

## AN ALTERNATIVE METHODOLOGY ADDRESSING UNITED NATIONS (UN) CLASSIFICATION TYPE FOR SELF-REACTIVE SUBSTANCES\*

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As an alternative to UN testing (such as A.5, C.1, C.2, E.1, E.2, etc.), one easy to perform 10 g ARSST test can produce the necessary information to determine the packaging Classification Type consistent with UN guidelines.

This approach is consistent with UN Guidelines which allow other procedures to be used provided that adequate correlation has been obtained with the classification tests on a representative range of substances.

### UN Guidelines

To demonstrate safe transportation the UN Guidelines include 7 Classifications (A-G) that are determined by performing specific tests including up to 8 Test Series (A-H). Self-reacting substances should be subjected to these classifications procedures unless their heat of decomposition is less than 300 J/g or their self-accelerating decomposition temperature (SADT) is greater than 75°C for a 50 kg package. Self-reactive substances are classified into seven types (A-G) according to the hazard, where the classification of types A to G is directly related to the maximum quantity allowed in one package. As such, the detailed classification procedures required by the UN guidelines can be simplified since the hazard potential to first order can be related directly to the energy release rate or the rate of pressure rise associated with the chemical decomposition.

\*Part II Classification Procedures, Test Methods and Criteria Relating to Self-Reactive Substances of Division 4.1 and Organic Peroxides of Division 5.2, Recommendations on the TRANSPORT of DANGEROUS GOODS, Manual of Tests and Criteria, Fifth revised edition, UNITED NATIONS, New York and Geneva, 2009.

The recommended sequences of testing is test series E, H, F, C and then A. Some tests may not be required. F is relevant only if the results from E is Low or No, and material is to be considered for transport in IBCs or tanks, or for exemption. Test G is relevant only if result from E is Violent.

In reviewing the UN Guidelines Flow Chart Scheme for Self-Reactive Substances and Organic Peroxides it is of interest to note that all exit gates referring to acceptable packing sizes for transport (Exits B through G) addresses the question) (Test Series E)

"What Is The Effect Of Heating It Under Defined Confinement?" (1)

as highlighted in Figure 1.

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If the answer to Question (1) is Medium the maximum package size is limited to 50 kg (Exits C and D). If the answer is Violent the package size is again limited to 50 kg (Exit C) if the answer to question (2) as highlighted in Figure 1 (Test Series G)

"Can It Explode As Packaged For Transport?" (2)

is No. If the answer is Yes, the package size is limited to 25 kg or less with "Explosive" subsidiary Risk Label (Exit B). The answer to this question depends on the package type. For the same reactive material the answer may be No for a card box (low pressure capability) while it is Yes for a stronger metal box.

If the answer to Question (1) is Low the maximum package size for transport is limited to 400 kg (Exit E), provided the substance in laboratory testing neither detonates nor deflagrates at all. This answer also implies that the material May Be Considered For Transport In IBCs, or Tanks (Exit F). If the answer to Question (1) is No, the transport requirement May Be Considered For Exemption (Exit G). If the answers to Question (1) are Low or No it is reasonable to conclude that answers to Question (3) as highlighted in Figure 1 (Test Series F)

"What is Its Explosive Power?" (3)

are also Low or No which are consistent with tests performed according to UN Guidelines.

The E-series tests relate directly to energy release rate or the rate of pressure rise associated with the chemical decomposition and is well illustrated by the E.2 Dutch pressure vessel tests.

The volume of the pressure vessel (50 mm diameter and height of 94.5 mm) is  $1.85 \cdot 10^{-4} \text{ m}^3$  and includes a 38 mm Bursting disc rated at  $620 \pm 60 \text{ kPa}$  at  $22^\circ\text{C}$ . A 10.0 g sample is located at the bottom of the pressure vessel and subjected to heating leading to a runaway reaction and gas evolution that can escape by testing different orifice sizes.

**Test criteria are**

"Violent" - Rupture of the disc with an orifice of 9.0 mm or greater and sample mass of 10.0 g.

"Medium" - No rupture of the disc with an orifice of 9 mm but rupture of the disc with an orifice of 3.5 mm or 6.0 mm and a sample mass of 10.0 g.

