



PDHonline Course G376 (3 PDH)

Globally Harmonized Systems – A Brave New OSHA HazComm

Instructor: Jeffrey R. Sotek, PE, CSP, CIH

2020

PDH Online | PDH Center

5272 Meadow Estates Drive
Fairfax, VA 22030-6658
Phone: 703-988-0088
www.PDHonline.com

An Approved Continuing Education Provider

APPENDIX B – PHYSICAL HAZARD CRITERIA (MANDATORY)

B.1 EXPLOSIVES

B.1.1 Definitions and general considerations

B.1.1.1 An explosive chemical is a solid or liquid chemical which is in itself capable by chemical reaction of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings. Pyrotechnic chemicals are included even when they do not evolve gases.

A *pyrotechnic chemical* is a chemical 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 chemical reactions.

An *explosive item* is an item containing one or more explosive chemicals.

A *pyrotechnic item* is an item containing one or more pyrotechnic chemicals.

An *unstable explosive* is an explosive which is thermally unstable and/or too sensitive for normal handling, transport, or use.

An *intentional explosive* is a chemical or item which is manufactured with a view to produce a practical explosive or pyrotechnic effect.

B.1.1.2 The class of explosives comprises:

- (a) Explosive chemicals;
- (b) Explosive items, except devices containing explosive chemicals in such quantity or of such a character that their inadvertent or accidental ignition or initiation shall not cause any effect external to the device either by projection, fire, smoke, heat or loud noise; and
- (c) Chemicals and items not included under (a) and (b) above which are manufactured with the view to producing a practical explosive or pyrotechnic effect.

B.1.2 Classification criteria

Chemicals and items of this class shall be classified as unstable explosives or shall be assigned to one of the following six divisions depending on the type of hazard they present:

- (a) Division 1.1 Chemicals and items which have a mass explosion hazard (a mass explosion is one which affects almost the entire quantity present virtually instantaneously);
- (b) Division 1.2 Chemicals and items which have a projection hazard but not a mass explosion hazard;
- (c) Division 1.3 Chemicals and items which have a fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard:
 - (i) combustion of which gives rise to considerable radiant heat; or
 - (ii) which burn one after another, producing minor blast or projection effects or both;
- (d) Division 1.4 Chemicals and items which present no significant hazard: chemicals and items which present only a small hazard in the event of ignition or initiation. The effects are largely confined to the package and no projection of fragments of appreciable size or range is to be expected. An external fire shall not cause virtually instantaneous explosion of almost the entire contents of the package;
- (e) Division 1.5 Very insensitive chemicals which have a mass explosion hazard: chemicals which have a mass explosion hazard but are so insensitive that there is very little probability of initiation or of transition from burning to detonation under normal conditions;
- (f) Division 1.6 Extremely insensitive items which do not have a mass explosion hazard: items which contain only extremely insensitive detonating chemicals and which demonstrate a negligible probability of accidental initiation or propagation.

B.1.3 Additional classification considerations

B.1.3.1 Explosives shall be classified as unstable explosives or shall be assigned to one of the six divisions identified in B.1.2 in accordance with the three step procedure in Part I of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*. The first step is to ascertain whether the substance or mixture has explosive effects (Test Series 1). The second step is the acceptance procedure (Test Series 2 to 4) and the third step is the assignment to a hazard division (Test Series 5 to 7). The assessment whether a candidate for “ammonium nitrate emulsion or suspension or gel, intermediate for blasting explosives (ANE)” is insensitive enough for inclusion as an oxidizing liquid (see B.13) or an oxidizing solid (see B.14) is determined by Test Series 8 tests.

NOTE: Classification of solid chemicals shall be based on tests performed on the chemical as presented. If, for example, for the purposes of supply or transport, the same chemical is to be presented in a physical form different from that which was tested and which is

considered likely to materially alter its performance in a classification test, classification must be based on testing of the chemical in the new form.

B.1.3.2 Explosive properties are associated with the presence of certain chemical groups in a molecule which can react to produce very rapid increases in temperature or pressure. The screening procedure in B.1.3.3 is aimed at identifying the presence of such reactive groups and the potential for rapid energy release. If the screening procedure identifies the chemical as a potential explosive, the acceptance procedure (see section 10.3 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*) is necessary for classification.

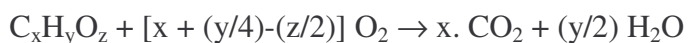
NOTE: Neither a Series 1 type (a) propagation of detonation test nor a Series 2 type (a) test of sensitivity to detonative shock is necessary if the exothermic decomposition energy of organic materials is less than 800 J/g.

B.1.3.3 If a mixture contains any known explosives, the acceptance procedure is necessary for classification.

