

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

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To demonstrate safe transportation the United Nations guidelines[1] define seven classification groups that are determined by performing specific tests. Self-reacting substance should be subject to these testing criteria and classification procedures, and classified into one of the seven types (A-G) which relates their hazard to an allowable quantity/package size for transport. This paper presents an alternative methodology to the prescribed UN testing regime by utilising one easy to perform 10g Advanced Reactive System Screening Tool (ARSST) test to produce the necessary information that allows the packaging classification type to be determined. The UN guidelines allow such alternative procedures to be used provided adequate correlation has been obtained with the classification tests on a representative range of substances and examples of this correlation will be given.

INTRODUCTION

As an alternative to UN recommended testing one easy to perform 10 g Advanced Reactive System Screening Tool (ARSST) test can produce the necessary information to determine the packaging Classification Type consistent with UN Guidelines.

The ARSST is a commercially available instrument manufactured by Fauske and Associates. This test typically uses 5,10 or 20 ml magnetically stirred samples contained in an open, well insulated glass test cell. This set up minimises heat sink effects associated with heavy walled test cells resulting in a phi factor typically of around 1.04. This low phi factor means that essentially all the reaction heat generated heats up the sample in an adiabatic type environment.

A schematic of the ARSST is shown in Figure 1.

UN GUIDELINES

Self-reactive substances and organic peroxides are classified into one of seven types (A-G) according to their hazard in the UN Guidelines.

- **A** – Not accepted for transport in that packaging.
- **B** – Accepted for transport in packages of not more than 25kg net mass with “explosive” subsidiary risk label.
- **C** – Accepted for transport in packages of not more than 50kg net mass.
- **D** – Accepted for transport in packages of not more than 50kg net mass.
- **E** – Accepted for transport in packages of not more than 400kg/450 litres
- **F** – May be considered for transport in IBC’s or tanks.
- **G** – Should be considered for exception

These classification types are determined by performing up to 8 specific tests that are described in Test Series (A-H) and the questions the tests are used to answer are summarised below along with the relevant test codes:

- A – “Does it propagate a detonation?” Test codes A.1, A.2, A.5 and A.6
- B – “Can it detonate as packaged for transport?” Test code B.1
- C – “Does it propagate a deflagration?” Test codes C.1 and C.2.
- D – “Does it deflagrate rapidly when packaged?” Test codes D.1
- E – “What is the effect of heating it under defined confinement?” Test codes E.1, E.2 and E.3.
- F – “What is its explosive power?” Test codes F.1, F.2, F.3, F.4 and F.5.
- G – “Can it explode as packaged for transport?” Test codes G.1 and G.2.
- H – “What is its T_{SADT} value?” Test codes H.1, H.2, H.3 and H.4.

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 packaging. 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 – data that a simple ARSST test can quickly and easily provide.

The recommended sequence 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 are 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) must address the question

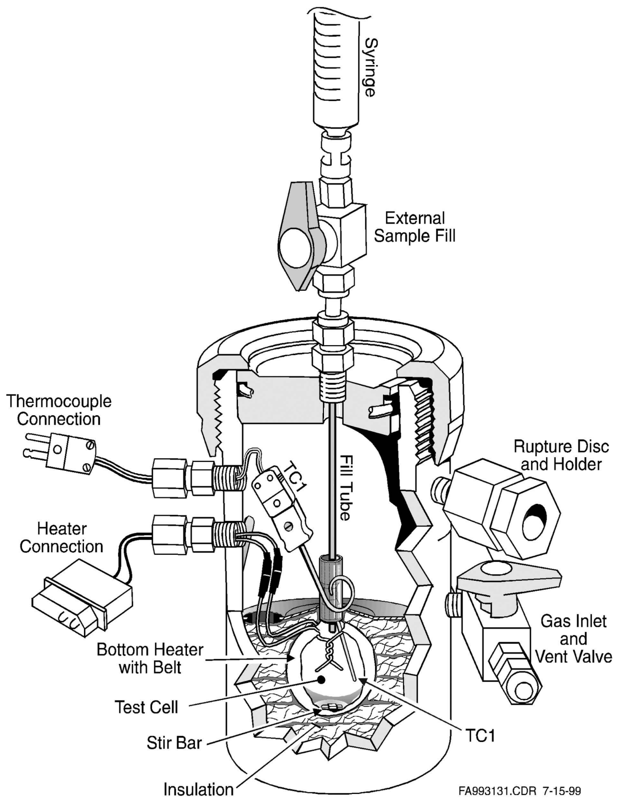

Figure 1. Schematic view of the Fauske ARSST

"What Is The Effect Of Heating It Under Defined Confinement?" (Test Series E) (Q1)

(Answer = Violent, Medium, Low or No)

as highlighted in Figure 2.