"Low" - No rupture of the disc with an orifice of 3.5 mm and a sample mass of 10.0 g but rupture of the disc with an orifice of 1.0 mm or 2 mm and a sample mass of 10 g or rupture of the disc with an orifice of 1mm and sample mass of 50 g.

"No" - No rupture of the disc with an orifice of 1.0 mm and a sample mass of 50.0 g.

**Alternative Methodology**

To first order the E.2 Dutch pressure vessel tests can be translated to simple ARSST tests by applying Fauske's generalized vent sizing equation for gassy decomposition reactions (Fauske, 2000)

$$A / V = \frac{3.5 \cdot 10^{-3}}{P} \dot{P} \quad (4)$$

where  $A \text{ (m}^2\text{)}$  is the vent area,  $V \text{ (m}^3\text{)}$  is the volume of reactant,  $\dot{P} \text{ (psi/min)}$  is the peak rate of pressure rise measured in the ARSST with a 10 g sample, and  $P \text{ (psia)}$  is the venting pressure. Setting  $V = 10^{-5} \text{ m}^3$  corresponding to a 10 g sample in the E.2 Dutch pressure vessel test (assuming a sample density of  $1 \text{ g/cm}^3$ ), and  $P \approx 80 \text{ psia}$  corresponding to the E.2 Dutch pressure vessel bursting disc pressure of 620-60 kPa, results in the following relationships between E series test criteria, ARSST peak rate of pressure rise measurements  $\dot{P}$  and Classification Types.

Table 1

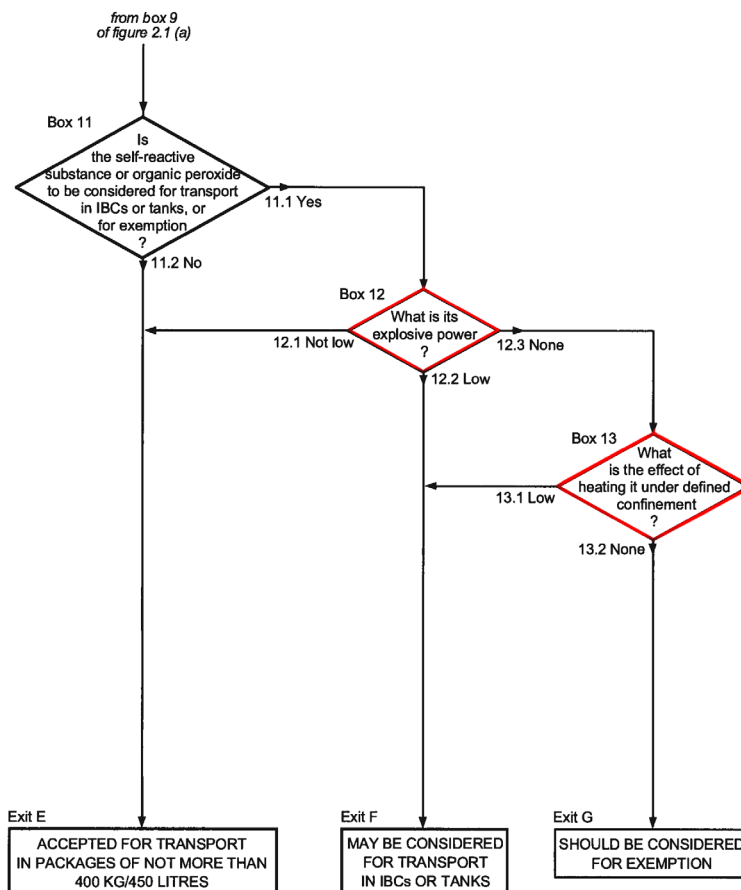
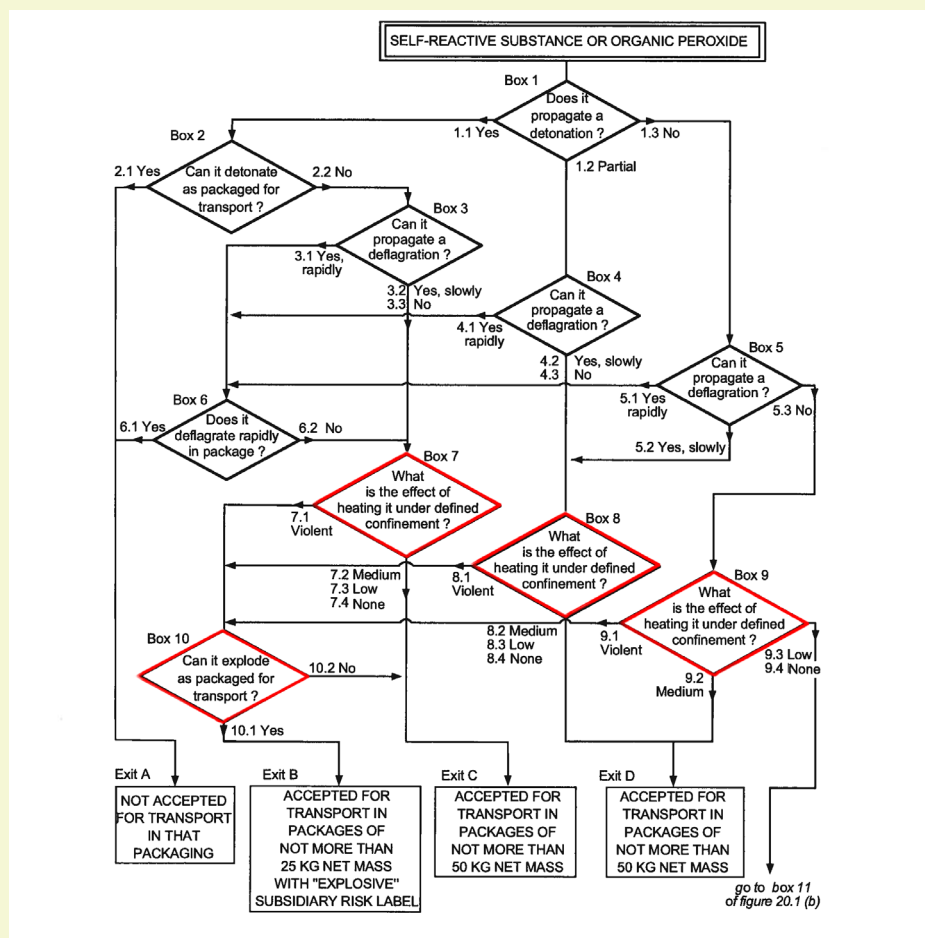
E-Series Test Criteria	ARSST Max $\dot{P}$ , psi min <sup>-1</sup>	Type
Violent	> 100,000	A, B, C
Medium	> 10,000	C, D
Low	> 400	E, F
No	< 400	G