B.1.3.4 A chemical is not classified as explosive if:

- (a) There are no chemical groups associated with explosive properties present in the molecule. Examples of groups which may indicate explosive properties are given in Table A6.1 in Appendix 6 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*; or
- (b) The substance contains chemical groups associated with explosive properties which include oxygen and the calculated oxygen balance is less than -200.

The oxygen balance is calculated for the chemical reaction:



using the formula: oxygen balance = $-1600 [2x + (y/2) - z]$ /molecular weight;

- (c) The organic substance or a homogenous mixture of organic substances contains chemical groups associated with explosive properties but the exothermic decomposition energy is less than 500 J/g and the onset of exothermic decomposition is below 500°C. The exothermic decomposition energy may be determined using a suitable calorimetric technique; or
- (d) For mixtures of inorganic oxidizing substances with organic material(s), the concentration of the inorganic oxidizing substance is:

less than 15 %, by mass, if the oxidizing substance is assigned to Category 1 or 2;

less than 30 %, by mass, if the oxidizing substance is assigned to Category 3.

B.2 FLAMMABLE GASES

B.2.1 Definition

Flammable gas means a gas having a flammable range with air at 20°C and a standard pressure of 101.3 kPa (14.7 psi).

B.2.2 Classification criteria

A flammable gas shall be classified in one of the two categories for this class in accordance with Table B.2.1:

Table B.2.1: Criteria for flammable gases

Category	Criteria
1	Gases, which at 20°C (68°F) and a standard pressure of 101.3 kPa (14.7 psi): (a) are ignitable when in a mixture of 13% or less by volume in air; or (b) have a flammable range with air of at least 12 percentage points regardless of the lower flammable limit.
2	Gases, other than those of Category 1, which, at 20°C (68°F) and a standard pressure of 101.3 kPa (14.7 psi), have a flammable range while mixed in air.

NOTE: Aerosols should not be classified as flammable gases. See B.3.

B.2.3 Additional classification considerations

Flammability shall be determined by tests or by calculation in accordance with methods adopted by ISO (see ISO 10156:1996 “Gases and gas mixtures – Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets”). Where insufficient data are available to use these methods, equivalent validated methods may be used.

B.3 FLAMMABLE AEROSOLS

B.3.1 Definition

Aerosol means any non-refillable receptacle containing a gas compressed, liquefied or dissolved under pressure, and fitted with a release device allowing the contents to be ejected as particles in suspension in a gas, or as a foam, paste, powder, liquid or gas.

B.3.2 Classification criteria

B.3.2.1 Aerosols shall be considered for classification as flammable if they contain any component which is classified as flammable in accordance with this Appendix, i.e.:

Flammable liquids (see B.6);

Flammable gases (see B.2);

Flammable solids (see B.7).

NOTE 1: Flammable components do not include pyrophoric, self-heating or water-reactive chemicals.

NOTE 2: Flammable aerosols do not fall additionally within the scope of flammable gases, flammable liquids, or flammable solids.

B.3.2.2 A flammable aerosol shall be classified in one of the two categories for this class in accordance with Table B.3.1.

Table B.3.1: Criteria for flammable aerosols

Category	Criteria
1	Contains $\geq 85\%$ of flammable components and the chemical heat of combustion is ≥ 30 kJ/g; or a) for spray aerosols, in the ignition distance test, ignition occurs at a distance ≥ 75 cm, or b) for foam aerosols, in the aerosol foam flammability test (i) the flame height is ≥ 20 cm and the flame duration ≥ 2 s; or (ii) the flame height is ≥ 4 cm and the flame duration ≥ 7 s
2	Contains $> 1\%$ flammable components, or the heat of combustion is ≥ 20 kJ/g; and a) for spray aerosols, in the ignition distance test, ignition occurs at a distance ≥ 15 cm, or in the enclosed space ignition test, the (i) time equivalent is ≤ 300 s/m ³ ; or (ii) deflagration density is ≤ 300 g/m ³ b) for foam aerosols, in the aerosol foam flammability test, the flame height is ≥ 4 cm and the flame duration is ≥ 2 s and it does not meet the criteria for Category 1

NOTE: Aerosols not submitted to the flammability classification procedures in this Appendix shall be classified as extremely flammable (Category 1).

B.3.3 Additional classification considerations

B.3.3.1 To classify a flammable aerosol, data on its flammable components, on its chemical heat of combustion and, if applicable, the results of the aerosol foam flammability test (for foam aerosols) and of the ignition distance test and enclosed space test (for spray aerosols) are necessary.

B.3.3.2 The chemical heat of combustion (ΔH_c), in kilojoules per gram (kJ/g), is the product of the theoretical heat of combustion (ΔH_{comb}), and a combustion efficiency, usually less than 1.0 (a typical combustion efficiency is 0.95 or 95%).

