CLASSIFICATION OF ENERGETIC INDUSTRIAL CHEMICALS FOR TRANSPORT

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The explosivity test data obtained by the Hazardous Materials section of HSE's Explosion and Flame laboratory on nitromethane, 77% 2, 4, 6-trinitrophenol, 2, 2'-azodi(isobutyronitrile), azodicarbonamide, ammonium nitrate, ammonium perchlorate and 1, 3-dinitrobenzene is presented. The results are discussed in terms of problems with the application of United Nations test methods and classification schemes and requirements for any new schemes.
Key words : United Nations, classification, energetic, explosive, transport, testing.

INTRODUCTION

The United Nations (UN) Committee of Experts on the Transport of Dangerous Goods (1) has made considerable progress in developing classification schemes, test methods and criteria for assessing the danger during transport from energetic industrial chemicals i.e. those which decompose exothermically to a dangerous extent. The Committee has introduced a generic system of classification for organic peroxides and has just agreed a similar system for self-reactive substances. Consolidated recommendations on tests and criteria for explosives, organic peroxides, self-reactive substances and "cigar burning" ammonium nitrate fertilisers have also been recently published by the UN (2). Until now, the principles for classification have tended to be developed by specialists on particular types of substances e.g. explosives, organic peroxides and self-reactive substances. However, some energetic chemicals fall into more than one category, or can be diluted or packaged to move from one category to another and it may now be desirable to develop a unified approach to the classification of all energetic industrial chemicals intended for international transport.

In order to assist in the development of such a unified approach, members of the International Group of Experts on the Explosion Risks of Unstable substances (see Thomson and von Zahn-Ullmann (3)) are performing round-robin tests on seven representative energetic industrial chemicals. This paper gives the results obtained by HSE's Explosion and Flame Laboratory(EFL). It is hoped this information will assist the development of a consistent set of principles for classification, test methods and criteria for the safe transport of energetic industrial chemicals.

The views expressed in this paper are the views of the authors and should not necessarily be taken to be those of the Health and Safety Executive.

TEST SUBSTANCES

The types of substances currently listed in the UN Recommendations which exhibit some explosive characteristics in laboratory testing, but which are not transported under the provisions of Class 1 (explosives), are:

- energetic flammable liquids of Class 3;
- desensitised explosives of Division 4.1 (flammable solids);
- energetic azo, nitro and nitrate compounds of Division 4.1;
- self-reactive substances of Division 4.1;
- energetic oxidizing agents of Division 5.1;
- types B and C organic peroxides of Division 5.2; and
- energetic organic nitro compounds of Division 6.1 (toxic substances).

Representative substances were chosen from each of these classes/divisions apart from Division 5.2 (test results for organic peroxides are given in reference (2)). The substances chosen, their physical form and any preparation, are summarised in Table 1. One of the substances, 65% 2, 4, 6-trinitrophenol, was received as a two phase mixture. As the worst case during transport is presented by the solid phase, excess water was decanted from the sample and the wet solid (77%) tested throughout.

TABLE 1 - Sample identification, form and preparation

UN NO.	CLASS	SAMPLE	CODE	FORM	PREPARATION
1942	5.1	AMMONIUM NITRATE	AN	Lumpy, white crystalline solid	Lumps broken up
1442	5.1	AMMONIUM PERCHLORATE	AP	White crystalline powder	Used as received
3242*	4.1	AZODICARBONAMIDE	AC	Fine yellow powder	Used as received
2952 (3234)**	4.1	2, 2'-AZODI(ISO-BUTYRONITRILE)	AZDN	White powder	Used as received
1597	6.1	1,3-DINITRO-BENZENE	DNB	Brownish-yellow crystals	Fraction pass 1.7 mm used
1261	3	NITROMETHANE	NM	Mobile, colourless liquid	Used as received
1344	4.1	2, 4, 6-TRINITRO-PHENOL + 23% WATER***	TNP	Yellow crystalline solid wetted with water	Excess water decanted

* Recently assigned to Division 4.1.

** Generic entry no. for SELF-REACTIVE SOLID, TYPE C, TEMPERATURE CONTROLLED

*** Nominal 65% material received with separate aqueous layer - excess water decanted leaving 77% wetted material (c.f. UN requirement for not less than 30% water)

IDENTIFICATION OF POTENTIALLY EXPLOSIVE SUBSTANCES

There are a number of literature references, e.g. Bretherick (4), ABPI Guide (5), which give guidance on identifying reactive chemical groups or combinations of groups, e.g. fuel and oxidizer, whose presence in a substance may lead to explosive properties and/or thermal instability at transport temperatures. In addition, computer programs such as CHETAH (new release described by Frurip et al (6)) are available which can give a guide to the potential hazard. New substances containing one or more reactive chemical groups would be considered by the authors as having the potential to decompose exothermically to a dangerous extent unless few reactive groups were present in a large chemical structure such as in some aromatic azo dyes. All the test substances would be identified as having the potential to decompose exothermically to a dangerous extent.

PRELIMINARY ASSESSMENT

For safety, it is essential to perform sensitivity tests on small quantities of substance before performing larger scale explosivity tests.Cutler (7) has indicated that the Hazardous Materials section normally assesses the response of small quantities of substance to sparks, flames, hot surfaces and to mechanical stimuli such as impact and friction. In addition, the section uses instrumental techniques such as differential scanning calorimetry (DSC) (8) to estimate the available energy and to obtain some indication of the temperature at which a significant exothermic reaction may commence. The results from such tests give an indication of how dangerous a substance is and if any special precautions, e.g. such as avoidance of tamping, are required in handling it. The results from DSC are given in Table 2, ad hoc ignitability tests in Table 3 and impact and friction sensitivity tests in Table 4. Brief descriptions of all the tests used are given, in order of reference, in the Appendix.