Table 1 is consistent with available UN and ARSST tests. As an example ARSST tests with dibenzoyl peroxide and t-butyl peroxybenzoate result in  $\dot{P} > 100,000 \text{ psi/min}$  as well as transition to propagating deflagrations as illustrated in Figure 2. These observations are consistent with UN tests. In case of dibenzoyl peroxide, E series tests lead to Violent, and C.1 and C.2 deflagration tests lead to Yes, Rapidly consistent with the ARSST test observations.

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Figure 1: UN flow chart scheme for self-reactive substance and organic peroxides (copyright).



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Dibenzoyl peroxide being a very energetic substance, UN guidelines suggest Classification Type A as appropriate as Test Series A exhibit sustained detonation characteristics which is consistent with the low ignition temperature of about 100°C indicated in Figure 2 and a heat of reaction  $> 800 \text{ J g}^{-1}$ . Consistent with UN Guidelines Samples exhibiting ARSST characteristics similar to Dibenzoyl peroxide belong to Classification Type A.

As for t-butyl peroxybenzoate, E-series tests lead to Violent, and C.1 and C.2 deflagration tests lead to Yes, Slowly, again consistent with the ARSST test observation indicating a relatively higher ignition temperature of about 165°C. In the absence of sustained detonation characteristics (Test Series A), UN Guidelines suggest Classification Types B or C, depending upon package type. Again, samples exhibiting ARSST characteristics similar to t-butyl peroxybenzoate belong to UN Classification Types B or C.

