COMMITTEE OF EXPERTS ON THE TRANSPORT OF DANGEROUS GOODS

Sub-Committee of Experts on the Transport of Dangerous Goods
(Geneva, 5-16 July 1999,
agenda item 5 (b))

MISCELLANEOUS DRAFT AMENDMENTS TO THE MODEL REGULATIONS ON THE TRANSPORT OF DANGEROUS GOODS

Lithium Batteries (Supplement to ST/SG/AC.10/C.3/1999/36)

Transmitted by the Expert from Canada

Introduction

Document ST/SG/AC.10/C.3/1999/36 identifies problems with the current approach to the regulation of lithium cells and batteries and calls for the establishment of an informal Working Group to address these. This supplement to that paper contains a "thought starter" presented in the form of amendments to the current Model Regulations.

Square brackets have been used to present points for discussion or to provide comment. The "thought starter" is presented later as Recommendations A and B.

Although no consistent differentiation has been identified between all "batteries" and all "cells" delegates might nevertheless wish to retain a difference in the size limits used to distinguish among small, intermediate and large units. [See paragraph 5 of Recommendation A.]

The distinction between lithium-ion and lithium which was introduced in the eleventh revised edition of the Model Regulations has been retained. Primary lithium batteries that contain lithium metal anodes were introduced commercially over twenty years ago and were soon followed by primary lithium batteries that contain lithium alloy anodes. Recent technologies include lithium-ion and lithium polymer batteries that use lithium-ion chemistries. Lithium-ion battery technologies are distinct from lithium metal and lithium alloy technologies in design and in reactivity. Lithium metal and lithium alloy technologies use metallic lithium and lithium alloy as the negative electrode. In contrast, lithium-ion technologies use a lithiated carbon material for the negative electrode and another intercalation compound for the positive electrode. Lithium-ion technologies are less reactive with water and are more thermally stable.

The final point to highlight with reference to the thought starter is that the 'threat analysis' [Table 1 of Paper ST/SG/AC.10/C.3/1999/36] shows the same threats for large and small batteries. Although this suggests that the purpose of testing should be the same for all ranges of batteries it does not mean that the tests used for these purposes must be the same for all ranges of batteries. Nevertheless, it appears that one series of tests may be acceptable and thus one series of tests is proposed in the thought starter for all ranges of batteries.

Thought Starter

Recommendation A: It is recommended that the Recommendations on the Transport of Dangerous Goods Model Regulations, eleventh revised edition, be amended as follows:

"Replace SP 188, 230 and 287 with
SP 188

1. A battery intended to use lithium (metal or alloy) or lithium-ion technology in its operation is a lithium battery. A battery includes a cell or module. [*It is suggested that there is no need to try to define a battery beyond its dictionary definition.*]

2. Each lithium battery must be designed or packaged in such a way as to prevent an external short circuit under conditions normal in transport.

3. To preclude a violent rupture under conditions normal in transport each lithium battery must incorporate a safety venting device or be designed to preclude such a rupture.

4. Each lithium battery must be packed in strong packagings or be contained in an equivalent case or device so as to prevent a puncture or crushing of the battery under conditions normal in transport.

5. Each lithium battery is assigned to Category A, B or C according to the following table, where Q is the maximum amount of lithium or lithium equivalent content which is expected to be in the battery at some point during its lifetime. Lithium content means the mass of lithium in the battery. Lithium equivalent content means, for a lithium-ion battery, 0.3 times the rated capacity of the battery in ampere-hours, with the result expressed as grams.

Category A		Category B		Category C	
Li (Li content)	Li-Ion (Li equivalent content)	Li (Li content)	Li-Ion (Li equivalent content)	Li (Li content)	Li-Ion (Li equivalent content)
Q <= 2g	Q <= 8g	Q <= 25g	Q <= 50g	Q > 25g	Q > 50g

[*The above table is proposed as adequate for all cells and batteries. Some delegates have suggested that two tables should be retained. One with Categories A, B and C defined for cells and the other with Categories A, B and C defined for batteries. If this were to be done there would have to be definitions establishing a relevant consistent difference between batteries and cells.*]

6. A lithium battery in Category A may be transported without meeting any requirements of these regulations other than paragraphs 2, 3 and 4 of this special provision.