TABLE 2 - Results from DSC (9)

SUBSTANCE	ONSET* TEMPERATURE (°C)	EXTRAPOLATED** ONSET TEMPERATURE (°C)	DECOMPOSITION ENERGY*** (J/g)
AMMONIUM NITRATE	284	295	961
AMMONIUM PERCHLORATE	389	Out of range	Out of range
AZODICARBONAMIDE	194	207	1105
2,2'-AZODI(ISOBUTYRONITRILE)	101	101	1301
1,3-DINITROBENZENE	268	c.a. 280	Out of range
NITROMETHANE	> 300	Out of range	Out of range
77% 2, 4, 6-TRINITROPHENOL	190	227	2854

* The temperature at which a deflection from the established baseline is first observed.

** The temperature found by extrapolating the baseline (prior to the peak) and the leading side of the peak to their intersection.

*** Not corrected for baseline shifts due to changes in specific heat.

As a conservative guide, based on DSC and explosivity test results on a wide variety of organic and inorganic energetic chemicals (to be published), substances with a low onset temperature (< 150° C) and a decomposition energy > 300 J/g may undergo dangerous self-heating at transport temperatures (up to 55°C). Substances with a decomposition energy > 500 J/g may have some explosive properties e.g. when heated under confinement, and substances with a decomposition energy > 800 J/g may be detonable. By these criteria, all the substances for which a decomposition energy could be measured may be detonable and AZDN may require temperature control during transport. Some of the substances tested did not give a measurable exotherm in the operating range (maximum temperature c.a. 300°C) of the sealed pan used. Onset temperatures and decomposition energies measured by DSC should be treated with some care. Onset temperatures are dependent on heating rate and instrument parameters and can be affected by catalysis of the decomposition by the pan materials and, particularly for the more energetic decompositions, Grewer and Duch (10) have shown that the decomposition energy measured can be an underestimate of the energy available in practice.
The results (Table 3) from ad hoc ignitability tests, indicate that AZDN,NM and TNP are ignitable, that DNB burns and AN gives flammable decomposition products on severe heating. AC and AP decompose without ignition of the fumes. No reports, indicating possible initiatory explosive behaviour, were heard in any tests.

TABLE 3 - Results from ad hoc ignitability tests (Koenen and Ide (11)) and the UN Princess Incendiary Spark Test (12)

SUBSTANCE	AD HOC IGNITABILITY			PRINCESS INCENDIARY SPARK TEST
	Gas flame	Red hot rod	Red hot dish	
AMMONIUM NITRATE	Melts and decomposes	Intermittent burning	Sustained burning	Failed to ignite
AMMONIUM PERCHLORATE	Decomposes on severe heating	Slight decomposition	Decomposition	Failed to ignite
AZODICARBON-AMIDE	Melts and decomposes	Melts and decomposes	Decomposes and fumes	Failed to ignite
2,2'-AZODI(ISO-BUTYRONITRILE)	Melts and ignites	Intermittent decomposition	Sustained burning	Failed to ignite
1,3-DINITRO-BENZENE	Melts and decomposes	Melts and decomposes	Sustained burning	Failed to ignite
NITROMETHANE	Ignites and burns gently	Slight fuming	Sustained burning	Failed to ignite
77% 2,4,6-TRI-NITROPHENOL	Melts and burns	Intermittent burning	Flashes and burns	Failed to ignite

Results from friction and impact sensitivity tests are given in Table 4. The Fallhammer impact test and the BAM friction test are normally used to decide if candidate substances for Class 1 are too sensitive for transport. Friction tests are not usually performed on liquids. The formal UN test prescriptions for the Fallhammer and BAM Friction tests do not treat complete decomposition or formation of considerable amounts of smoke without a report or flash as a positive event although their occurrence is reported. In some relatively low energy materials, complete reaction of the packaged material can be initiated by impact or friction but these substances may not give a report or flash in these tests. The results indicate that only ammonium perchlorate is close to the borderline criteria for being too impact sensitive for transport, that AZDN, NM and DNB show some sensitivity to impact and that AN, AC and TNP are relatively insensitive. Only AZDN shows some sensitivity to initiation by friction.

TABLE 4 - Results from impact (13) and friction (14) tests

SUBSTANCE	FALLHAMMER TEST Limiting impact energy* (J)	BAM FRICTION TEST Limiting load** (N)
AMMONIUM NITRATE	> 50	> 363
AMMONIUM PERCHLORATE	5 (report)	> 363
AZODICARBONAMIDE	> 50	> 363
2, 2'-AZODI(ISOBUTYRONITRILE)	3 (smoke)	363 (smoke)
1, 3-DINITROBENZENE	20 (smoke)	> 363
NITROMETHANE	40 (report)	Not performed
77% 2, 4, 6-TRINITROPHENOL	> 50	> 363

* The UN consider the result "positive" if the limiting energy ≤ 2 J

** The UN consider the result "positive" if the limiting load < 80 N

Some care has to be taken in interpreting impact and friction results as only small quantities of substance are used in a form which may not be found during transport e,g. cast materials may be broken up for testing. In addition, some thermally unstable materials may give a positive reaction just from the heating effects from the striking surfaces and low melting solids can vaporize giving the appearance of smoke.

