

Recommendations on the

TRANSPORT OF DANGEROUS GOODS

Manual of Tests and Criteria

Third revised edition

Amendment 1: Lithium batteries



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FOREWORD

The recommendations in the Manual of Tests and Criteria supplement the "Recommendations on the Transport of Dangerous Goods" and the Model Regulations annexed thereto. The third revised edition of the Manual of Tests and Criteria results from the decisions of the United Nations Committee of Experts on the Transport of Dangerous Goods up to its twentieth (1998) session.

Corrections to the third revised edition are included in Part I of this publication.

The amendments contained in Part II have been adopted by the Committee at its twenty-first (2000) session (refer to ST/SG/AC.10/27/Add.2). They concern new provisions for the classification criteria and testing procedures for lithium batteries. They are published at the request of the United Nations Economic and Social Council in its resolution 2001/34 of 26 July 2001.

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PART I

CORRIGENDUM TO THE ENGLISH VERSION OF THE THIRD REVISED EDITION OF THE MANUAL OF TESTS AND CRITERIA

Page 1

1.1.2 **Replace "and" with "are" in the last sentence.**

Page 2

1.3.1 **Replace "2.0.3.1" with "2.0.3.3".**

Page 11

10.1.2 **Replace "2.1.1.3" with "2.1.1.4".**

Page 16

10.4.1.1 **Replace "2.1.1.3" with "2.1.1.4".**

Page 29

11.4.1.5 **Add "-" in the last line under the heading "Result".**

Page 104

13.5.1.2.2 **Replace "13.5.1.1" with "13.5.1.2".**

Page 123

Table 14.1 **For 4(a), insert "unpackaged" after "test for" under the heading "Name of Test".**

Page 124

14.4.1.4 (b) **Replace "It" with "It".**
and (c)

Page 150

16.4.1.4 **Replace "in chapter 4 of the Recommendations" with "in Chapter 2.1" of the Model Regulations".**

Page 165

17.6.1.2.5 **Replace "1, 2 and 3" with "(C)".**

Page 173

17.8.1.3.1 **Replace "16.6.1" with "16.6.1.3".**

Page 185

20.2.3 (a) **Replace "2.4.2.3.1" with "2.4.2.3.1.1".**

Page 186

20.2.6 **Replace "section 33.2" with "section 33.3".**

Page 205

Replace "TN0" with "TNO".

Page 241

25.4.2.5 **Replace "morpholinobenzene-diazonium" with "morpholinobenzenediazonium" (twice).**

- Page 265**
26.4.4.2 **Replace** "26.4.4" **with** "26.4.4.2".
- Page 309**
32.2.5 **Replace** "(see section 32.6)" **with** "(see section 32.5.2)".
- Page 310**
32.3.1.5 **Replace** "32.3.1.6" **with** "32.3.1.7".
- 32.3.1.6 (c) **Insert** "provided the nitrocellulose contains not more than 12.6% nitrogen by dry mass" after "nitrocellulose".
- Page 337**
34.1.1 **Replace** "paragraphs 2.5.2.2.1 and 2.5.2.2.2" **with** "2.5.2.2 and 2.5.2.3".
- 34.2.1 **Insert** "or 2.5.2.3.1 and 2.5.2.3.2" after "and 2.5.2.2.2".
- 34.3.1 and
34.3.2 **Replace** "Chapter 2.0" **with** "section 2.0.3".
- Page 340**
34.4.1.4.2 In the paragraph immediately before 34.4.1.5, **replace** "paragraph 1.44" **with** "section 2.0.3".
- Page 364**
38.3.4.2.2.1 In the last sentence, **replace** "38.2.3.2.3.2" **with** "38.3.4.2.3.2".
- Page 366**
38.3.4.3.2.1 In the last sentence, **replace** "38.2.3.2.3.2" **with** "38.3.4.3.3.2".
- Page 369**
38.3.4.5.2.1 In the last sentence, **replace** "38.2.3.5.3.2" **with** "38.3.4.5.3.2".
- Page 392**
Appendix 5 In paragraph 3, for "Mt", **insert** "or self-reactive substance" after "organic peroxide".
- Page 393**
Appendix 5 In the example, for "Mt" and in paragraph 4. (first and second paragraphs), **insert** "or self-reactive substance" after "organic peroxide".
- Page 397**
Appendix 6 In the Note, **delete** the reference to footnote 1 after "800 J.g".
- Page 399**
Appendix 6 In paragraph 5.1 (a), **replace** "self-heating" **with** "self-reactive".