The consequences of the various answers are summarized below:

Medium – then the maximum package size is limited to 50 kg (Exits C and D).
Violent – the package size is again limited to 50 kg (Exit C) but only if the answer to question (Q2) as highlighted in Figure 1, box 10 is No

"Can It Explode As Packaged For Transport?" (Test Series G) (Q2)

(Answer = Yes or No)

If the answer to Q2 is **Yes**, the package size is limited to 25 kg or less with "Explosive" subsidiary Risk Label (Exit B). Of course 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 may be Yes for a stronger metal box.

Low – the maximum package size for transport is limited to 400 kg (Exit E), provided the substance

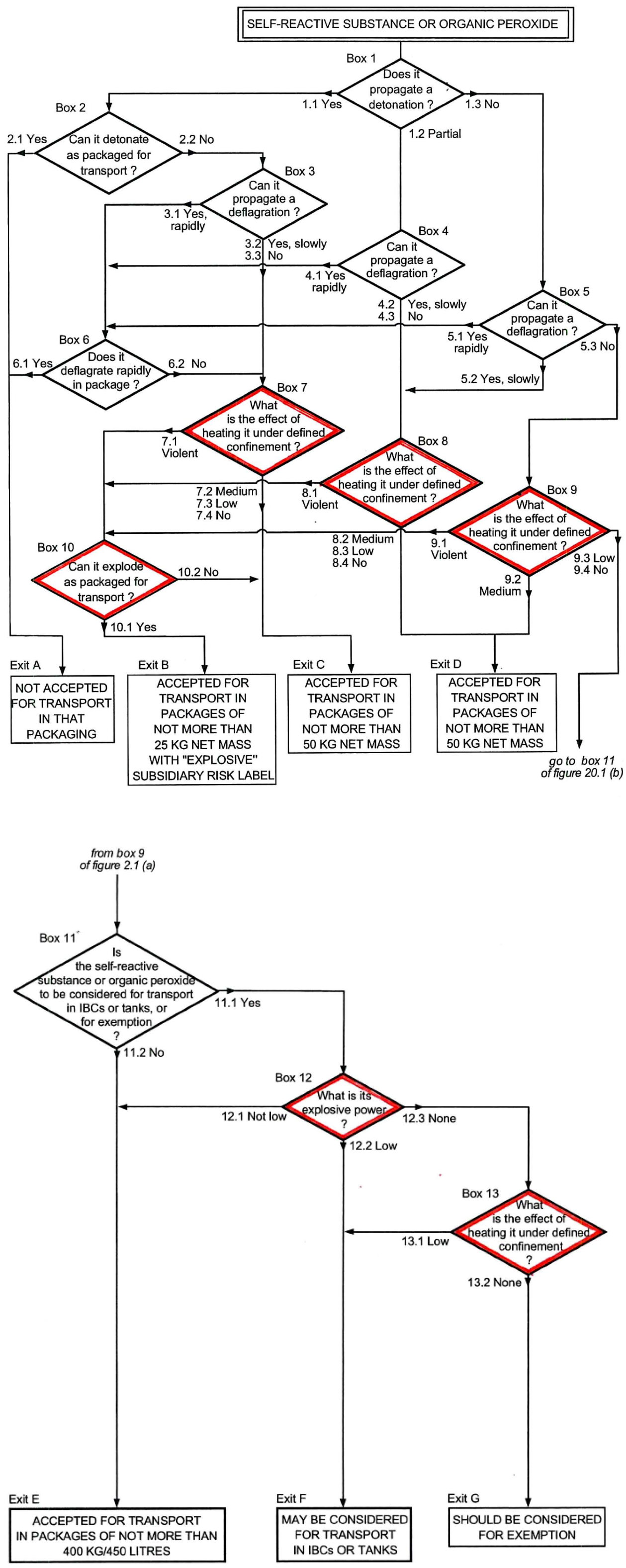

Figure 2. UN flow chart scheme for self-reactive substance and organic peroxides

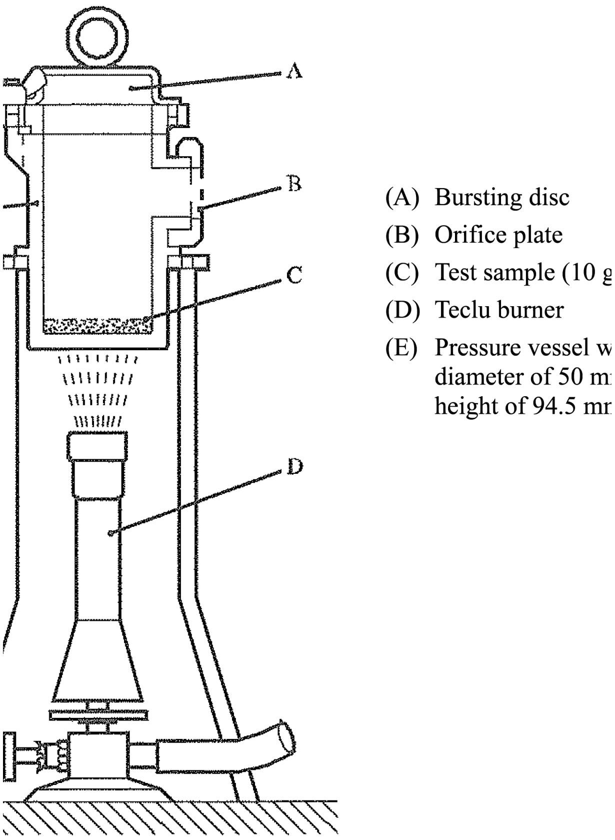

Figure 3. Schematic view of the Dutch Pressure Vessel

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).

No – the transport requirement May Be Considered For Exemption (Exit G). If the answers to Question (Q1) are **Low** or **No** it is reasonable to conclude that answers to Question (Q3) as highlighted in Figure 2 (Test Series F)

"What Is Its Explosive Power?" (Q3)

(Answer = None, Low, Not Low)

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

The UN guidelines also suggest that in order to select the appropriate exit gate requires an answer to the question:

"Does It Propagate a Deflagration?" (Q4)
(Test Series C)

(Answer = Yes- rapidly, Yes-slowly, or No)

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 $1.85 \bullet 10^{-4}$ m^3 and includes a 38 mm Bursting disc rated at 620 ± 60 kPa at 22°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)[2]