CLASS 1 ACCEPTANCE PROCEDURE

In paragraph 4.1.6 of the UN Recommendations, (see section on Transport of energetic substances not accepted into Class 1), substances suspected of having explosive properties should first be considered for inclusion in Class 1 i.e. subjected to the Class 1 acceptance procedure (15). This procedure is used to decide whether a substance is too insensitive for inclusion in Class 1 or too sensitive for transport. Figure 1 illustrates the Class 1 acceptance procedure, as it relates to substances not intended for explosive use, expressed in terms of the property determined. The flowchart shows the sequence of evaluating the results rather than the order in which the properties are determined. The experimental procedure involves first assessing the sensitiveness of the substance to mechanical stimuli(impact and friction), and to heat or flame. The sensitivity to heat is assessed by an isothermal test performed at 75°C for 48 hours and the sensitivity to flame is a small scale deflagration to detonation test. Normally the Hazardous Materials section would use a self-accelerating decomposition temperature (SADT) test to assess thermal stability and the ad hoc ignitability tests would indicate if the sensitivity to flame need be determined. The thermal stability test would normally only be performed on those substances to be classified in Class 1. Provided the substance is not too sensitive for transport, then the next step is to determine the sensitiveness to detonative shock and the effects of heating or ignition under confinement. Tests relating to propagation of detonation are used to assess the explosive nature of the substance and are not strictly necessary for application of the acceptance procedure.

For organic peroxides and self-reactive substances it has been proposed to the UN Committee of Experts (16) that a combination of results from an explosive power test and two different heating under confinement tests may be used to assess if it is necessary to perform detonability tests which require expensive test facilities and means for storing explosives. Hence explosive power tests may be performed before detonability tests.

The DSC onset temperatures in table 2 indicate that only AZDN is likely to fail the thermal stability tests and these were only performed on AZDN(Table 5). Although the thermal stability test at 75°C indicates that AZDN is too sensitive for transport in Class 1, the heat accumulation storage test indicates that the SADT is 50°C (for a 50 kg package) and that, as it meets the definition, it may be transported as a Division 4.1 self-reactive substance under temperature control at a maximum temperature of 40°C.

TABLE 5 - Thermal stability results on 2, 2'-azodi(isobutyronitrile) from the heat accumulation storage test (17) and the thermal stability test (18) at 75°

HEAT ACCUMULATION STORAGE TEST		THERMAL STABILITY TEST AT 75°C
Temperature(°C)	Result	Result
45	No apparent change	Runaway reaction
50	Mild reaction	

The results in Table 6 from explosive power tests may be taken into consideration when assessing candidates for Class 1 but are normally used to decide if organic peroxides or self-reactive substances may be transported in tanks or Intermediate Bulk Containers (IBCs). Of the test substances, only 2, 2'-azodi(isobutyronitrile) meets the newly agreed definition of a self-reactive substance and the "LOW" result would not ban it from transport in IBCs or tanks. In the future, if a "NO" result is obtained in an explosive power test and a "LOW" or "NO" result is obtained from two different heating under confinement tests then it may not be necessary to perform a detonability test on an organic peroxide or a self-reactive substance. The "LOW" result from AZDN means that a detonability test would be required.

At present, the high pressure autoclave is the only UN test of explosive power not involving detonator initiation and clearly it would be advantageous if this test could be used to assess the explosive power of all types of energetic substances. However, some problems were found on performing this test on substances with electrical conducting properties and/or which were very stable. These problems may be overcome if an insulated heating wire is used which will not "short out". A ballistic mortar value > 50% the value given by picric acid is a reasonable indication that a substance may be detonable but substances with values as low as 8% can be detonable e.g. dibenzoyl peroxide.

When assessing candidates for Class 1 no distinction is made in detonability testing (Table 7) between a "PARTIAL" reaction, e.g. deflagration, and a "NO" reaction. A test using a detonator plus booster charge initiation is used to assess if a detonation can be propagated and a test using detonator only initiation is used to assess the sensitivity to detonative shock of those substances which propagate detonation. The results indicate that the AN, AP, DNB, NM and TNP samples all propagate detonation but only the DNB is sensitive to detonative shock.

TABLE 6 - Explosive power results from the Ballistic Mortar Mk.IIId test(19) and the High Pressure Autoclave test (20)

SUBSTANCE	BALLISTIC MORTAR TEST		HIGH PRESSURE AUTOCLAVE	
	% value of picric acid (%)	Result	F value (J/g)	Result
AMMONIUM NITRATE	58	NOT LOW	14.3	LOW
AMMONIUM PERCHLORATE	60	NOT LOW	Partial reaction*	
AZODICARBONAMIDE	1	NO	46.7	LOW
2,2'-AZODI(ISOBUTYRONITRILE)	4	LOW	47.1	LOW
1,3-DINITROBENZENE	74	NOT LOW	Variable reaction**	
NITROMETHANE	113	NOT LOW	> 100	NOT LOW
77% 2, 4, 6-TRINITROPHENOL	1	NO	Variable reaction***	

* Propagation throughout the mass in only one of five tests
** Violent reaction (bursting disk broken) in one of five tests
*** Pressure of 45 MPa generated from 12.5 g

TABLE 7 - Detonability results from BAM 50/60 tube tests (21,22)