A further example that a single ARSST test can satisfy UN Classification for transport is provided by considering dicumyl peroxide. This organic peroxide is transported in IBCs (Classification Type F). The measured ARSST peak rate of pressure rise,  $\dot{P}$ , for dicumyl peroxide is about 4000 psi/min with no indication of transition to a propagating deflagration as illustrated in Figure 2, and according to Table 1 is consistent with UN Classification Type F. Furthermore, UN deflagration tests (C.1 and C.2), detonation tests (A series) and explosive power tests (F series) with dicumyl peroxide lead to No, No and Low, respectively. The latter observations appear to be consistent with all available UN test results where E-series Test Criteria Low is satisfied. This suggests that if E-series Test Criteria Low is satisfied as illustrated by a simple ARSST test eliminates the need for E-series tests but also A-, C- and F-series tests.

## References

Hans K. Fauske, 2000, "Properly Size Vents for Nonreactive and Reactive Chemicals," Chemical Eng. Progress, February 2000.

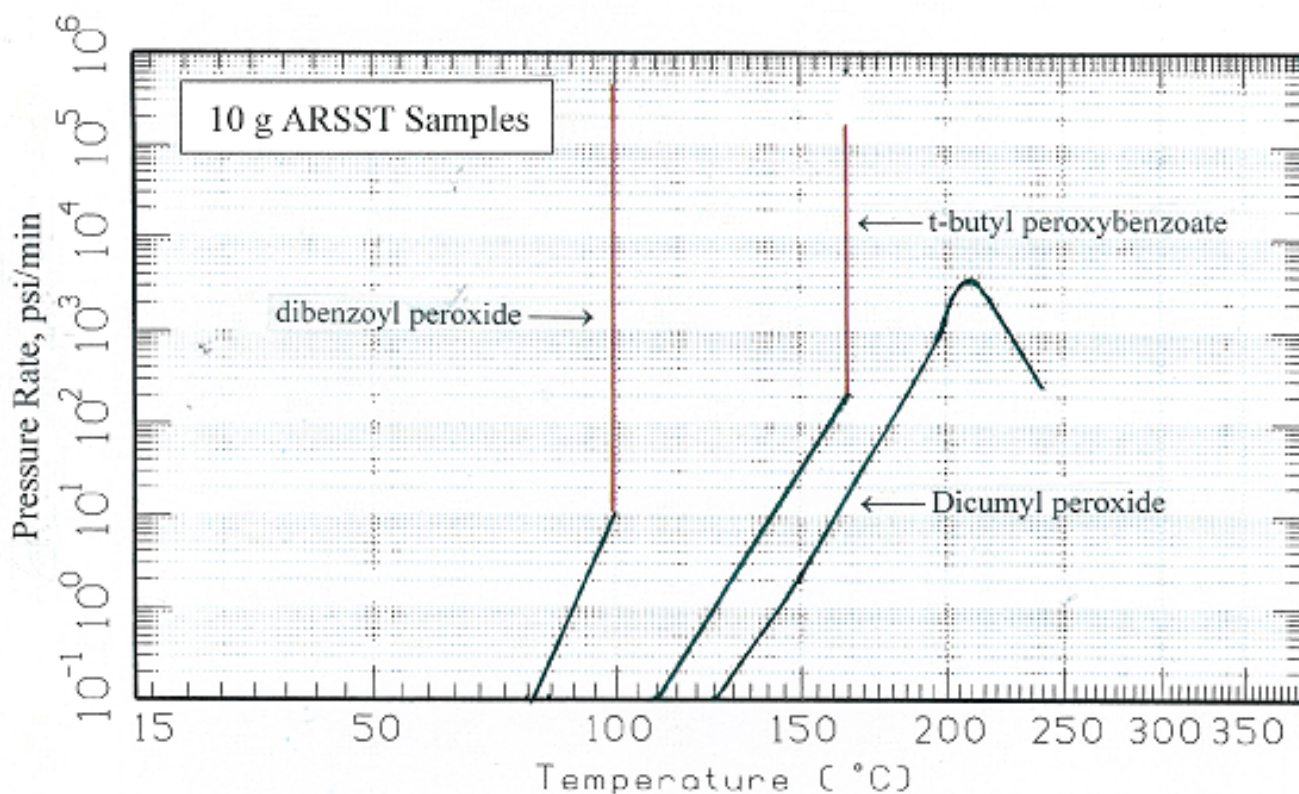


Figure 2: ARSST tests illustrating peak rates of pressure rise, and the presence (dibenzoyl peroxide and t-butyl peroxybenzoate) or absence (Dicumyl peroxide) of transition from Arrhenius to propagating reaction behavior.