



# Energetic properties and testing methodologies of oxidising substances

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# 1. Oxidising substances

Substances or mixtures which, while in themselves not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other materials.

(Regulation (EC) No 1272/2008 – The CLP regulation)

- High reactivity: due to their oxygen content.
- No external ignition source required for combustion.
- Considers organic peroxides ( $\text{H}_2\text{O}_2$  derivatives) –O-O-
- Liable to explosive decomposition if contaminated.

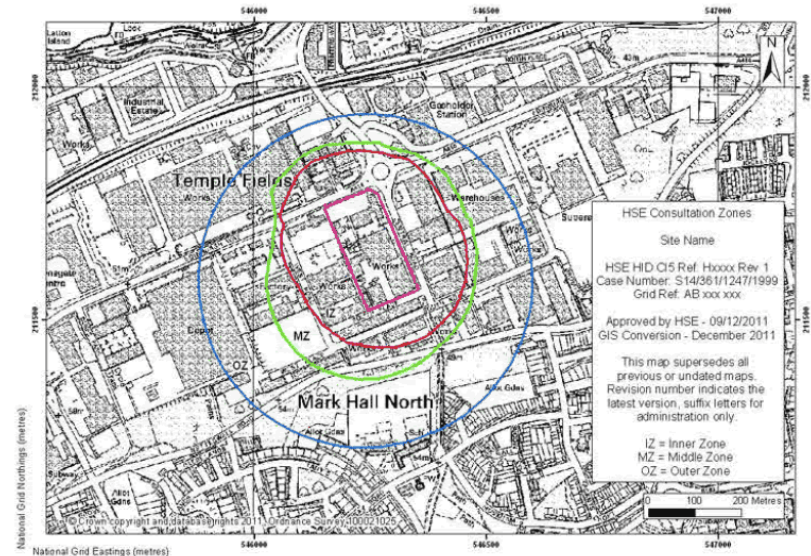


## 2. Hazardous Substance Consent (HSC):

- HSC application for Land-Use Planning (LUP) purposes.



### LUP – Consultation zones



- HSE Guidance: assessment of the overall explosive yield for the quantity of oxidising substances stored.
- Current oxidiser assessments require HSL / HSE expert assessment on a case by case basis

## 2. Hazardous Substance Consent (HSC):

✓ ‘Worst-case’ contaminant scenario:

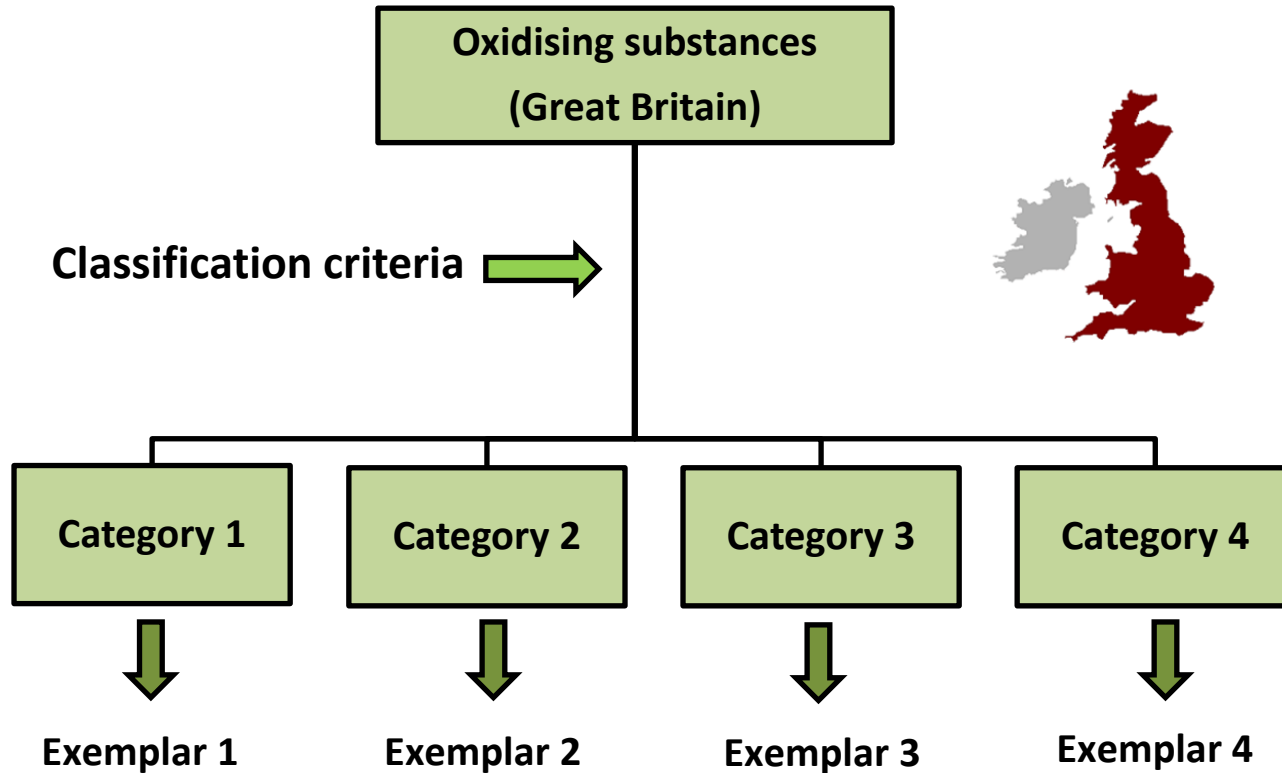
**‘Oxidiser’ + ‘non-explosive substance’ to produce the worst case explosive overpressure by detonation.**