7. A lithium battery in Category B may be transported without meeting any requirements of these regulations other than paragraphs 2, 3 and 4 of this special provision provided its battery type has been tested according to Part III, sub-section 38.3 of the Manual of Tests and Criteria and has passed the tests. [*Should a "mark" be required on a battery to show its type has been tested?*]

8. A lithium battery in Category C may be transported provided its battery type has been tested according to Part III, sub-section 38.3 of the Manual of Tests and Criteria and has passed the tests. In this case the these regulations apply and the primary class is Class 9. [*Should a “mark” be required on a battery to show its type has been tested?*]

9. A lithium battery which does not satisfy the provisions of paragraph 6, 7 or 8 may only be transported with special authorization granted by the competent authority.

10. New, uncycled and uncharged lithium ion batteries are not subject to these Regulations if:

(a) the electrolyte does not meet the definition of any class or division in these Regulations; or

(b) the electrolyte meets the definition of a class or division in these Regulations but the electrolyte will not flow from a ruptured or cracked case and there is no free liquid to flow.”

Recommendation B: It is recommended that sub-section 38.3 of the Manual of Tests and Criteria be amended to read as follows:

"38.3 Lithium Batteries

38.3.1 This section sets out the tests to be applied in determining if lithium batteries may be transported under Special Provision 188 of the Model Regulations.

38.3.2 For the purposes of the tests, the following definitions apply:

Cycle means one sequence of fully charging and fully discharging a rechargeable battery.

Distortion means the change in any dimension of a battery beyond its design tolerances.

Fully charged battery means a rechargeable battery which has been charged to its designed starting condition or a primary battery with at least 95% of its rated capacity.

Fully discharged battery means either:

a primary battery which has been discharged to remove 100% of its rated capacity; or
a rechargeable battery at its lowest voltage limit.

Primary means a battery which is not designed to be charged or recharged electrically.

Rated capacity means the capacity, in ampere-hours, of a battery as measured by subjecting it to a load, temperature and voltage cutoff point specified by the manufacturer.

Rechargeable means a battery which is designed to be recharged electrically.

Type means a particular electrochemical system and physical design of battery. A battery which differs from a tested type by:

(a) a change of more than 20% by mass to the cathode, anode or electrolyte; or

(b) a change that would materially affect the test results

is a new type and must be tested as a new type.

Vent means the intended activation of the pressure relief device of a battery to allow excessive internal pressure to be safely reduced without fire or rupture.

38.4 **Test Series ST**

38.4.1 *Introduction*

These tests are intended for batteries identified in Special Provision 188 as being subject to these tests. The pressure differential, expansion and contraction, vibration and shock tests are designed to determine the ability of batteries to withstand exposure to environmental conditions encountered during transport without a resulting internal short circuit or rupture. [See attached analysis, Table 1.] A comparison of the battery appearance before and after these tests is intended to detect battery damage such as leakage or abnormal venting, the disintegration, cracking, swelling or distortion of the battery pack, or any other observation which could indicate the occurrence of an internal short circuit or constitute a transportation safety hazard.

38.4.2 *Apparatus and materials*

38.4. 2.1 The following apparatus is required for this test: a balance with sufficient accuracy to detect mass losses identified in paragraph 38.4.4.1 (b), a vacuum chamber, a controlled temperature chamber, a vibration machine and a shock test apparatus.

38.4.2.2 The number and state of batteries to be tested for each battery type are:

(a) For primary batteries; eight, of which four must be tested in the fully charged state and four must be tested in the fully discharged state;

(b) For rechargeable batteries; eight, of which four must be tested after 50 deep cycles ending in the fully charged state, and four must be tested after 50 deep cycles ending in the fully discharged state.

38.4.3 *Procedure*

Each battery is subjected in sequence to the test procedures described below.

38.4.3.1 Pressure Differential [*To test for a design in which containment fails due to a high (relative) internal pressure. This can arise through external depressurization or the generation of internal pressure.*]

Batteries are stored at ambient temperature for at least 6 hours at an absolute pressure equal to 11.6 kPa or less.

38.4.3.2 Expansion and Contraction [*To test for a design in which internal connections are not adequate enough to avoid an internal short circuit.*]

Batteries are stored for at least 6 hours at a temperature equal to 75 °C, followed by at least 6 hours at a temperature equal to -20 °C. The maximum time between temperature extremes is 30 minutes. The cycle is repeated for a total of 10 times, after which the batteries are stored at room temperature for at least 24 hours.