SUBSTANCE	BAM 50/60 TUBE TEST (detonator + 50 g RDX)		BAM 50/60 TUBE TEST (detonator only)	
	Fragmented length (cm)	Result	Fragmented length (cm)	Result
AMMONIUM NITRATE	50 (split)*	PARTIAL	Not performed	
AMMONIUM PERCHLORATE	50	DETONATION	0	NO
AZODICARBONAMIDE	15	NO	Not performed	
2, 2'-AZODI(ISOBUTYRONITRILE)	14	DEFLAGRATION	Not performed	
1, 3-DINITROBENZENE	50	DETONATION	50	DETONATION
NITROMETHANE	50	DETONATION	10	PARTIAL?
77% 2, 4, 6-TRINITROPHENOL	50	DETONATION	0	NO
(sand)	13			

* 5% unreacted material left

The deflagration tests used by EFL (Table 8) are those required when assessing the properties of organic peroxides and self-reactive substances.The time/pressure test is also used in the Class 1 acceptance procedure as a test for the effect of ignition under confinement, i.e. a thermal response test, and may be used as an alternative to a test for the effect of heating under confinement. In the authors view, these are two distinct properties and both should be determined. Any substance, apart from an organic peroxide or a self-reactive substance, which gives a "YES, RAPIDLY" result in the time/pressure test should be submitted to the Class 1 assignment procedure. On this basis, AP and AZDN (if it were not considered a self-reactive substance) should be considered for assignment to Class 1.The deflagration test result for nitromethane is typical of that for a flammable liquid i.e. combustion rate and not deflagration rate has been measured.

TABLE 8 - Deflagration results from the Time/Pressure test (23) and the deflagration test (24)

SUBSTANCE	TIME/PRESSURE TEST Pressure rise time (ms)	Result	DEFLAGRATION TEST Deflagration rate (mm/s)	Result
AMMONIUM NITRATE	No ign.	NO	No ign.	NO
AMMONIUM PERCHLORATE	24	YES, RAPIDLY	No ign.	NO
AZODICARBONAMIDE	94	YES, SLOWLY	0.38	YES, SLOWLY
2, 2'-AZODI(ISOBUTYRO-NITRILE)	28.5	YES, RAPIDLY	0.81	YES, SLOWLY
1,3-DINITROBENZENE	< 2070 kPa	NO	No ign.	NO
NITROMETHANE	112	YES, SLOWLY	0.01	NO
77% 2, 4, 6-TRINITROPHENOL	No ign.	NO	No ign.	NO

The results from heating under confinement tests are given in Table 9. The Koenen test is used in the Class 1 acceptance procedure and for classification of organic peroxides and self-reactive substances. The Dutch Pressure Vessel test is currently only used for classification of organic peroxides and self-reactive substances. The thermal explosion vessel test is not currently used for classification but is a new test which may be used for classification once sufficient experience has been gained in its operation. A "VIOLENT" result from the Koenen test would require that a substance be submitted to the Class 1 assignment procedure. Hence, by the Koenen test, both ammonium perchlorate and 77% 2,4,6-trinitrophenol should be submitted to the Class 1 assignment procedure but not 2,2'-azodi-(isobutyronitrile).

TABLE 9 - Effect of heating under confinement results from the Koenen (25), Dutch Pressure Vessel (26) and Thermal Explosion Vessel (27) tests

SUBSTANCE	KOENEN TEST		DUTCH PRESSURE VESSEL TEST		THERMAL EXPLOSION VESSEL TEST	
	Critical diameter (mm)	Result	Critical diameter (mm)	Result	Maximum rate x maximum pressure (MPa^2/s)	Result
AN	1.0	LOW	1.0	LOW	0.16	LOW
AP	3.0	VIOLENT	6.0	MEDIUM	> 403	VIOLENT
AC	1.5	MEDIUM	1.5	LOW	14.7	MEDIUM
AZDN	1.5	MEDIUM	11.0	VIOLENT	81.8	MEDIUM
DNB	1.0	NO	1.0	LOW	No effect at 320°C	
NM	<1.0	NO	<1.0	NO	< 0.005	NO
77% TNP	5.0	VIOLENT	5.0	MEDIUM	> 599	VIOLENT

The overall assessment of the results by the Class 1 acceptance procedure are summarised in Table 10. If the results from all the tests which are part of the Class 1 acceptance procedure are used then ammonium perchlorate, 2, 2'-azodi(isobutyronitrile), 1, 3-dinitrobenzene and 77% 2, 4, 6-trinitrophenol (70% is exempted and the sample received was 65%) should be submitted to the Class 1 assignment procedure. Although detonable, nitromethane is considered too insensitive for provisional acceptance into Class 1.

TABLE 10 - Overall assessment of results from application of the Class 1 acceptance procedure

SUBSTANCE	Is it thermally unstable?	Is it too hazardous for transport in form tested?	Is it too insensitive for acceptance into Class 1?	Is it an explosive substance?*
AN	NO**	NO	YES	YES
AP	NO**	NO	NO	YES
AC	NO**	NO	YES	YES
AZDN	YES	YES***	NO	YES
DNB	NO**	NO	NO	YES
NM	NO**	NO	YES	YES
77% TNP	NO**	NO	NO	YES
Test types used to answer question (see Figure 1)	3(c)	3(a)+3(b) +3(c)+3(d)	2(a)+2(b)	1(a)+1(b)

* Some explosive properties but not necessarily an explosive
** Not tested - result estimated from DSC results and literature data
*** As a Class 1 substance but not as a self-reactive substance