PART II

AMENDMENTS TO THE THIRD REVISED EDITION OF THE MANUAL OF TESTS AND CRITERIA

Section 38.3 Replace section 38.3 of the Manual Test and Criteria with the following:

"38.3 Lithium batteries

38.3.1 Purpose

This section presents the procedures to be followed for the classification of lithium cells and batteries (see UN Nos. 3090 and 3091, and the applicable special provisions of Chapter 3.3 of the Model Regulations).

38.3.2 Scope

38.3.2.1 Lithium cells and batteries shall be subjected to the tests, as required by special provisions 188 and 230 of Chapter 3.3 of the Model Regulations prior to the transport of a particular cell or battery type. Lithium cells or batteries which differ from a tested type by:

- (a) a change of more than 0.1 g or 20% by mass, whichever is greater, to the cathode, to the anode, or to the electrolyte; or
- (b) a change that would materially affect the test results,

shall be considered a new type and shall be subjected to the required tests. In the event that a lithium cell or battery type does not meet one or more of the test requirements, steps shall be taken to correct the deficiency or deficiencies that caused the failure before such cell or battery type is retested.

38.3.2.2 For the purposes of classification, the following definitions apply:

Aggregate lithium content means the sum of the grams of lithium content or lithium equivalent content contained by the cells comprising a battery.

Battery means one or more cells which are electrically connected together by permanent means, including case, terminals, and markings.

NOTE: Units that are commonly referred to as "battery packs" having the primary function of providing a source of power to another piece of equipment are for purposes of these Regulations treated as batteries.

Button cell or battery means a round small cell or battery when the overall height is less than the diameter.

Cell means a single encased electrochemical unit (one positive and one negative electrode) which exhibits a voltage differential across its two terminals. Under these Regulations, to the extent the encased electrochemical unit meets the definition of "cell" herein, it is a "cell", not a "battery", regardless of whether the unit is termed a "battery" or a "single cell battery" outside of these Regulations.

Component cell means a cell contained in a battery.

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

Disassembly means a vent or rupture where solid matter from any part of a cell or battery penetrates a wire mesh screen (annealed aluminium wire with a diameter of 0.25 mm and grid density of 6 to 7 wires per cm) placed 25 cm away from the cell or battery.

Effluent means a liquid or gas released when a cell or battery vents or leaks.

Equivalent lithium content is defined in the definition of lithium content.

First cycle means the initial cycle following completion of all manufacturing processes.

Fully charged means a rechargeable cell or battery which has been electrically charged to its design rated capacity.

Fully discharged means either:

a primary cell or battery which has been electrically discharged to remove 100% of its rated capacity; or

a rechargeable cell or battery which has been electrically discharged to its endpoint voltage as specified by the manufacturer.

Large battery means a battery in which the aggregate lithium content of all anodes, when fully charged, is more than 500 g.

Large cell means a cell in which the lithium content or lithium equivalent content of the anode, when fully charged, is more than 12 g.

Leakage means the escape of material from a cell or battery.

Lithium content is applied to lithium metal and lithium alloy cells and batteries, and for a cell means the mass of lithium in the anode of a lithium metal or lithium alloy cell, which for a primary cell is measured when the cell is in an undischarged state and for a rechargeable cell is measured when the cell is fully charged. The lithium content of a battery equals the sum of the grams of lithium content contained in the component cells of the battery.

Lithium-equivalent content is applied to lithium-ion cells and batteries, and for a cell is measured as 0.3 times the rated capacity of the cell in ampere-hours, with the result expressed in grams. The lithium-equivalent content of a battery equals the sum of the grams of lithium-equivalent content contained in the component cells of the battery.