For a composite aerosol formulation, the chemical heat of combustion is the summation of the weighted heats of combustion for the individual components, as follows:

$$\Delta H_c (\text{product}) = \sum_i^n [w_i\% \times \Delta H_c(i)]$$

where:

ΔH_c	=	chemical heat of combustion (kJ/g);
$w_i\%$	=	mass fraction of component i in the product;
$\Delta H_c(i)$	=	specific heat of combustion (kJ/g) of component i in the product;

The chemical heats of combustion shall be found in literature, calculated or determined by tests (see ASTM D240-02(2007) – Standard Test Methods for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter, ISO/FDIS 13943:1999, 86.1 to 86.3 – Fire safety – Vocabulary, and NFPA 30B – Code for the Manufacture and Storage of Aerosol Products, 2007 Edition).

B.3.3.3 The Ignition distance test, Enclosed space ignition test and Aerosol foam flammability test shall be performed in accordance with sub-sections 31.4, 31.5 and 31.6 of the of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*.

B.4 OXIDIZING GASES

B.4.1 Definition

Oxidizing gas means any gas which may, generally by providing oxygen, cause or contribute to the combustion of other material more than air does.

NOTE: “Gases which cause or contribute to the combustion of other material more than air does” means pure gases or gas mixtures with an oxidizing power greater than 23.5% (as determined, by a method specified in ISO 10156:1996 or 10156-2:2005 or an equivalent testing method.)

B.4.2 Classification criteria

An oxidizing gas shall be classified in a single category for this class in accordance with Table B.4.1:

Table B.4.1: Criteria for oxidizing gases

Category	Criteria
1	Any gas which may, generally by providing oxygen, cause or contribute to the combustion of other material more than air does.

B.4.3 Additional classification considerations

Classification shall be in accordance with tests or calculation methods as described in ISO 10156:1996 “Gases and gas mixtures – Determination of fire potential and oxidizing ability for the selection of cylinder valve outlet” and ISO 10156-2:2005 “Gas cylinders, Gases and gas mixtures. Part 2: Determination of oxidizing ability of toxic and corrosive gases and gas mixtures”.

B.5 GASES UNDER PRESSURE

B.5.1 Definition

Gases under pressure are gases which are contained in a receptacle at a pressure of 200 kPa (29 psi) (gauge) or more, or which are liquefied or liquefied and refrigerated.

They comprise compressed gases, liquefied gases, dissolved gases and refrigerated liquefied gases.

B.5.2 Classification criteria

Gases under pressure shall be classified in one of four groups in accordance with Table B.5.1:

Table B.5.1: Criteria for gases under pressure

Group	Criteria
Compressed gas	A gas which when under pressure is entirely gaseous at -50°C (-58°F); including all gases with a critical temperature ¹ $\leq -50^{\circ}\text{C}$ (-58°F).
Liquefied gas	A gas which when under pressure is partially liquid at temperatures above -50°C (-58°F). A distinction is made between: (a) High pressure liquefied gas: a gas with a critical temperature ¹ between -50°C (-58°F) and $+65^{\circ}\text{C}$ (149°F); and (b) Low pressure liquefied gas: a gas with a critical temperature ¹ above $+65^{\circ}\text{C}$ (149°F).
Refrigerated liquefied gas	A gas which is made partially liquid because of its low temperature.
Dissolved gas	A gas which when under pressure is dissolved in a liquid phase solvent.

(1) *The critical temperature is the temperature above which a pure gas cannot be liquefied, regardless of the degree of compression.*

B.6 FLAMMABLE LIQUIDS

B.6.1 Definition

Flammable liquid means a liquid having a flash point of not more than 93°C (199.4°F).

B.6.2 Classification criteria

A flammable liquid shall be classified in one of four categories in accordance with Table B.6.1:

Table B.6.1: Criteria for flammable liquids

Category	Criteria
1	Flash point < 23°C (73.4°F) and initial boiling point ≤ 35°C (95°F)
2	Flash point < 23°C (73.4°F) and initial boiling point > 35°C (95°F)
3	Flash point ≥ 23°C (73.4°F) and ≤ 60°C (140°F)
4	Flash point > 60°C (140°F) and ≤ 93°C (199.4°F)

B.6.3 Additional classification considerations

The flash point shall be determined in accordance with Standard Method of Test for Flash Point by Tag Closed Tester (ASTM D 56-93), Standard Methods of Test for Flash Point of Liquids by Setaflash Closed Tester (ASTM D 3278-96), Standard Methods of Test for Flash Point by Small Scale Closed Tester (ASTM D 3828-93), Standard Method of Test for Flash Point by Pensky-Martens Closed Tester (ASTM D 0093-96), or any other method specified in GHS Revision 3, Chapter 2.6.

