prior to use.

35. The use of glassware with ground glass joints should be avoided as manipulations of these can cause friction and a possible explosion.

36. Excessive use of heat, including naked flames and sparks should be avoided when handling energetic materials. Physical shock and friction that could be caused by crushing or grinding should be completely prevented, as often only a small amount of energy is required to cause the decomposition of these substances which may lead to an explosion. (E.g. silver fulminate will detonate under its own weight and there has been an accident in the University where apparently friction generated by the movement of a powder in a glass tube was sufficient to cause it to explode).

Storage Considerations

37. Solvents prone to autoxidation must be stored safely by keeping the bottles sealed, preferably under an inert atmosphere, when not in use to prevent ingress of air. They should be kept in dark bottles and in a dark cupboard as autoxidation can be photoinitiated. These solvents should also be kept in a cool place as autoxidation, like most chemical reactions, occurs more quickly at elevated temperatures.

38. The segregation of incompatible substances is essential to prevent dangerous interactions. Like substances should be stored with like substances. All newly purchased chemicals are labelled by the supplier to identify their hazard category, (e.g. flammable, oxidising, corrosive, toxic etc.) and are supplied with a Safety Data Sheet (SDS). Information regarding chemical incompatiblities can be found in Section 10 of the SDS.

39. Only the minimum stock levels of hazardous chemicals should be stored in the laboratory. Chemicals should be purchased only in the in the quantities that are likely to be needed. Some chemical companies have a facility to enable the purchaser to specify how much of a particular chemical is required and they will sell chemicals in bespoke amounts, provided they are contacted.

40. Hazardous chemicals that are no longer required should be disposed of on a timely basis via the School procedures and/ or protocols, ensuring that waste streams such as organic halogenated solvents, non-halogenated solvents, organic and aqueous acids and bases, are kept separate from each other.

41. Large breakable containers, particularly of liquids, should be stored below shoulder height and in a tray (bund) equivalent to 110% of the volume of the container.

42. It should be ensured that containers and bottle tops are sealed appropriately to avoid unnecessary leakage of fumes and vapours (note that it may, in labs that are not air conditioned, be necessary to cap materials more loosely to allow small expansion and contraction of the liquids to accommodate diurnal and seasonal temperature changes).

43. Containers should only be filled to the shoulder with liquids to allow with liquids a headspace of at least 10% by volume.

44. Bottles containing chemicals must never be carried only by the top. Winchesters (2.5L bottles) must always be transported in carriers or baskets that provide proper support and support the base of bottles in use.

45. Use by dates provided by the manufacturer must be checked and such chemicals must be either used or disposed of by the date shown. E.g. Concentrated nitric acid has a shelf life of 18 months from the date of manufacture.

46. When new bottles of solvents prone to autoxidation are obtained, it is good practice to ensure they are dated by the User, so that it is easier to identify when the shelf life has expired and the contents should be disposed of according to local procedures.

47. If chemicals are meant to be stored under a liquid, e.g. alkali metals under paraffin, some explosive materials under water (e.g. picric acid), this requirement must be noted and a system for checking that the liquid levels for these chemicals are maintained must be instigated.

48. Containers must be checked regularly for degradation of either the label or the container and as soon as deterioration is noted, the chemical and container must be disposed of according to School procedures and/or protocols.

49. More detailed information about packed chemical storage can be found in the HSE Publication HSE Chemical Warehousing, HSG71, HSE, 2009.

Notes – Oxygen balance, (OB% or Ω)

50. Oxygen balance is the amount of oxygen, expressed as a % weight that is required to fully oxidise all the fuel elements (carbon to carbon dioxide, hydrogen to water and any metals to their oxide) from within the explosive substance. If the amount of oxygen is insufficient to complete the oxidation, then the oxygen balance of the explosive will be negative and formation of toxic gases will occur as products of the explosion. If there is more oxygen than is required the oxygen balance will be positive. However, it is when the oxygen balance approaches zero, that the sensitivity, strength and brisance of the explosive tend to be maximised.

    General formula to calculate Ω for explosive with formula $C_aH_bN_cO_d$ and molecular mass M

    $$\Omega = \frac{[d - (2a) - (b/2)] \times 1600}{M}$$

Glossary

51. Detonation is a type of combustion involving a supersonic (faster than the speed of sound) exothermic (giving out heat) front accelerating through a medium that eventually drives a shock front propagating directly in front of it.

52. Deflagration is a subsonic combustion propagating through heat transfer where hot burning material heats the next layer of cold material and ignites it.

53. Deflagration to detonation transition is a phenomenon in ignitable mixtures of flammable gases and air (or oxygen) when a sudden transition takes place from a subsonic to a supersonic combustion.

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