$$A/V = \frac{3.5 \cdot 10^{-3}}{P} \dot{P} \qquad (1)$$

where A (m^2) is the vent area, V (m^3) is the volume of reactant, $\dot{P}$ (psi/min) is the peak rate of pressure rise measured in the ARSST with a 10 g sample, and P (psia) is the venting pressure. Setting $V = 10^{-5}$ m^3 corresponding to a 10 g sample in the E.2 Dutch pressure vessel test (assuming a sample density of 1 g/cm^3), and $P \approx 80$ 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 is consistent with available UN and ARSST tests. As an example ARSST tests with dibenzoyl peroxide and t-butyl peroxybenzoate result in $\dot{P} > 100{,}000$ psi/min as well as transition to propagating deflagrations as illustrated in Figure 4. These observations are consistent with UN tests. In the case of dibenzoyl peroxide, E series tests lead to Violent, and C.1 and C.2 deflagration tests lead to Yes (Rapidly), which is consistent with the

Table 1.

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

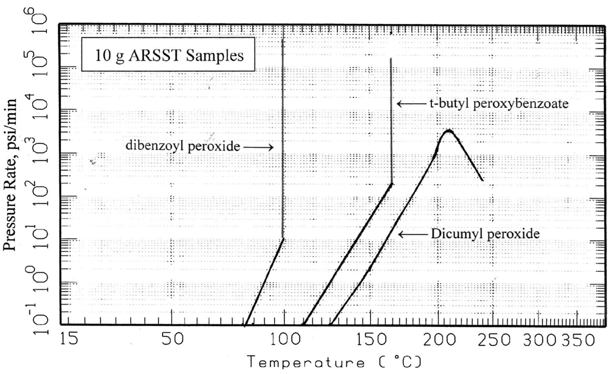

Figure 4. ARSSST tests illustrating peak rates of pressure rise, and the presence (dibenzoyl peroxide and t-butyl peroxybenzoate) or absence (Dicumyl peroxide) of transition from Arrhenius to propagating reaction behavior

ARSST test observations. 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 4 and a heat of reaction >800 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, P, for dicumyl peroxide is about 4000 psi/min with no indication of transition to a propagating deflagration as illustrated in Figure 4, 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 then this not only eliminates the need for E-series tests but also A-, C-, and F-series tests.