Lithium-ion cell or battery means a rechargeable electrochemical cell or battery in which the positive and negative electrodes are both intercalation compounds (intercalated lithium exists in an ionic or quasi-atomic form with the lattice of the electrode material) constructed with no metallic lithium in either electrode. A lithium polymer cell or battery that uses lithium-ion chemistries, as described herein, is regulated as a lithium-ion cell or battery.

Mass loss means a loss of mass that exceeds the values in table 1 below. In order to quantify the mass loss, the following procedure is provided:

$$\text{Mass loss (\%)} = \frac{(M_1 - M_2)}{M_1} \times 100$$

where M_1 is the mass before the test and M_2 is the mass after the test. When mass loss does not exceed the values in table 1, it shall be considered as "no mass loss".

Table 1: Mass loss limit

Mass M of cell or battery	Mass loss limit
$M < 1 \text{ g}$	0.5 %
$1 \text{ g} < M < 5 \text{ g}$	0.2 %
$M \geq 5 \text{ g}$	0.1 %

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

Prismatic cell or battery means a cell or battery whose ends are similar, equal and parallel rectilinear figures, and whose sides are parallelograms.

Protective devices means devices such as fuses, diodes and current limiters which interrupt the current flow, block the current flow in one direction or limit the current flow in an electrical circuit.

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

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

Rupture means the mechanical failure of a cell container or battery case induced by an internal or external cause, resulting in exposure or spillage but not ejection of solid materials.

Short circuit means a direct connection between positive and negative terminals of a cell or battery that provides a virtual zero resistance path for current flow.

Small battery means a battery composed of small cells, and in which the aggregate lithium content of all cell anodes, when fully charged, is not more than 500 g.

Small cell means a cell in which the lithium content of the anode, when fully charged, is not more than 12 g.

Type means a particular electrochemical system and physical design of cells or batteries.

Undischarged means a primary cell or battery that has not been wholly or partly discharged.

Venting means the release of excessive internal pressure from a cell or battery in a manner intended by design to preclude rupture or disassembly.

38.3.3 When a cell or battery type is to be tested under this sub-section, the number and condition of cells and batteries of each type to be tested are as follows:

- (a) When testing primary cells and batteries under tests 1 to 5 the following shall be tested:
 - (i) ten cells in undischarged states,
 - (ii) ten cells in fully discharged states,
 - (iii) four batteries in undischarged states, and
 - (iv) four batteries in fully discharged states.

- (b) When testing rechargeable cells and batteries under tests 1 to 5 the following shall be tested:
 - (i) ten cells, at first cycle, in fully charged states,
 - (ii) ten cells, at first cycle, in fully discharged states,
 - (iii) four batteries, at first cycle, in fully charged states,
 - (iv) four batteries, at first cycle, in fully discharged states,
 - (v) four batteries after fifty cycles ending in fully charged states, and
 - (vi) four batteries after fifty cycles ending in fully discharged states.

- (c) When testing primary and rechargeable cells under test 6, the following shall be tested:
 - (i) for primary cells, five cells in undischarged states and five cells in fully discharged states,
 - (ii) for component cells of primary batteries, five cells in undischarged states and five cells in fully discharged states,
 - (iii) for rechargeable cells, five cells at first cycle at 50% of the design rated capacity and five cells after 50 cycles ending in fully discharged states, and
 - (iv) for component cells of rechargeable batteries, five cells at first cycle at 50% of the design rated capacity and five cells after 50 cycles ending in fully discharged states.

For prismatic cells, ten test cells are required for each of the states of charge being tested, instead of the five described above, so that the procedure can be carried out on five cells along the longitudinal axes and, separately, five cells along the other axes. In every case, the test cell is only subjected to one impact.

- (d) When testing rechargeable batteries under test 7, the following shall be tested:
 - (i) four rechargeable batteries, at first cycle, in fully charged states, and
 - (ii) four rechargeable batteries after fifty cycles ending in fully charged states.