✓ Quantification equivalent to a mass of TNT:

$$TNT_{\text{mass equivalent}} = \text{Explosive power} \times \text{Explosion efficiency} \times \text{Mass}_{\text{oxidiser}}$$

✓ For generic oxidisers, ‘worst-case’ exemplar:  
**89% Hydrogen peroxide; explosive yield = 0.69**

# 3. Oxidiser League Table: Proposal



### 3. Oxidiser League Table: List compilation

Compilation of a of list of oxidisers commonly used in GB.

- Trade bodies and associations in GB: CEFIC, CIA.
- International bodies: **IGUS-EOS** Group → **DATATOP 2013**



- HSE Records (TRIM).
- Survey – HSE Inspectors specialized in risk assessment.
- Planning Regulations for Hazardous Substances (2009).
- UN Manual of Test and Criteria

# 3. Oxidiser League Table: List generation

Refined list of oxidisers arranged by:

- ✓ UN Class (5.1, 5.2, others risks)
- ✓ Tonnage
- ✓ Frequency

Apparent lack of available explosive power data, specially for 'standard oxidisers'.

**DATATOP 2013 – Exclusive to OP**

**UN Test F.1 Ballistic Mortar Mk III – few OP**

Common oxidisers Great Britain - TONNAGE (Including common used subclass-oxidisers materials)			
Oxidiser name	Class	Total tonnage (te) *	Frequency
Zinc oxide raw material	9	828	4
Hydrogen peroxide	5.1	450.5	24
Sodium chlorite	5.1	316.0	3
Calcium hypochlorite	5.1	315.7	7
Oxidising solids (UN1479)	5.1	301.4	6
Potassium nitrate	5.1	199.8	5
Chromium trioxide	5.1	174.9	4
Sodium nitrite	5.1	144.0	6
Sodium nitrate	5.1	141.7	9
Peroxyacetic acid	5.2	109.9	6
Trichloroisocyanuric Acid	5.1	104.1	3
Metal nitrates (UN 1477)	5.1	79.6	10
Sodium chlorate	5.1	63.0	5
Sodium carbonate peroxyhydrate	5.1	62.0	2
Ammonium persulphate	5.1	60.3	4
Nickel nitrate	5.1	50.0	3
Oxidising solids (UN3085)	5.1	42.4	4
Sodium persulphate	5.1	38.5	6
Persulphates	5.1	37.0	2
Permanganates - Inorganics	5.1	26.7	1
Potassium chlorate	5.1	25.0	1
Aluminium nitrate	5.1	20.5	4
Zinc nitrate	5.1	20.0	1
Nitric acid	8(5.1)	17.0	5
Potassium permanganate	5.1	14.0	1
Magnesium nitrate	5.1	14.0	3
Ammonium nitrate	5.1	13.8	5
Di-tert-butyl peroxide	5.2	9.60	3
Potassium mono-persulphate	5.1	6.00	2
Dicumyl peroxide	5.2	4.60	1
Di-tert-amyl peroxide	5.2	4.24	1
Methyl Ethyl Ketone Peroxide (MEKP)	5.2	3.65	1
Diisopropyl benzene hydroperoxide	5.2	3.60	1
Sodium perborate monohydrate	5.1	2.80	2
Barium nitrate	5.1	2.70	1
tert-butyl hydroperoxide (TBHP)	5.2	2.70	3
Potassium hydrogen sulphate	8	1.40	1
1,1-di-(tert-butylperoxy)cyclohexane	5.2	1.18	1
Di-(2-tert-butylperoxyisopropyl) benzene	5.2	1.00	3
Methyl isobutyl ketone peroxide	5.2	1.00	1
Silver nitrate	5.1	1.00	2
2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane	5.2	0.60	1
Ruthenium nitrosyl nitrate	8(5.1)	0.50	1
Ammonium thioglycolate	8(6.1)	0.26	1
Sodium dichromate (as Alchrom)	6.1(5.1)	0.25	2
Acetyl acetone peroxide	5.2	0.23	1
n-butyl-4,4-di(t-butylperoxy)valerate	5.2	0.20	1
1,1-Bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane	5.2	0.18	1
tert-butylperoxy 2-ethylhexyl carbonate	5.2	0.75	1
T-Amyl peroxy 2-ethylhexanoate	5.2	0.050	1
Lauroyl peroxide	5.2	0.050	1
Potassium dichromate (as Alchrom)	6.1(5.1)	0.0004	1
tert-butyl peroxibenzoate (TBPB)	5.2	(-)	1
tert-butyl peroxy (2-ethylhexanoate) (TBP6H)	5.2	(-)	1
Sodium permanganate	5.1	(-)	1

\* The tonnage was not always available.

## 4. Other classification criterion

Consistent criterion to cover all (or most) of the oxidisers included in the refined list obtained.

- Packing group (UN Manual)
- Hazard Rating (NFPA 704)
  
- NFPA 430 Code for the storage of Liquid and Solid Oxidisers



**National Fire Protection Association**  
The authority on fire, electrical, and building safety



# 5. NPFA 430 Code



**National Fire Protection Association**  
The authority on fire, electrical, and building safety

Class	Criteria
<b>CLASS 1</b>	Does not moderately increase the burning rate of combustible materials with which it comes into contact.
<b>CLASS 2</b>	Causes a moderate increase in the burning rate of combustible materials with which it comes into contact.
<b>CLASS 3</b>	Causes a severe increase in the burning rate of combustible materials with which it comes into contact.
<b>CLASS 4</b>	Generally meets the Class 3 criteria plus can undergo an explosive reaction due to contamination or exposure to thermal or physical shock with which it comes into contact.

✓ **Flammability criteria**

# 6. HSE CS21 Guidance



Type	Criteria
Type 1	This contains both explosive-labelled packaged peroxides and packaged peroxides which burn very intensely.
Type 2	This contains packaged peroxides which burn in a way which is intermediate between Type 1 and 3.
Type 3	This contains packaged peroxides which burn in the range 'gently' up to something akin to solvents and hydrocarbons.
Type 4	This contains packaged peroxides which are non-combustible and from which the available oxygen is not more than 5%.