APPLICATION OF ALTERNATIVE METHODOLOGY

With the above observations supporting the alternative methodology, further illustration is provided by one 10 g

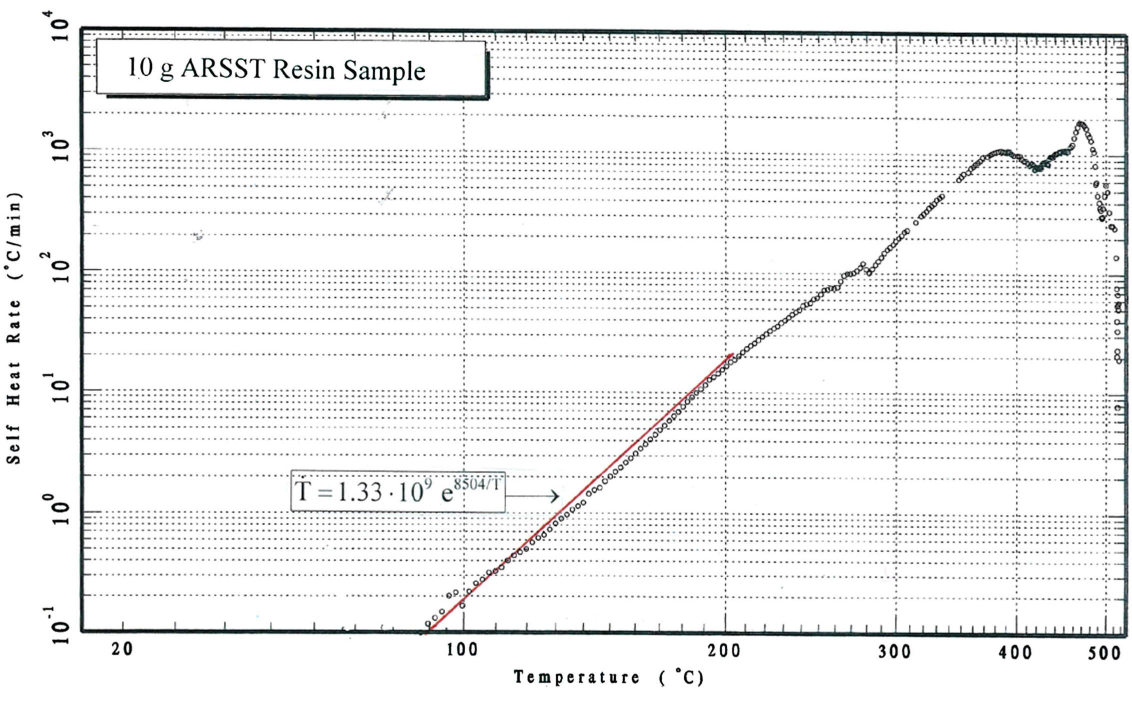

Figure 5. Adiabatic runaway data providing heat of reaction and kinetic parameters for the curing reaction