CLASS 1 ASSIGNMENT PROCEDURE

The Class 1 assignment procedure (28) applies to all products that are candidates for Class 1 by the acceptance procedure except those declared to have a mass explosion hazard (assigned to Division 1.1 of Class 1). In this procedure, the results from three types of package test are used to assess the behaviour of a product if a load is involved in a fire resulting from internal or external sources or an explosion from internal sources. As these tests are expensive to perform, they will be shared amongst participating laboratories once all the small scale test data is available. Results from some package tests, although not on these particular samples, have been published in the literature (29). The three types of test to be performed are:

(a) a test on a single package for the purpose of determining whether initiation or ignition in the package causes burning or explosion in the package;

(b) a test on a stack of packages for the purpose of determining whether an explosion in the stack is propagated from one package to another; and

(c) a test on a stack of packages for the purpose of determining how the packages in the stack behave when involved in an external fire simulating a realistic accident.In each test, it is observed whether, and in what way, the surroundings are endangered by blast waves, heat radiation and/or fragment projection. The second type of test (b) may be waived if the contents of the package fail to explode, or explode so feebly as would exclude propagation of the explosive effect from one package to another. For an industrial chemical to be exempted from Class 1, it must not show explosive properties in any of these tests. An exemption should only apply to the type of packaging, quantity of substance and size of package tested.

TRANSPORT OF ENERGETIC SUBSTANCES NOT ACCEPTED INTO CLASS 1

Although the UN recommendations state (30) that "any substance or article having or suspected of having explosive properties shall first be considered for inclusion in Class 1", in practice this is not always done as certain primary characteristics are always given precedence (31). For energetic substances, the types of substance whose primary characteristics always take precedence are:

- self-reactive substances and wetted explosives of Division 4.1; and
- organic peroxides of Division 5.2.

Of the seven test substances, only two (AZDN and 77% TNP) have primary characteristics which are given precedence.

An organic peroxide is defined as an organic substance which contains the bivalent -O-O- structure and a self-reactive substance is defined by the UN(16) as a substance with an exothermic decomposition energy > 300 J/g and a self-accelerating decomposition temperature ≤ 75°C. Self-reactive substances with no explosive properties and of sufficient thermal stability (SADT > 55°C) may be exempted after testing. It is necessary to give these characteristics precedence as, by the Class 1 acceptance procedure, nearly all organic peroxides and self-reactive substances requiring temperature control would be thermally unstable by the thermal stability at 75°C test and would, in theory, be banned from transport. In addition, detonable organic peroxides and self-reactive substances have to pass a more severe detonation in the package test than substances exempted from Class 1 by package tests and hence they could be rejected from Division 5.2 or 4.1 as being too dangerous and not accepted into Class 1 as being insufficiently dangerous. Clearly this gap needs to be closed. The test results were consistent with the classification of 2, 2'-azodi (isobutryonitrile) as a self-reactive substance of Division 4.1.
A wetted explosive of Division 4.1 should be "so packed that the percentage of water will not fall below that stated at any time during transport" and be such that "it is not capable of being detonated by means of a No. 8 test blasting cap at a temperature of 24-27°C or capable of mass detonation through a powerful booster". This last statement is somewhat ambiguous as it implies that either a test of propagation of detonation, a less severe test of sensitivity to detonative shock or a communication test between packages may be used. 70% 2, 4, 6-trinitrophenol is currently considered to be a wetted explosive of Division 4.1 although the solid phase could be considered capable of mass detonation through a powerful booster (see Table7). The results from tests for the effect of heating under confinement suggest that it could explode in a fire. This substance is currently allowed for transport in 225 kg steel drums. It is not clear whether the particular types of drum used have been subjected to fire engulfment tests. If substances with some explosive

properties do not have one of the"primary characteristics" then they are considered for other classes and divisions on an ad hoc basis. This usually means that :

- if an organic liquid, it would be considered for Class 3 (flammable liquids) if its flash-point were ≤ 60.5°C;

- if a solid with oxidizing properties, it would be subjected to a test (32) to see if it increased the burning rate or intensity of fuel when mixed with it and would be considered for Division 5.1 (oxidizing agents);

- if an organic solid, it would be subjected to a burning rate test (33) and would be considered as a readily combustible solid of Division 4.1; and

- if toxic, it would be considered as a poisonous substance of Division 6.1.

Other properties may need to be considered, e.g. susceptibility to oxidative self-heating or corrosivity, but most energetic industrial chemicals would be covered by those given above. Any substance may exhibit more than one of these characteristics and the relative importance of each is decided by the UN Hazard Precedence table. Warning of explosive properties is not always given.

The test substances without "primary characteristics" are currently classified as follows.

Ammonium perchlorate is classified as an explosive (Class 1) or as an oxidising agent according to the particle size involved. It has recently been involved in a major incident at Henderson (29) and may only be considered as an oxidising agent (Division 5.1) if it is rejected from Class 1 by the acceptance or assignment procedure. The substance involved in the Henderson disaster was a nominal 200 micron size propellant-grade ammonium perchlorate. The sample tested by EFL was of a similar specification (0.3% > 300 micron; 14.6% < 300 and ≤ 250 micron; 50.05% < 250 and ≤ 150 micron; 25.65% < 150 and ≤ 106 micron; 11.54% < 106 micron).The results from tests for the effects of ignition and heating under confinement indicate that this particular sample should be subjected to the package tests which are part of the Class 1 assignment procedure. Ammonium perchlorate is an oxidising agent by the UN solid oxidizer test.