- (e) When testing primary and rechargeable cells under test 8, the following shall be tested:
 - (i) ten primary cells in fully discharged states,
 - (ii) ten rechargeable cells, at first cycle in fully discharged states, and
 - (iii) ten rechargeable cells after fifty cycles ending in fully discharged states.

When batteries that have passed all applicable tests are electrically connected to form a battery assembly in which the aggregate lithium content of all anodes, when fully charged, is more than 500 g, that battery assembly does not need to be tested if it is equipped with a system capable of monitoring the battery assembly and preventing short circuits, or over discharge between the batteries in the assembly and any overheat or overcharge of the battery assembly.

38.3.4 Procedure

Each cell and battery type must be subjected to tests 1 to 8. Tests 1 to 5 must be conducted in sequence on the same cell or battery. Tests 6 and 8 should be conducted using not otherwise tested cells or batteries. Test 7 may be conducted using undamaged batteries previously used in Tests 1 to 5 for purposes of testing on cycled batteries.

38.3.4.1 *Test 1: Altitude simulation*

38.3.4.1.1 *Purpose*

This test simulates air transport under low-pressure conditions.

38.3.4.1.2 *Test procedure*

Test cells and batteries shall be stored at a pressure of 11.6 kPa or less for at least six hours at ambient temperature (20 ± 5 °C).

38.3.4.1.3 *Requirement*

Cells and batteries meet this requirement if there is no mass loss, no leakage, no venting, no disassembly, no rupture and no fire and if the open circuit voltage of each test cell or battery after testing is not less than 90% of its voltage immediately prior to this procedure. The requirement relating to voltage is not applicable to test cells and batteries at fully discharged states.

38.3.4.2 *Test 2: Thermal test*

38.3.4.2.1 *Purpose*

This test assesses cell and battery seal integrity and internal electrical connections. The test is conducted using rapid and extreme temperature changes.

38.3.4.2.2 *Test procedure*

Test cells and batteries are to be stored for at least six hours at a test temperature equal to 75 ± 2 °C, followed by storage for at least six hours at a test temperature equal to -40 ± 2 °C. The maximum time interval between test temperature extremes is 30 minutes. This procedure is to be repeated 10 times, after which all test cells and batteries are to be stored for 24 hours at ambient temperature (20 ± 5 °C). For large cells and batteries the duration of exposure to the test temperature extremes should be at least 12 hours.

38.3.4.2.3 *Requirement*

Cells and batteries meet this requirement if there is no mass loss, no leakage, no venting, no disassembly, no rupture and no fire and if the open circuit voltage of each test cell or battery after testing is not less than 90% of its voltage immediately prior to this procedure. The requirement relating to voltage is not applicable to test cells and batteries at fully discharged states.

38.3.4.3 **Test 3: Vibration**

38.3.4.3.1 *Purpose*

This test simulates vibration during transport.

38.3.4.3.2 *Test procedure*

Cells and batteries are firmly secured to the platform of the vibration machine without distorting the cells 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 cell. 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 1 g_n 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 8 g_n occurs (approximately 50 Hz). A peak acceleration of 8 g_n is then maintained until the frequency is increased to 200 Hz.

38.3.4.3.3 *Requirement*

Cells and batteries meet this requirement if there is no mass loss, no leakage, no venting, no disassembly, no rupture and no fire and if the open circuit voltage of each test cell or battery after testing is not less than 90% of its voltage immediately prior to this procedure. The requirement relating to voltage is not applicable to test cells and batteries at fully discharged states.

38.3.4.4 **Test 4: Shock**

38.3.4.4.1 *Purpose*

This test simulates possible impacts during transport.

38.3.4.4.2 *Test procedure*

Test cells and batteries shall be secured to the testing machine by means of a rigid mount which will support all mounting surfaces of each test battery. Each cell or battery shall be subjected to a half-sine shock of peak acceleration of 150 g_n and pulse duration of 6 milliseconds. Each cell or battery shall be subjected to three shocks in the positive direction followed by three shocks in the negative direction of three mutually perpendicular mounting positions of the cell or battery for a total of 18 shocks.