38.4.3.3 Vibration [*To test for a design in which internal connections are not adequate enough to avoid an internal short circuit or the integrity of the unit fails due to vibration.*]

Batteries are firmly secured to the platform of the vibration machine without distorting the batteries in such a manner as to faithfully transmit the vibration. The vibration shall be a sinusoidal waveform with a logarithmic sweep between 7 Hz and 200 Hz and back to 7 Hz, traversed in 15 minutes. This cycle shall be repeated 12 times for a total of 3 hours for each of three mutually perpendicular mounting positions of the battery. One of the directions of vibration must be perpendicular to the terminal face.

The logarithmic frequency sweep is as follows: from 7 Hz a peak acceleration of 10 m/s^2 (approximately 1 g) is maintained until 18 Hz is reached. The amplitude is then maintained at 0.8 mm (1.6 mm total excursion) and the frequency increased until a peak acceleration of 80 m/s^2 occurs (approximately 50 Hz). A peak acceleration of 80 m/s^2 is then maintained until the frequency is increased to 200 Hz.

38.4.3.4 Shock [*To test for a design in which internal connections are not adequate enough to avoid an internal short circuit or the integrity of the unit fails due to shock.*]

Batteries are secured to the shock test apparatus by means of a rigid mount in such a manner as to faithfully transmit the shock impact without distorting the batteries. Each battery is subjected to three shocks in the positive direction, followed by three shocks in the negative direction, in each of three mutually perpendicular mounting positions of the cell, for a total of 18 shocks. One of the directions of the shock must be perpendicular to the terminal face. The minimum peak acceleration should be 50 g in a half-sine waveform over a minimum duration of 11 milliseconds.

38.4.4 ***Series ST test criteria and method of assessing results***

38.4.4.1 A lithium battery does not pass the test if, for any one of the units of that type required to be tested

(a) venting [other than venting of gases during the expansion and contraction test], leaking, distortion, rupture, short circuit or fire is evident;

(b) for a battery with a mass more than 1.0g, the maximum mass loss is not greater than 0.2%; or

(c) in the case of rechargeable batteries, the four batteries which were fully charged at the beginning of the test are fully discharged and after repeated cycling, any one battery’s capacity does not recover to within 10% of the average capacity of the four batteries which were fully discharged at the beginning of the test.”

Table 1:

	Concerns during Transport	Potential Solutions (Lithium devices)	Potential Solutions (Lithium-Ion devices)
1	Electrical Current External to Device	- protect during transport by isolating anode from cathode or transport device without a charge	- protect during transport by isolating anode from cathode or transport device without a charge
2.	Generation of Heat by: - short circuit - burning of lithium - burning of lithium-ion - voltage reversal or forced discharge (- re-charging)	- build and package to resist defined test values for shock, vibration, expansion and contraction; package to resist crush - prevent release of lithium, see row 3 below - ... - protect during transport by isolating anode from cathode or transport batteries without a charge. Otherwise, not an issue in transport - not an issue in transport	- build and package to resist defined test values for shock, vibration, expansion and contraction; package to resist crush - ... - prevent access to lithium ion, see row 3 below. - protect during transport by isolating anode from cathode or transport batteries without a charge. Otherwise, not an issue in transport - not an issue in transport
3.	Release of lithium, access to lithium-ion or release of electrolyte (possible consequences include corrosive gases lithium monoxide, lithium hydroxide, lithium carbonate; hydrogen if released into water; fire; and corrosive electrolyte) resulting from: - puncture - crush - internal pressure * opens * explodes	- package to resist puncture. - package to resist crush. - protect from heat, including heat generated as described in number 2 above. Altitude consideration.	- package to resist puncture. - package to resist crush. - protect from heat, including heat generated as described in number 2 above. Altitude consideration.

Comments: -The above suggests the use of tests to cover shock (drop test for large mass units?), vibration, expansion and contraction as these contribute to short circuit and tests to cover shock pressure differential (altitude) as these contribute to rupture. Protection from puncture and crush is to be derived from packaging requirements.

-Pass criteria to be: no evidence of short circuit, no visible leakage or deformation.