Ammonium nitrate, provided that it contains less than 0.2% combustible matter, is currently classified as an oxidizing agent (Division 5.1). All the test results on the crystalline material are consistent with this although it is known (34) that medium and low density ammonium nitrate prills, which can be transported under the same UN entry, are detonable.

1, 3-dinitrobenzene is classified in the Division 6.1 of the UN Recommendations. No warning is given of any explosive properties and there is no restriction on the crystal size. DNB was the only substance found to be sensitive to detonative shock. However, the sample tested (pass 1.7 mm) was of a finer crystal size than the "as received" technical grade chemical. 1, 3-dinitrobenzene is the reference substance for determining explosive properties in relation to the European Community Directive (79/831/EEC) on classification, packaging and labelling of dangerous substances (35). Clearly, if this particular sample was used as a reference substance, it could result in incorrect EC classifications.

Nitromethane (flash-point 35°C) is currently classified as a flammable liquid (Class 3) and it is indicated by special provision that it possesses some dangerous explosive properties. It has been involved (see Merrifield and Roberts (36)) in a number of transport incidents and has been banned from transport in tanks. The test results are consistent with this.

Some formulations of azodicarbonamide have an SADT less than 75°C and should be considered as self-reactive substances. The UN Committee classified the technically pure chemical as a substance "related" to a self-reactive substance in Division 4.1. It deflagrates slowly and gives a "medium" effect when heated under confinement. It is not a readily combustible solid of Division 4.1 by the burning rate test.

TEST METHODS

The UN Recommendations allow a competent authority the discretion to dispense with certain tests, to vary the details of tests, and to require additional tests to obtain reliable and realistic assessments of the hazards of a product. As has been shown, the Hazardous Materials section uses more tests than are strictly necessary to assess the hazards of a product in order that:

(a) an assessment can be made of which tests are most suitable for which types of substance and, in particular, which tests most accurately predict the behaviour of the substance packaged as for transport; and

(b) some of the older test methods, which rank substances by performance, can eventually be replaced by more informative tests which assess the properties under conditions which allow the behaviour of the substance as packaged for transport to be more accurately predicted.

It is already clear from the results obtained that some test methods are better than others for assessing particular properties of different types of substances and that if the minimum level of testing is performed then dangerous properties will be missed. For example, both the Koenen test and the time/pressure test are used as tests for thermal response. The Keonen test indicates that ammonium perchlorate and 77% 2, 4, 6-trinitrophenol should be provisionally accepted into Class 1 but the time/pressure test indicates that ammonium perchlorate and 2, 2'-azodi (isobutyronitrile) should be provisionally accepted. If the Dutch Pressure Vessel test (currently only allowed for organic peroxides and self-reactive substances) was used, it would indicate that only 2, 2'-azodi (isobutyronitrile) should be provisionally accepted. The thermal explosion vessel test (not currently used for classification) would indicate that ammonium perchlorate and 77% 2, 4, 6-trinitrophenol should be provisionally accepted i.e. the same substances as indicated by the Koenen test.

In the OECD-IGUS round-robin (3), it is hoped that more than one laboratory will perform each of the small scale explosivity tests given in the UN Recommendations. When this data is available, it should be possible to obtain a much better idea of the circumstances in which a particular test should be used, the reproducibility of the tests and where test prescriptions should be improved.

CLASSIFICATION SCHEMES

At present there are defined classification schemes for explosives and organic peroxides and one just agreed for self-reactive substances. As indicated earlier, the organic peroxide/self-reactive substance schemes are not yet properly interfaced with the explosive schemes. If a substance has some explosive properties but is not covered by the provisions of another class or division then the current UN Recommendations allow it to be considered non-dangerous i.e. not covered by the Recommendations. This creates a number of problems:

(a) Substances detonable by the Class 1 acceptance procedure but too insensitive for inclusion in Class 1 can be regarded as non-dangerous although they clearly have some explosive properties. Very insensitive substances could be non-dangerous under transport conditions but the question arises as to how well the small scale tests are related to realistic circumstances.

(b) For a chemical desensitised to avoid provisional acceptance into Class 1, there is no provision for it to be regarded as dangerous. If it is not regarded as dangerous then it cannot be restricted to the concentration required for non-inclusion in Class 1 unless there is a Class 1 entry for the higher concentration or it is included in another class or division. Such substances could be treated as desensitised explosives of Division 4.1. However, a level of dilution could be used so as to make the formulation non-dangerous. Principles for classification are required which assess the degree of hazard and allow the more innocuous formulations to be classified as non-dangerous.

(c) Some dangerous substances may leave Class 1 after not exhibiting any explosive hazard in package tests. Clearly, in such cases the substances should still be regarded as dangerous. If they are not, there is no means to restrict them to the packaging which allowed them to pass the package tests.

The UN Committee is increasingly using generic or not otherwise specified entries where a particular property at a particular hazard level is described and substances with those properties may be transported under the general proper shipping name. For example, generic systems of classification have been agreed for organic peroxides and self-reactive substances offering the following benefits:

- ease of introduction of new products and formulations into international transport;
- ability to transport new products once competent authority approval (of the country of origin only) has been given;
- ability to transport samples in quantities up to 10 kg per transport unit;
- more consistent approach to packaging and labelling; and
- ability to transport the less dangerous substances in IBCs or tanks and to obtain exemption from control.