The initial boiling point shall be determined in accordance with “Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure (ASTM D86-07a) or Standard Test Method for Distillation Range of Volatile Organic Liquids (ASTM D1078-05).

B.7 FLAMMABLE SOLIDS

B.7.1 Definitions

Flammable solid means a solid which is a readily combustible solid, or which may cause or contribute to fire through friction.

Readily combustible solids are powdered, granular, or pasty chemicals which are dangerous if they can be easily ignited by brief contact with an ignition source, such as a burning match, and if the flame spreads rapidly.

B.7.2 Classification criteria

B.7.2.1 Powdered, granular or pasty chemicals shall be classified as flammable solids when the time of burning of one or more of the test runs, performed in accordance with the test method described in the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*, Part III, sub-section 33.2.1, is less than 45 s or the rate of burning is more than 2.2 mm/s.

B.7.2.2 Powders of metals or metal alloys shall be classified as flammable solids when they can be ignited and the reaction spreads over the whole length of the sample in 10 min or less.

B.7.2.3 Solids which may cause fire through friction shall be classified in this class by analogy with existing entries (e.g., matches) until definitive criteria are established.

B.7.2.4 A flammable solid shall be classified in one of the two categories for this class using Method N.1 as described in Part III, sub-section 33.2.1 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*, in accordance with Table B.7.1:

Table B.7.1: Criteria for flammable solids

Category	Criteria
1	Burning rate test: Chemicals other than metal powders: (a) wetted zone does not stop fire; and (b) burning time < 45 s or burning rate > 2.2 mm/s Metal powders: burning time ≤ 5 min
2	Burning rate test: Chemicals other than metal powders: (a) wetted zone stops the fire for at least 4 min; and (b) burning time < 45 s or burning rate > 2.2 mm/s Metal powders: burning time > 5 min and ≤ 10 min

NOTE: Classification of solid chemicals shall be based on tests performed on the chemical as presented. If, for example, for the purposes of supply or transport, the same chemical is to be presented in a physical form different from that which was tested and which is considered likely to materially alter its performance in a classification test, classification must be based on testing of the chemical in the new form.

B.8 SELF-REACTIVE CHEMICALS

B.8.1 Definitions

Self-reactive chemicals are thermally unstable liquid or solid chemicals liable to undergo a strongly exothermic decomposition even without participation of oxygen (air). This definition excludes chemicals classified under this section as explosives, organic peroxides, oxidizing liquids or oxidizing solids.

A self-reactive chemical is regarded as possessing explosive properties when in laboratory testing the formulation is liable to detonate, to deflagrate rapidly or to show a violent effect when heated under confinement.

B.8.2 Classification criteria

B.8.2.1 A self-reactive chemical shall be considered for classification in this class unless:

- (a) It is classified as an explosive according to B.1 of this appendix;
- (b) It is classified as an oxidizing liquid or an oxidizing solid according to B.13 or B.14 of this appendix, except that a mixture of oxidizing substances which contains 5% or more of combustible organic substances shall be classified as a self-reactive chemical according to the procedure defined in B.8.2.2;
- (c) It is classified as an organic peroxide according to B.15 of this appendix;
- (d) Its heat of decomposition is less than 300 J/g; or
- (e) Its self-accelerating decomposition temperature (SADT) is greater than 75°C (167°F) for a 50 kg package.

B.8.2.2 Mixtures of oxidizing substances, meeting the criteria for classification as oxidizing liquids or oxidizing solids, which contain 5% or more of combustible organic substances and which do not meet the criteria mentioned in B.8.2.1 (a), (c), (d) or (e), shall be subjected to the self-reactive chemicals classification procedure in B.8.2.3. Such a mixture showing the properties of a self-reactive chemical type B to F shall be classified as a self-reactive chemical.

B.8.2.3 Self-reactive chemicals shall be classified in one of the seven categories of “types A to G” for this class, according to the following principles:

- (a) Any self-reactive chemical which can detonate or deflagrate rapidly, as packaged, will be defined as **self-reactive chemical TYPE A**;
- (b) Any self-reactive chemical possessing explosive properties and which, as packaged, neither detonates nor deflagrates rapidly, but is liable to undergo a

thermal explosion in that package will be defined as **self-reactive chemical TYPE B**;