✓ **Flammability criteria**

# 7. Flammability type classification criteria

## Oxidising substances: NFPA 430 Code

Common oxidisers Great Britain - FREQUENCY & NFPA 430 Modified Methodology Sub-classes			
Frequency	Oxidiser name	Class	NFPA Modified Methodology <sup>1</sup>
24	Hydrogen peroxide	5.1.	1 (>8% - 27.5%)
10	Metal nitrates (UN 1477)	5.1.	1
9	Sodium nitrate	5.1.	1
7	Calcium hypochlorite	5.1.	1 (80% nominal + MgSO <sub>4</sub> )
6	Oxidising solids (UN1479) - Nitrates (Co, Gd, Pd, Ce)	5.1.	1
6	Sodium persulphate	5.1.	1
6	Sodium nitrite	5.1.	1
5	Potassium nitrate	5.1.	1
4	Ammonium persulphate	5.1.	1
4	Aluminium nitrate	5.1.	1
3	Nickel nitrate	5.1.	1
3	Trichloroisocyanuric Acid	5.1.	1
3	Magnesium nitrate	5.1.	1
2	Sodium perborate monohydrate	5.1.	1
2	Potassium mono-persulphate	5.1.	1
2	Sodium carbonate peroxyhydrate	5.1.	1
2	Silver nitrate	5.1.	1
1	Zinc nitrate	5.1.	1
1	Barium nitrate	5.1.	1
24	Hydrogen peroxide	5.1.	2 (>27.5% - 52)
7	Calcium hypochlorite	5.1.	2 (50% or less w/w)
4	Chromium trioxide (Chromic acid)	5.1.	2
4	Oxidising solids (UN3085) (Bromo-chloro dimethylhydantoin)	5.1.	2
3	Sodium chlorite	5.1.	2 (40% or less w/w)
1	Potassium permanganate	5.1.	2
1	Sodium permanganate	5.1.	2
24	Hydrogen peroxide	5.1.	3 (>52% - 91)
7	Calcium hypochlorite	5.1.	3 (>50% w/w)
5	Sodium chlorate	5.1.	3
3	Sodium chlorite	5.1.	3 (>40% w/w)
1	Potassium chlorate	5.1.	3
24	Hydrogen peroxide	5.1.	4 (>91%)

## Organic peroxides: HSE CS21 Guidance

Frequency	Oxidiser name	UN Class	CS21
3	Di-tert-butyl peroxide	5.2 (Type E)	Type 1 (≤ 100%)
1	2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane	5.2 (Type C)	Type 1 (53-100%)
1	Methyl Ethyl Ketone Peroxide (MEKP)	5.2 (Type B)	Type 1 (≤ 45%)
1	T-Amyl peroxy 2-ethylhexanoate	5.2 (Type D)	Type 2 (≤ 100%)
1	Methyl isobutyl ketone peroxide	5.2 (Type D)	Type 1 (≤ 62%)
1	tert-butyl peroxibenzoate (TBPB)	5.2 (Type C)	Type 1 (78-100%)
1	tert-butyl peroxy (2-ethylhexanoate) (TBPEH)	5.2 (Type C)	Type 1 (53-100%)
Part A - Named Subst.	tert-butyl peroxyisobutyrate (>80%)	5.2 (Type D)	Type 1 (≤ 52%)
Part A - Named Subst.	tert-butyl peroxyisobutyrate (>80%)	5.2 (Type B)	Type 1 (53-77%)
