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Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

Sub-Committee of Experts on the Transport of Dangerous Goods

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Listing, classification and packing

Sodium batteries: Amendment to Special Provision 239

Transmitted by the expert from the United States of America[1]

Background

1. The Model Regulations currently authorize the transport of sodium cells and batteries under the description "Batteries containing sodium or Cells containing sodium" (UN 3292). Special Provision 239 applies and limits the types of dangerous goods which may be contained in such batteries to sodium, sulphur, and polysulphides.

2. In recent years, however, other sodium battery chemistries have emerged and become more widely used and commonly transported. For example, some batteries with sodium metal chloride chemistries use sodium tetrachloroaluminate as a secondary electrolyte (see annex).

3. Sodium metal chloride batteries present no additional hazards in transport as compared to sodium sulphur batteries. In addition, the active components are hermetically sealed in steel enclosures as required by Special Provision 239. It is therefore suggested that the first sentence of Special Provision 239 be revised to more comprehensively address sodium compounds utilized in sodium batteries.

[1] In accordance with the programme of work of the Sub-Committee for 2009-2010 approved by the Committee at its fourth session (refer to ST/SG/AC.10/C.3/68, para. 118 (d) and ST/SG/AC.10/36, para. 14).

Proposal

4. Revise Special Provision 239 as follows:

239 Batteries or cells shall not contain dangerous goods other than sodium, sulphur and/or polysulphides. **sodium, sulphur and/or sodium compounds (e.g. sodium polysulphides, sodium tetrachloroaluminate etc.).** Batteries or cells shall not be offered for transport at a temperature such that liquid elemental sodium is present in the battery or cell unless approved and under the conditions established by the competent authority.

Cells shall consist of hermetically sealed metal casings which fully enclose the dangerous goods and which are so constructed and closed as to prevent the release of the dangerous goods under normal conditions of transport.

Batteries shall consist of cells secured within and fully enclosed by a metal casing so constructed and closed as to prevent the release of the dangerous goods under normal conditions of transport.

Except for air transport, batteries installed in vehicles (UN 3171) are not subject to these Regulations.

Annex

[English only]

Additional information on Sodium Metal Chloride Batteries

1. The chemistry of a sodium metal chloride battery using sodium tetrachloroaluminate secondary electrolyte is detailed in the write-up below. Information is presented to demonstrate that this battery technology attains the same level of safety as the sodium sulphur battery technology.

2. **The Sodium Sulphur Cell** behaves as follows: The sodium sulphur cell, when first built is in the fully **charged** state. This means that the negative electrode compartment is full of sodium and the positive compartment is full of sulphur. At room temperature (25°C) all components of the cell are solid. As the cell is heated, the sodium (98°C), and then the sulphur (114°C) melt. At this point the cell begins to exhibit a voltage across the terminals. The sodium sulphur cell cannot be practically used, however, until a temperature of at least 250°C is obtained, at which point the cell can be discharged. In this process, sodium is transferred electrochemically through the **solid** beta alumina and reacts with the sulphur to produce sodium polysulphide.

(*charged*) $2Na + xS \rightarrow Na_2Sx$ (*discharged*) where x usually varies between 3 and 5

3. When fully discharged, the negative compartment contains only a small amount of sodium and the positive electrode comprises mainly sodium trisulphide (Na_2S_3).

4. For **the Sodium Metal Chloride Cell,** the mechanical construction is very similar to the sodium sulphur cell, but the chemistry differs. The sodium metal chloride cell behaves as follows: A newly built cell begins in the fully **discharged** state, in contrast with the initially charged sodium sulphur cell. This means that the negative electrode compartment is completely empty of elemental sodium and the positive compartment is full of a non-flammable intimate mixture of a metal powder, sodium chloride (table salt) and sodium tetrachloroaluminate (see below). At room temperature (25°C) all components of the cell are solid. As the sodium metal chloride cell is heated, the sodium tetrachloroaluminate melts at 156°C but the remaining components remain solid. At this point there is still no sustainable voltage on the cell terminals. The sodium metal chloride cell cannot be practically used, however, until a temperature of at least 250°C is obtained, at which point the cell can be charged. In this process, the metal and sodium chloride are converted into metal chloride and elemental sodium and the sodium is transferred electrochemically through the solid beta alumina electrolyte to fill the negative electrode compartment. When fully charged, the negative compartment is partially full of sodium and the positive electrode comprises mainly metal chloride.

$$M + xNaCl \rightarrow MClx + Na$$

5. Where M is the metal concerned and x may vary depending upon the metal concerned. For example, to use the metal nickel, the equation would be:

(discharged) $Ni + 2NaCl \rightarrow NiCl_2 + 2Na$ (charged)

6. Discharge reverses this process, sodium passing back through the beta alumina into the positive compartment, reacting with the metal chloride to reform sodium chloride and metal, whilst leaving the negative compartment nearly, but not completely, empty. From this point onwards there will always be a small amount of elemental sodium present, even in the discharged state..

$$\text{(charged) } 2Na + NiCl_2 \rightarrow 2NaCl + Ni \text{ (discharged)}$$

7. It should be noted that, at all times, both compartments are completely sealed from each other and from the outside world.