- (c) Any self-reactive chemical possessing explosive properties when the chemical as packaged cannot detonate or deflagrate rapidly or undergo a thermal explosion will be defined as **self-reactive chemical TYPE C**;
- (d) Any self-reactive chemical which in laboratory testing:
 - (i) detonates partially, does not deflagrate rapidly and shows no violent effect when heated under confinement; or
 - (ii) does not detonate at all, deflagrates slowly and shows no violent effect when heated under confinement; or
 - (iii) does not detonate or deflagrate at all and shows a medium effect when heated under confinement;will be defined as self-reactive chemical TYPE D;
- (e) Any self-reactive chemical which, in laboratory testing, neither detonates nor deflagrates at all and shows low or no effect when heated under confinement will be defined as **self-reactive chemical TYPE E**;
- (f) Any self-reactive chemical which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows only a low or no effect when heated under confinement as well as low or no explosive power will be defined as **self-reactive chemical TYPE F**;
- (g) Any self-reactive chemical which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows no effect when heated under confinement nor any explosive power, provided that it is thermally stable (self-accelerating decomposition temperature is 60°C (140°F) to 75°C (167°F) for a 50 kg package), and, for liquid mixtures, a diluent having a boiling point greater than or equal to 150°C (302°F) is used for desensitization will be defined as **self-reactive chemical TYPE G**. If the mixture is not thermally stable or a diluent having a boiling point less than 150°C (302°F) is used for desensitization, the mixture shall be defined as self-reactive chemical TYPE F.

B.8.3 Additional classification considerations

B.8.3.1 For purposes of classification, the properties of self-reactive chemicals shall be determined in accordance with test series A to H as described in Part II of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*.

B.8.3.2 Self-accelerating decomposition temperature (SADT) shall be determined in accordance with the *UN Recommendations for the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*, Part II, section 28.

B.8.3.3 The classification procedures for self-reactive substances and mixtures need not be applied if:

- (a) There are no chemical groups present in the molecule associated with explosive or self-reactive properties; examples of such groups are given in Tables A6.1 and A6.2 in the Appendix 6 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*; or
- (b) For a single organic substance or a homogeneous mixture of organic substances, the estimated SADT is greater than 75°C (167°F) or the exothermic decomposition energy is less than 300 J/g. The onset temperature and decomposition energy may be estimated using a suitable calorimetric technique (see 20.3.3.3 in Part II of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*).

B.9 PYROPHORIC LIQUIDS

B.9.1 Definition

Pyrophoric liquid means a liquid which, even in small quantities, is liable to ignite within five minutes after coming into contact with air.

B.9.2 Classification criteria

A pyrophoric liquid shall be classified in a single category for this class using test N.3 in Part III, sub-section 33.3.1.5 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*, in accordance with Table B.9.1:

Table B.9.1: Criteria for pyrophoric liquids

Category	Criteria
1	The liquid ignites within 5 min when added to an inert carrier and exposed to air, or it ignites or chars a filter paper on contact with air within 5 min.

B.9.3 Additional classification considerations

The classification procedure for pyrophoric liquids need not be applied when experience in production or handling shows that the chemical does not ignite spontaneously on coming into contact with air at normal temperatures (i.e. the substance is known to be stable at room temperature for prolonged periods of time (days)).

B.10 PYROPHORIC SOLIDS

B.10.1 Definition

Pyrophoric solid means a solid which, even in small quantities, is liable to ignite within five minutes after coming into contact with air.

B.10.2 Classification criteria

A pyrophoric solid shall be classified in a single category for this class using test N.2 in Part III, sub-section 33.3.1.4 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition* in accordance with Table B.10.1:

Table B.10.1: Criteria for pyrophoric solids

Category	Criteria
1	The solid ignites within 5 min of coming into contact with air.

NOTE: Classification of solid chemicals shall be based on tests performed on the chemical as presented. If, for example, for the purposes of supply or transport, the same chemical is to be presented in a physical form different from that which was tested and which is considered likely to materially alter its performance in a classification test, classification must be based on testing of the chemical in the new form.

B.10.3 Additional classification considerations

The classification procedure for pyrophoric solids need not be applied when experience in production or handling shows that the chemical does not ignite spontaneously on coming into contact with air at normal temperatures (i.e. the chemical is known to be stable at room temperature for prolonged periods of time (days)).

B.11 SELF-HEATING CHEMICALS

B.11.1 Definition

A *self-heating chemical* is a solid or liquid chemical, other than a pyrophoric liquid or solid, which, by reaction with air and without energy supply, is liable to self-heat; this chemical differs from a pyrophoric liquid or solid in that it will ignite only when in large amounts (kilograms) and after long periods of time (hours or days).

NOTE: Self-heating of a substance or mixture is a process where the gradual reaction of that substance or mixture with oxygen (in air) generates heat. If the rate of heat production exceeds the rate of heat loss, then the temperature of the substance or mixture will rise which, after an induction time, may lead to self-ignition and combustion.