Part A - Named Subst.	tert-butyl peroxyisopropylcarbonate (>80%)	5.2 (Type C)	Type 1 (≤ 77%)
Part A - Named Subst.	tert-butyl peroxyisovalerate (>77%)	5.2 (Type C)	Type 1
Part A - Named Subst.	Di-n-propyl peroxydicarbonate (>80%)	5.2 (Type C)	Type 1 (53-100%)
3	Di-(2-tert-butylperoxyisopropyl) benzene	5.2 (Type D)	Type 2 (43 - 100%)
3	tert-butyl hydroperoxide (TBHP) (70%)	5.2 (Type F)	Type 2 (≤ 72%)
1	2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane	5.2 (Type C)	Type 2 (≤ 52%)
1	Dicumyl peroxide	5.2 (Type F)	Type 2 (43 - 100%)
1	1,1-Bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane	5.2 (Type B)	Type 2 (≤ 57%)
1	1,1-di-(tert-butylperoxy)cyclohexane	5.2 (Type B)	Type 2 (52%, ≥ 48% Diluent)
1	Acetyl acetone peroxide	5.2 (Type D)	Type 2 (≤ 42%)
1	tert-butyl peroxibenzoate (TBPB)	5.2 (Type C)	Type 2 (≤ 52%)
Part A - Named Subst.	2,2-Bis(tert-butylperoxy) butane (>70%)	5.2 (Type C)	Type 2 (≤ 52%)
Part A - Named Subst.	tert-butyl peroxyacetate (>70%)	5.2 (Type B)	Type 2 (≤ 52%)
Part A - Named Subst.	tert-butyl peroxyvalerate (>80%)	5.2 (Type E)	Type 2 (≤ 42% as a paste)
Part A - Named Subst.	tert-butyl peroxyvalerate (>80%)	5.2 (Type C)	Type 2 (≤ 52%)
Part A - Named Subst.	Di-n-propyl peroxydicarbonate (>80%)	5.2 (Type C)	Type 2 (≤ 52%)
Part A - Named Subst.	Di-sec-butyl peroxydicarbonate (>80%)	5.2 (Type C)	Type 2 (≤ 52%)
6	Peroxyacetic acid	5.2 (Type E - F)	Type 3 (≤ 43%)
1	n-butyl-4,4-di(t-butylperoxy)valerate	5.2 (Type C)	Type 3 (≤ 52%)
1	1,1-Bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane	5.2 (Type B)	Type 3 (≤ 57%, ≥ 43% Diluent)
1	1,1-di-(tert-butylperoxy)cyclohexane	5.2 (Type B)	Type 3 (≤ 27%, ≥ 36% Diluent)
1	Acetyl acetone peroxide	5.2 (Type D)	Type 3 (≤ 32%, paste)
Part A - Named Subst.	Di-n-propyl peroxydicarbonate (>80%)	5.2	Type 3 (10%)
Part A - Named Subst.	3,3,6,6,9,9-hexamethyl-1,2,4,5-tetroxacyclononane (>75%)	5.2 (Type D)	Type 3 (≤ 52%)
3	Di-(2-tert-butylperoxyisopropyl) benzene	5.2 (Type D)	Type 4 (≤ 42%)
1	Dicumyl peroxide	5.2 (Type F)	Type 4 (≤ 42%)
1	1,1-di-(tert-butylperoxy)cyclohexane	5.2 (Type B)	Type 4 (≤ 42%, ≥ 13% Diluent)