However, large cells and large batteries shall be subjected to a half-sine shock of peak acceleration of 50 g_n and pulse duration of 11 milliseconds. Each cell or battery is subjected to three shocks in the positive direction followed by three shocks in the negative direction of each of three mutually perpendicular mounting positions of the cell for a total of 18 shocks.

38.3.4.4.3 *Requirement*

Cells and batteries meet this requirement if there is no mass loss, no leakage, no venting, no disassembly, no rupture and no fire and if the open circuit voltage of each test cell or battery after testing is not less than 90% of its voltage immediately prior to this procedure. The requirement relating to voltage is not applicable to test cells and batteries at fully discharged states.

38.3.4.5 **Test 5: External short circuit**

38.3.4.5.1 *Purpose*

This test simulates an external short circuit.

38.3.4.5.2 *Test procedure*

The cell or battery to be tested shall be temperature stabilized so that its external case temperature reaches $55 \pm 2^\circ\text{C}$ and then the cell or battery shall be subjected to a short circuit condition with a total external resistance of less than 0.1 ohm at $55 \pm 2^\circ\text{C}$. This short circuit condition is continued for at least one hour after the cell or battery external case temperature has returned to $55 \pm 2^\circ\text{C}$. The cell or battery must be observed for a further six hours for the test to be concluded.

38.3.4.5.3 *Requirement*

Cells and batteries meet this requirement if their external temperature does not exceed 170°C and there is no disassembly, no rupture and no fire within six hours of this test.

38.3.4.6 **Test 6: Impact**

38.3.4.6.1 *Purpose*

This test simulates an impact.

38.3.4.6.2 *Test procedure*

The test sample cell or component cell is to be placed on a flat surface. A 15.8 mm diameter bar is to be placed across the centre of the sample. A 9.1 kg mass is to be dropped from a height of 61 ± 2.5 cm onto the sample.

A cylindrical or prismatic cell is to be impacted with its longitudinal axis parallel to the flat surface and perpendicular to the longitudinal axis of the 15.8 mm diameter curved surface lying across the centre of the test sample. A prismatic cell is also to be rotated 90 degrees around its longitudinal axis so that both the wide and narrow sides will be subjected to the impact. Each sample is to be subjected to only a single impact. Separate samples are to be used for each impact.

A coin or button cell is to be impacted with the flat surface of the sample parallel to the flat surface and the 15.8 mm diameter curved surface lying across its centre.

38.3.4.6.3 *Requirement*

Cells and component cells meet this requirement if their external temperature does not exceed 170°C and there is no disassembly and no fire within six hours of this test.

38.3.4.7 **Test 7: Overcharge**

38.3.4.7.1 *Purpose*

This test evaluates the ability of a rechargeable battery to withstand an overcharge condition.

38.3.4.7.2 *Test procedure*

The charge current shall be twice the manufacturer's recommended maximum continuous charge current. The minimum voltage of the test shall be as follows:

- (a) when the manufacturer's recommended charge voltage is not more than 18V, the minimum voltage of the test shall be the lesser of two times the maximum charge voltage of the battery or 22V.
- (b) when the manufacturer's recommended charge voltage is more than 18V, the minimum voltage of the test shall be 1.2 times the maximum charge voltage.

Tests are to be conducted at ambient temperature. The duration of the test shall be 24 hours.

38.3.4.7.3 *Requirement*

Rechargeable batteries meet this requirement if there is no disassembly and no fire within seven days of the test.

38.3.4.8 **Test 8: Forced discharge**

38.3.4.8.1 *Purpose*

This test evaluates the ability of a primary or a rechargeable cell to withstand a forced discharge condition.

38.3.4.8.2 *Test procedure*

Each cell shall be forced discharged at ambient temperature by connecting it in series with a 12V D.C. power supply at an initial current equal to the maximum discharge current specified by the manufacturer.

The specified discharge current is to be obtained by connecting a resistive load of the appropriate size and rating in series with the test cell. Each cell shall be forced discharged for a time interval (in hours) equal to its rated capacity divided by the initial test current (in Ampere).

38.3.4.8.3 *Requirement*

Primary or rechargeable cells meet this requirement if there is no disassembly and no fire within seven days of the test."