B.11.2 Classification criteria

B.11.2.1 A self-heating chemical shall be classified in one of the two categories for this class if, in tests performed in accordance with test method N.4 in Part III, sub-section 33.3.1.6 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*, the result meets the criteria shown in Table B.11.1.

Table B.11.1: Criteria for self-heating chemicals

Category	Criteria
1	A positive result is obtained in a test using a 25 mm sample cube at 140°C (284°F)
2	A negative result is obtained in a test using a 25 mm cube sample at 140°C (284°F), a positive result is obtained in a test using a 100 mm sample cube at 140°C (284°F), and: (a) the unit volume of the chemical is more than 3 m ³ ; or (b) a positive result is obtained in a test using a 100 mm cube sample at 120°C (248°F) and the unit volume of the chemical is more than 450 liters; or (c) a positive result is obtained in a test using a 100 mm cube sample at 100°C (212°F).

B.11.2.2 Chemicals with a temperature of spontaneous combustion higher than 50°C (122°F) for a volume of 27 m³ shall not be classified as self-heating chemicals.

B.11.2.3 Chemicals with a spontaneous ignition temperature higher than 50°C (122°F) for a volume of 450 liters shall not be classified in Category 1 of this class.

B.11.3 Additional classification considerations

B.11.3.1 The classification procedure for self-heating chemicals need not be applied if the results of a screening test can be adequately correlated with the classification test and an appropriate safety margin is applied.

B.11.3.2 Examples of screening tests are:

- (a) The Grewer Oven test (VDI guideline 2263, part 1, 1990, Test methods for the Determination of the Safety Characteristics of Dusts) with an onset temperature 80°K above the reference temperature for a volume of 1 *l*;
- (b) The Bulk Powder Screening Test (Gibson, N. Harper, D. J. Rogers, R. Evaluation of the fire and explosion risks in drying powders, Plant Operations Progress, 4 (3), 181-189, 1985) with an onset temperature 60°K above the reference temperature for a volume of 1 *l*.

B.12 CHEMICALS WHICH, IN CONTACT WITH WATER, EMIT FLAMMABLE GASES

B.12.1 Definition

Chemicals which, in contact with water, emit flammable gases are solid or liquid chemicals which, by interaction with water, are liable to become spontaneously flammable or to give off flammable gases in dangerous quantities.

B.12.2 Classification criteria

B.12.2.1 A chemical which, in contact with water, emits flammable gases shall be classified in one of the three categories for this class, using test N.5 in Part III, sub-section 33.4.1.4 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*, in accordance with Table B.12.1:

**Table B.12.1: Criteria for chemicals which, in contact with water,
emit flammable gases**

Category	Criteria
1	Any chemical which reacts vigorously with water at ambient temperatures and demonstrates generally a tendency for the gas produced to ignite spontaneously, or which reacts readily with water at ambient temperatures such that the rate of evolution of flammable gas is equal to or greater than 10 liters per kilogram of chemical over any one minute.
2	Any chemical which reacts readily with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 20 liters per kilogram of chemical per hour, and which does not meet the criteria for Category 1.
3	Any chemical which reacts slowly with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 1 liter per kilogram of chemical per hour, and which does not meet the criteria for Categories 1 and 2.

NOTE: Classification of solid chemicals shall be based on tests performed on the chemical as presented. If, for example, for the purposes of supply or transport, the same chemical is to be presented in a physical form different from that which was tested and which is considered likely to materially alter its performance in a classification test, classification must be based on testing of the chemical in the new form.

B.12.2.2 A chemical is classified as a chemical which, in contact with water, emits flammable gases if spontaneous ignition takes place in any step of the test procedure.

B.12.3 Additional classification considerations

The classification procedure for this class need not be applied if:

- (a) The chemical structure of the chemical does not contain metals or metalloids;

- (b) Experience in production or handling shows that the chemical does not react with water, (e.g., the chemical is manufactured with water or washed with water); or
- (c) The chemical is known to be soluble in water to form a stable mixture.

B.13 OXIDIZING LIQUIDS

B.13.1 Definition

Oxidizing liquid means a liquid which, while in itself not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other material.