The authors consider that it would be advantageous to work towards a generic system of classification for other types of energetic substances e.g. desensitised explosives. However, it is clear that the currently available tests for assessing explosive properties are not all suitable for all types of substance. An essential prerequisite for setting up such generic systems of classification is to have agreed test methods and criteria for assessing the degree of hazard.

CONCLUSIONS

The EFL test results indicate that all the substances tested have some explosive properties although not necessarily sufficient for classification as an explosive. The divergence in results from tests for nominally the same property suggests that some energetic substances may be not be classified appropriately. It may be necessary to reclassify some substances or to place additional restrictions on their physical form or packaging. In order to ensure that these substances are correctly packaged and labelled for transport, it is necessary to:

(a) improve the test prescriptions, combining the best features of similar tests where possible;

(b) *give clearer guidance on the applicability of particular tests;*

(c) improve the way in which different tests are used in combination;

(d) ensure that the test criteria are set at levels corresponding to the behaviour of the substance in realistic incidents; and

(e) establish principles for classification for thermally stable energetic substances.

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18) Ref. (2), Part I, Test 3(c).

19) Ref. (2), Part III, Test F.1.

20) Ref. (2), Part III, Test F.5.

21) Ref. (2), Part III, Test A.1 (c.f. Part I, test 1(a)(i))

22) Ref .(2), Part I, Test 2(a)(i).

23) Ref. (2), Part III, Test C.1. (c.f. Part I,Test 2(b)(iii))

24) Ref. (2), Part III, Test C.2.

25) *Ref. (2), Part III, Test E.1 (c.f. Part I, Test 1(b)(i) and 2(b)(i))*

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APPENDIX. BRIEF DESCRIPTIONS OF TEST METHODS

Ad hoc ignitability. The reaction of the sample is observed when heated with a gas flame, touched with a red hot rod or thrown into a red hot dish.

Princess incendiary spark test. A 3 g sample in a 15 mm diameter glass tube is bombarded with the sparks from a safety fuse. Observations are made on ignitability and the vigour of any burning.

BAM Fallhammer test. Impact energy is imparted to the sample by subjecting it to the impact from a falling weight. The lowest impact energy at which a positive reaction occurs is recorded. Positive reactions are explosions, flashes or flames.

BAM Friction Apparatus. The sample is spread onto a porcelain plate which is then dragged under a loaded porcelain peg, thereby subjecting the sample to friction. The reaction is noted as the load on the peg is varied, a maximum force of 363 N is available. Positive reactions are explosions, flashes or flames.

Heat accumulation storage test. The sample, contained in a Dewar vessel with heat loss characteristics similar to the transport package, is placed in an oven and kept at the oven temperature until runaway reaction occurs or for up to 7 days with the sample at oven temperature. The lowest temperature for self-accelerating decomposition is determined to the nearest 5°C.

Thermal stability test at 75°C. 100 g of sample and inert reference substance are put into separate glass vessels inside an oven at 75°C. The temperature difference (if any) between the sample and reference substance is measured for 48 hours after they have reached oven temperature. The sample is thermally unstable if the sample temperature exceeds the reference temperature by 3°C.

Ballistic Mortar Mk.IIId test. The explosive power of a substance is measured by subjecting a 10 g sample to the shock from a detonator under heavy confinement in a suspended mortar. The recoil of the mortar is used to assess the explosive power in terms of a percentage of that of the picric acid standard. A value more than 7% that given by picric acid is considered "not low", 2% to 7% "low" and 1% or less "no".

High Pressure Autoclave. Samples of different mass are heated by an electrical heating wire in a pressure vessel and the variation of pressure with time measured. The specific energy (J/g) is determined as a function of the maximum pressure by plotting the ratio of the pressure vessel volume to the sample mass against the reciprocal of the maximum pressure. Specific energy values greater than 100 J/g are considered "not low", 5 to 100 J/g"low" and less than 5 J/g "no".

BAM 50/60 steel tube test. The sample is loose-filled into a steel tube of length 500 mm, internal diameter 50 mm and external diameter 60 mm and is subjected to the detonative shock from a 50 g high explosive donor charge. The detonability of the sample is assessed from the damage to the steel tube and, if necessary, by measurement of the rate of propagation.

BAM 50/60 steel tube test. As above but with initiation by a detonator only.

Time/Pressure test. A 5 g sample is confined in a pressure vessel (fitted with a bursting disk) and subjected to the incendive flame from a match-head surrounded by cambric which has been primed with a pyrotechnic composition.The variation of pressure with time is recorded and the time for the pressure to rise from 690 kPa to 2070 kPa (100-300 psi) is used to assess the hazard that the substance presents of explosion by deflagration. Deflagration is considered "rapid" if the time measured is less than 30 ms, "slow" if a pressure of 2070 kPa is achieved and "no" if this pressure is not achieved. If the time is less than 30 ms, the substance is considered to be thermally sensitive.

Deflagration test. The downward rate of a reaction front is measured by igniting the sample (at 50°C or the emergency temperature) in a Dewar vessel which has vertical observation windows on opposite sides. The rate is deemed to be "rapid" if greater than 5 mm/s, "slow" if between 0.35 and 5 mm/s or"no" if less than or equal to 0.35 mm/s.