<sup>1</sup> Oxidizer Classification Research Project: Tests & Criteria (Ed. 2009) NFPA Request - Flammability type  
NC = Not classified

## 8. Conclusions

- ✓ The 'oxidiser league table' is a practical concept.
- ✓ Shortage of available explosive yield data.
- ✓ Arrangement by burning rate is possible and allows some fit with other international systems.
- ✓ No correlation proven between burning rate and explosive yield.

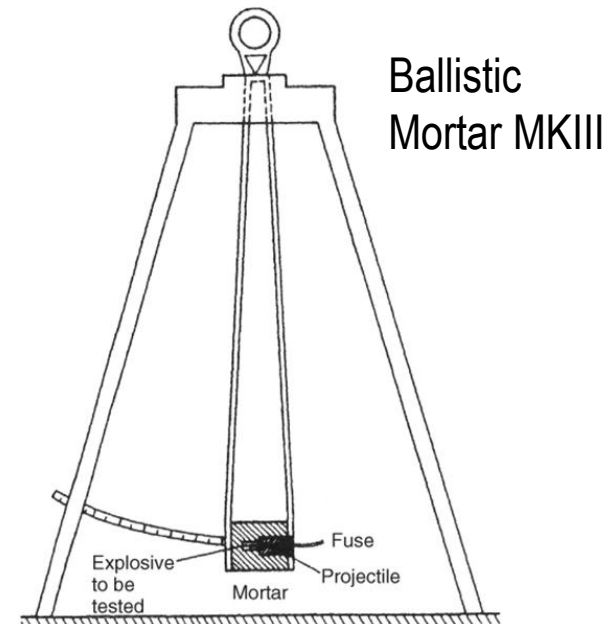
## 9. Future work: Oxidising substances

### ➤ Characterization: Experimental test campaign.



Carious tube

- ✓ Test of oxidisers when contaminated.
- ✓ Use of paraffin wax ( $C_nH_{2n+2}$ ) instead of cellulose.
- ✓ Paraffin at certain temperature improves the mixing 'oxidiser – contaminant'.
- ✓ Mixing independent of the particle size.





## 9. Future work: Oxidising substances

- Correlation burning rate  $\leftrightarrow$  explosive yield
- Classification

# Thank you for your time!



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