B.13.2 Classification criteria

An oxidizing liquid shall be classified in one of the three categories for this class using test O.2 in Part III, sub-section 34.4.2 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*, in accordance with Table B.13.1:

Table B.13.1: Criteria for oxidizing liquids

Category	Criteria
1	Any chemical which, in the 1:1 mixture, by mass, of chemical and cellulose tested, spontaneously ignites; or the mean pressure rise time of a 1:1 mixture, by mass, of chemical and cellulose is less than that of a 1:1 mixture, by mass, of 50% perchloric acid and cellulose;
2	Any chemical which, in the 1:1 mixture, by mass, of chemical and cellulose tested, exhibits a mean pressure rise time less than or equal to the mean pressure rise time of a 1:1 mixture, by mass, of 40% aqueous sodium chlorate solution and cellulose; and the criteria for Category 1 are not met;
3	Any chemical which, in the 1:1 mixture, by mass, of chemical and cellulose tested, exhibits a mean pressure rise time less than or equal to the mean pressure rise time of a 1:1 mixture, by mass, of 65% aqueous nitric acid and cellulose; and the criteria for Categories 1 and 2 are not met.

B.13.3 Additional classification considerations

B.13.3.1 For organic chemicals, the classification procedure for this class shall not be applied if:

- (a) The chemical does not contain oxygen, fluorine or chlorine; or
- (b) The chemical contains oxygen, fluorine or chlorine and these elements are chemically bonded only to carbon or hydrogen.

B.13.3.2 For inorganic chemicals, the classification procedure for this class shall not be applied if the chemical does not contain oxygen or halogen atoms.

B.13.3.3 In the event of divergence between tests results and known experience in the handling and use of chemicals which shows them to be oxidizing, judgements based on known experience shall take precedence over test results.

B.13.3.4 In cases where chemicals generate a pressure rise (too high or too low), caused by chemical reactions not characterizing the oxidizing properties of the chemical, the test described in Part III, sub-section 34.4.2 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition* shall be repeated with an inert

substance (e.g., diatomite (kieselguhr)) in place of the cellulose in order to clarify the nature of the reaction.

B.14 OXIDIZING SOLIDS

B.14.1 Definition

Oxidizing solid means a solid which, while in itself is not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other material.

B.14.2 Classification criteria

An oxidizing solid shall be classified in one of the three categories for this class using test O.1 in Part III, sub-section 34.4.1 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*, in accordance with Table B.14.1:

Table B.14.1: Criteria for oxidizing solids

Category	Criteria
1	Any chemical which, in the 4:1 or 1:1 sample-to-cellulose ratio (by mass) tested, exhibits a mean burning time less than the mean burning time of a 3:2 mixture, by mass, of potassium bromate and cellulose.
2	Any chemical which, in the 4:1 or 1:1 sample-to-cellulose ratio (by mass) tested, exhibits a mean burning time equal to or less than the mean burning time of a 2:3 mixture (by mass) of potassium bromate and cellulose and the criteria for Category 1 are not met.
3	Any chemical which, in the 4:1 or 1:1 sample-to-cellulose ratio (by mass) tested, exhibits a mean burning time equal to or less than the mean burning time of a 3:7 mixture (by mass) of potassium bromate and cellulose and the criteria for Categories 1 and 2 are not met.

NOTE 1: Some oxidizing solids may present explosion hazards under certain conditions (e.g., when stored in large quantities). For example, some types of ammonium nitrate may give rise to an explosion hazard under extreme conditions and the “Resistance to detonation test” (IMO: Code of Safe Practice for Solid Bulk Cargoes, 2005, Annex 3, Test 5) may be used to assess this hazard. When information indicates that an oxidizing solid may present an explosion hazard, it shall be indicated on the Safety Data Sheet.

NOTE 2: Classification of solid chemicals shall be based on tests performed on the chemical as presented. If, for example, for the purposes of supply or transport, the same chemical is to be presented in a physical form different from that which was tested and which is considered likely to materially alter its performance in a classification test, classification must be based on testing of the chemical in the new form.

B.14.3 Additional classification considerations

B.14.3.1 For organic chemicals, the classification procedure for this class shall not be applied if:

- (a) The chemical does not contain oxygen, fluorine or chlorine; or

- (b) The chemical contains oxygen, fluorine or chlorine and these elements are chemically bonded only to carbon or hydrogen.

B.14.3.2 For inorganic chemicals, the classification procedure for this class shall not be applied if the chemical does not contain oxygen or halogen atoms.

B.14.3.3 In the event of divergence between tests results and known experience in the handling and use of chemicals which shows them to be oxidizing, judgements based on known experience shall take precedence over test results.

B.15 ORGANIC PEROXIDES

B.15.1 Definition

B.15.1.1 *Organic peroxide* means a liquid or solid organic chemical which contains the bivalent -O-O- structure and as such is considered a derivative of hydrogen peroxide, where one or both of the hydrogen atoms have been replaced by organic radicals. The term organic peroxide includes organic peroxide mixtures containing at least one organic peroxide. Organic peroxides are thermally unstable chemicals, which may undergo exothermic self-accelerating decomposition. In addition, they may have one or more of the following properties:

- (a) be liable to explosive decomposition;
- (b) burn rapidly;
- (c) be sensitive to impact or friction;
- (d) react dangerously with other substances.