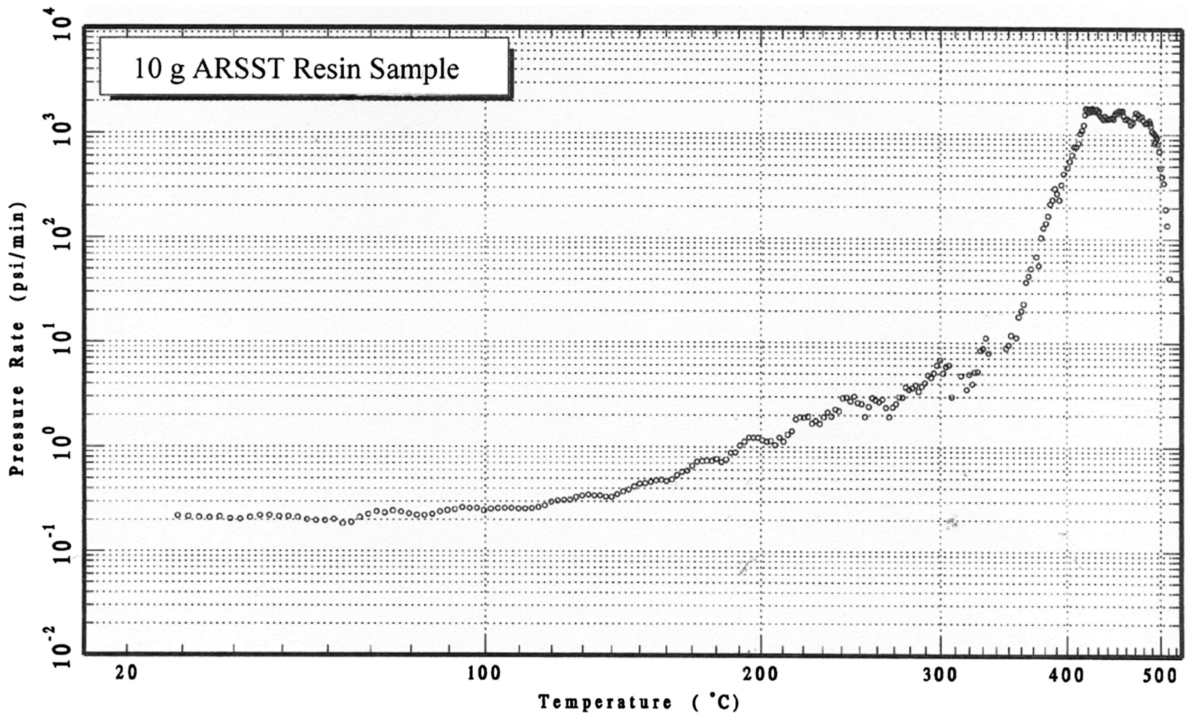

Figure 6. ARSST test illustrating peak rate of pressure rise and absence of transition to propagating reaction behaviour.

ARSST test performed with a fresh resin sample. The resulting adiabatic self-heat rate data is provided in Figure 5 illustrating the thermal reaction (resin curing) followed by a decomposition reaction at a temperature above 300°C. With a resin specific heat value of about $C = 2\ J\ g^{-1}$, the ARSST test indicates a decomposition heat of reaction of which is well

$$\Delta H_R = \Delta T \cdot c \approx 220 \cdot 2 = 440\ J\ g^{-1} \tag{2}$$

above 300 J/g therefore requiring the resin sample to be subjected to UN classification procedures. The data illustrated in Figure 5 also provide the necessary kinetic parameters to estimate the T_{SADT} for the resin sample applying the simple methodology proposed by Fauske (Fauske, 2009)[3] for determining T_{SADT}

$$T_{SADT} = \frac{-B}{\ell n \dfrac{T_{SADT}^2\ \delta_c\ \alpha}{R^2\ B\ A}} \tag{3}$$

where $B = 8504$ K, $A = 2.22 \bullet 10^7\ K\ s^{-1}$, $\delta_c = 2.09$, $\alpha = 10^{-7}\ m^2\ s^{-1}$ and $R = 0.212$ m considering a 50 kg resin package and results in

$$T_{SADT} = 318.3\ K \text{ or } 45.3°C \tag{4}$$

which is consistent with the UN H.4 Heat Accumulation Storage Test resulting in

$$T_{SADT} = 45°C \tag{5}$$

Table 2. Summary of UN tests versus ARSST data for 3 peroxides

	U.N. Tests			ARSST Tests
Chemical	A.1	C.2	E.3	
Dibenzoyl Peroxide	Yes	Yes, rapidly	Violent	$\sim 10^6$
t-Butyl Peroxybenzoate	Partial	Yes, slowly	Medium*	$\sim 10^5$
Dicumyl Peroxide	No	No	Low+	$\sim 4 \bullet 10^3$

*E.2 Violent, E.1 violent
+E.2 Medium, E.1 No

Table 3. UN Tests on Resin Sample

Test	Result
C.1: Time/pressure test	"No"
C.2: Deflagration test	"No"
E.1: Koenen tube test	"Low"
E.2: Dutch Pressure Vessel test	"Low"

Furthermore, the resulting rate of pressure rise data provided in Figure 6 illustrating a peak rate of pressure rise of $\dot{P} \approx 2000$ psi min^{-1} from the decomposition reaction with no sign of transition to propagating deflagration. According to these observations and Table 2, this leads to Classification Type E.

This observation is consistent with detailed UN tests performed with the resin sample summarised below in Table 3.

CONCLUSIONS

It has been demonstrated how one simple ARSST test, using only 10 g of material, can help classify self-reactive substances into their correct classification group for transport as detailed in the UN guidelines for transport of dangerous goods. The data has been correlated with the recommended UN tests for several reactive materials and shown to be consistent in assigning the correct classification group.

REFERENCES

1. 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 TRANPORT of DANGEROUS GOODS, Manual of Tests and Criteria, Fifth revised edition, UNITED NATIONS, New York and Geneva, 2009.
2. Fauske, H.K., February 2000, "Properly Size Vents for Nonreactive and Reactive Chemicals," *Chemical Eng. Progress*.
3. Fauske, H.K., May 2009, "A Simple and Cost Effective Method for Determination of the Self-Accelerating Decomposition Temperature (SADT)," *Fauske Process Safety Newsletter*.