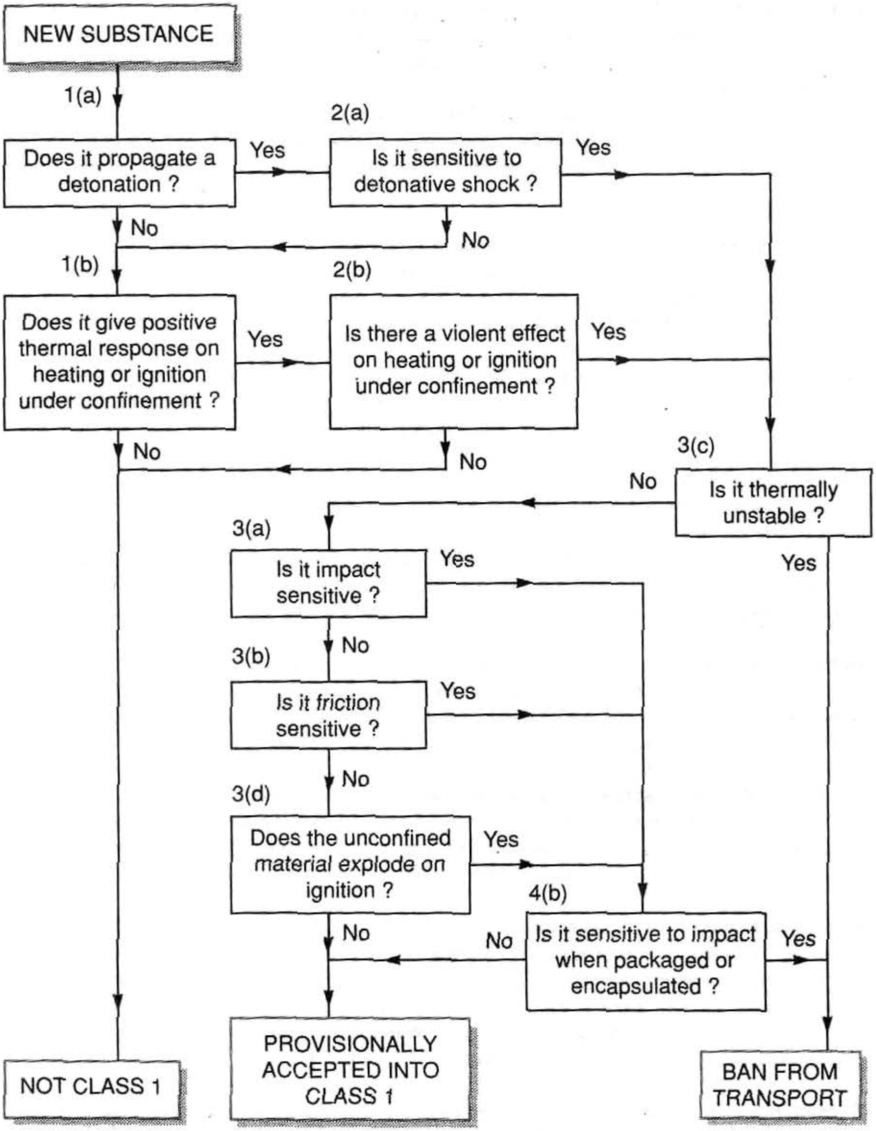
Koenen test. The sample is poured (for liquids) or tamped into a steel tube of 25 mm diameter and 75 mm length to a level 15 mm from the top. The tube is then closed off with an orifice plate and the whole assembly is heated by the flames from 4 burners positioned around the tube. The orifice diameter is decreased from 20 mm until the increased confinement causes the reaction to burst the tube. The largest diameter at which an explosion occurs is termed the "critical" or "limiting" diameter and its value is used to classify the behaviour of the sample when heated under confinement. The mean time, t1, from start of heating to commencement of jetting through the orifice and t2, the subsequent mean duration of jetting to explosion or end of reaction, are also recorded. A critical diameter of 1 mm or 1.5 mm indicates that the substance has some thermal explosive properties and 2 mm or more that it is "thermally sensitive".

Dutch pressure vessel test. The sample is heated in a pressure vessel fitted with an orifice plate and a bursting disk. By successively reducing the orifice diameter the largest diameter is found at which failure of the disk occurs. The time to jetting and duration of jetting is recorded as in the Koenen test. A critical diameter of 9 mm or more indicates a "violent" effect.

Thermal explosion vessel test. A 5 g sample is heated in a sealed steel vessel on a hot plate and the temperature and pressure measured. A "violent"effect on heating under confinement is considered to have occurred if the product of the maximum pressure (MPa) and maximum rate of pressure rise(MPa/s) is greater than 100 MPa^2/s.

Solid oxidizer test. 1:1 and 1:4 mixtures (30 g) of oxidiser to sawdust are formed into a conical pile which is ignited by a loop of electrically heated wire inside the base of the cone. The shortest time from the first observable signs of combustion to end of reaction as compared with that given by 1:1 mixtures of ammonium persulphate, potassium perchlorate and potassium bromate.If the reaction time is faster than that given by the ammonium persulphate mixture then the substance may be considered to be an oxidizing substance of Division 5.1.

Burning rate test. The sample is formed into a 250 mm long train with a triangular cross-section and a small zone near one end wetted with water. The train is ignited at the other end with a gas flame and the rate of propagation of combustion determined and it is noted whether or not combustion continues through the wetted zone. If the burning rate is greater than 2.2 mm/s then the substance is considered to be a readily combustible solid.



Note. The numbers and letters indicate the UN test series and test type.

FIGURE 1 - Class 1 acceptance procedure for new substances not intended to produce a practical explosive or pyrotechnic effect expressed in terms of the properties assessed