B.15.1.2 An organic peroxide is regarded as possessing explosive properties when in laboratory testing the formulation is liable to detonate, to deflagrate rapidly or to show a violent effect when heated under confinement.

B.15.2 Classification criteria

B.15.2.1 Any organic peroxide shall be considered for classification in this class, unless it contains:

- (a) not more than 1.0% available oxygen from the organic peroxides when containing not more than 1.0% hydrogen peroxide; or
- (b) not more than 0.5% available oxygen from the organic peroxides when containing more than 1.0% but not more than 7.0% hydrogen peroxide.

NOTE: The available oxygen content (%) of an organic peroxide mixture is given by the formula:

$$16 \times \sum_i^n \left(\frac{n_i \times c_i}{m_i} \right)$$

where:

- n_i = number of peroxygen groups per molecule of organic peroxide i;
- c_i = concentration (mass %) of organic peroxide i;
- m_i = molecular mass of organic peroxide i.

B.15.2.2 Organic peroxides shall be classified in one of the seven categories of “Types A to G” for this class, according to the following principles:

- (a) Any organic peroxide which, as packaged, can detonate or deflagrate rapidly shall be defined as **organic peroxide TYPE A**;
- (b) Any organic peroxide possessing explosive properties and which, as packaged, neither detonates nor deflagrates rapidly, but is liable to undergo a thermal explosion in that package shall be defined as **organic peroxide TYPE B**;
- (c) Any organic peroxide possessing explosive properties when the chemical as packaged cannot detonate or deflagrate rapidly or undergo a thermal explosion shall be defined as **organic peroxide TYPE C**;
- (d) Any organic peroxide which in laboratory testing:
 - (i) detonates partially, does not deflagrate rapidly and shows no violent effect when heated under confinement; or
 - (ii) does not detonate at all, deflagrates slowly and shows no violent effect when heated under confinement; or
 - (iii) does not detonate or deflagrate at all and shows a medium effect when heated under confinement;shall be defined as **organic peroxide TYPE D**;
- (e) Any organic peroxide which, in laboratory testing, neither detonates nor deflagrates at all and shows low or no effect when heated under confinement shall be defined as **organic peroxide TYPE E**;
- (f) Any organic peroxide which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows only a low or no effect when heated under confinement as well as low or no explosive power shall be defined as **organic peroxide TYPE F**;
- (g) Any organic peroxide which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows no effect when heated under confinement nor any explosive power, provided that it is thermally stable (self-accelerating decomposition temperature is 60°C (140°F) or higher for a 50 kg package), and, for liquid mixtures, a diluent having a boiling point of not less than 150°C (302°F) is used for desensitization, shall be defined as **organic peroxide TYPE G**. If the organic peroxide is not thermally stable or a diluent having a boiling point less than 150°C (302°F) is used for desensitization, it shall be defined as organic peroxide TYPE F.

B.15.3 Additional classification considerations

B.15.3.1 For purposes of classification, the properties of organic peroxides shall be determined in accordance with test series A to H as described in Part II of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*.

B.15.3.2 Self-accelerating decomposition temperature (SADT) shall be determined in accordance with the *UN Recommendations for the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*, Part II, section 28.

B.15.3.3 Mixtures of organic peroxides may be classified as the same type of organic peroxide as that of the most dangerous ingredient. However, as two stable ingredients can form a thermally less stable mixture, the SADT of the mixture shall be determined.

B.16 CORROSIVE TO METALS

B.16.1 Definition

A *chemical which is corrosive to metals* means a chemical which by chemical action will materially damage, or even destroy, metals.

B.16.2 Classification criteria

A chemical which is corrosive to metals shall be classified in a single category for this class, using the test in Part III, sub-section 37.4 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth Revised Edition*, in accordance with Table B.16.1:

Table B.16.1: Criteria for chemicals corrosive to metal

Category	Criteria
1	Corrosion rate on either steel or aluminium surfaces exceeding 6.25 mm per year at a test temperature of 55°C (131°F) when tested on both materials.

NOTE: Where an initial test on either steel or aluminium indicates the chemical being tested is corrosive the follow-up test on the other metal is not necessary.

B.16.3 Additional classification considerations

The specimen to be used for the test shall be made of the following materials:

- (a) For the purposes of testing steel, steel types S235JR+CR (1.0037 resp.St 37-2), S275J2G3+CR (1.0144 resp.St 44-3), ISO 3574, Unified Numbering System (UNS) G 10200, or SAE 1020;
- (b) For the purposes of testing aluminium: non-clad types 7075-T6 or AZ5GU-T6.