8. Electrochemically, the two systems are similar in that they rely on the ability of the solid sodium beta alumina (a ceramic like material) to conduct sodium ions in both directions when heated above about 250°C, whilst remaining an electronic insulator, thus making the perfect electrolyte.

9. One difference between sodium sulphur and sodium metal chloride cells, is the presence, in the positive electrode, of the substance sodium tetrachloroaluminate. This acts as a secondary electrolyte for the following reason. Whilst, at operating temperature (250°C or above), both sodium and sulphur/sodium polysulphides are liquid in the sodium sulphur cell, only the sodium is molten at similar temperatures in the sodium metal chloride cell. It is necessary, therefore, to have a substance which is liquid to enable the sodium ions more easily to travel between the beta alumina surface and the active positive electrode materials. This substance takes no other part in the cell reaction but is vital for the action of the cell.

Figure 1.1 Sodium sulphur cell schematic

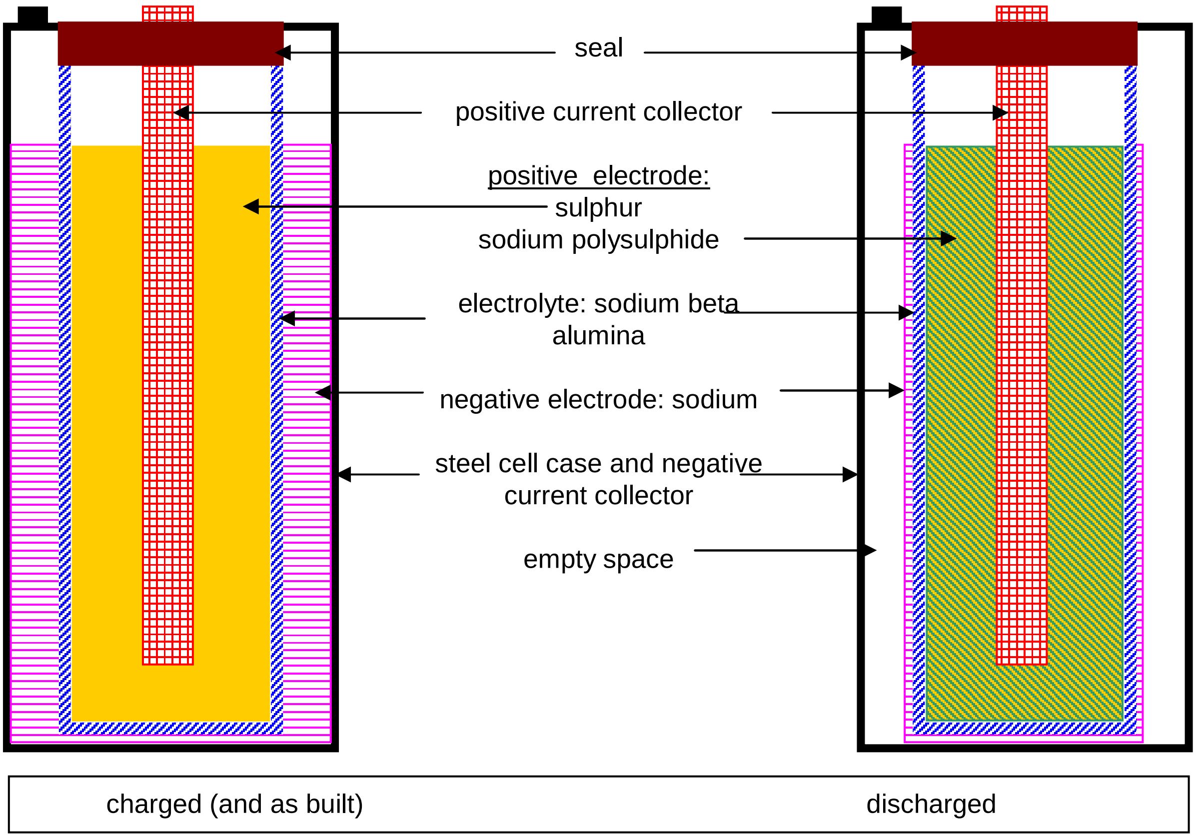

Figure 1.2 Sodium metal chloride cell schematic (differences highlighted in blue)