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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

Fifty-fourth session

Geneva, 26 November-4 December 2018 Item 2 (d) of the provisional agenda Recommendations made by the Sub-Committee on its fifty-first, fifty-second and fifty-third sessions and pending issues: electric storage systems

Sodium-Nickel chloride (Na-NiCl₂)

Transmitted by the expert from Switzerland*

Summary

Executive summary: The extensive experience in the technology of Sodium-Nickel Chloride

(Na-NiCl2) secondary batteries in electric and hybrid vehicles, in which the safety requirements are more restrictive than those of stationary storage applications, depicts batteries based in the Na-NiCl2 technology as a non-dangerous goods for transport. The risk of fire is negligible because of the intrinsic safety of the cell chemical reactions, related to the sodium-tetrachloroaluminate (NaAlCl4) content into the cell, which acts as a secondary electrolyte (the primary electrolyte being the ceramic

 β "-alumina electrolyte as common for Na-Beta batteries).

Action to be taken: Exempt the carriage of cells and batteries containing sodium

tetrachloroaluminate in a cold state from the Regulations.

Background documents: ST/SG/AC.10/C.3/R.294 (United States of America),

ST/SG/AC.10/C.3/2010/30 (United States of America)

ST/SG/AC.10/C.3/106, paragraphs 83-85

Informal documents INF.45 and 45/Add.1 (fifty-third session)

(Switzerland)

^{*} In accordance with the programme of work of the Sub-Committee for 2017–2018 approved by the Committee at its eighth session (see ST/SG/AC.10/C.3/100, paragraph 98 and ST/SG/AC.10/44, para. 14).

Introduction

- 1. At the fifty-third session of the Sub-Committee, the expert from Switzerland presented two informal documents INF.45 and INF.45/Add.1 proposing to exempt the carriage of cells and batteries containing sodium tetrachloroaluminate in a cold state form the Regulations. These presented informal documents provided:
 - (a) A hystory of Sodium/Nickel Chloride battery technology and its classification UN 3292;
 - (b) A background to Sodium/Nickel Chloride battery technology and composition;
 - (c) Explained the differences in comparison to sodium-sulphur battery technology;
 - (d) Explained the status of "non-battery" in "cold" state (temperature lower than 90 °C) since there is no possibility of any current to circulate through the cell at room temperature;
 - (e) Showed market overview and applications, with a fast growing cell demand in the next years; and
 - (f) Reported additional safety consideration during operation and examples of tests performed.
- 2. During the discussion the risk of electrochemical reaction in the case of cold transport was excluded and experts who took the floor noted that a certain amount of sodium remained in the battery even at the discharged state and consequently the chemical hazard could not be ignored.
- 3. We stressed the fact that no incidents related to the transport of this type of cells and batteries had been reported for many years. This safety record should be borne in mind when considering less stringent transport requirements.
- 4. On the risk generated by the presence of metallic sodium during transport, we remind you that the amount of sodium in the discharged state is around 7 g (1% of the cell weight) while in the charged state is 40 g (6% of the cell weight).
- 5. The battery is not a container of chemicals but a complex system designed to also withstand stress and accidents, overcoming the tests conducted by third-party bodies of international importance according to specific standards, in particular:
 - · Crash Barrier Penetration
 - Drop Test (10m)
 - · EuroNCAP Crash Test
 - · Vibration Test
 - · Petrol Fire Test
 - Salt Water Immersion Test
 - · Fire Extinguishing on a Damaged Battery
 - · Shock Test
 - · Impact Test

6. However, if we want to make some comparisons with the provisions for the transport of sodium/nickel chloride batteries and other types of batteries, we see that it satisfies the safety requirements, and this can explain the lack of accident reports.

Packagings

- 7. The sodium/nickel chloride battery container is very robust, in fact, when compared to the packagings required for sodium metal we see that:
- 8. For sodium metal (UN 1428), an approved packaging of packing group (PG) I is required, which must pass drop tests of 1.8 m. Relating to the packing provisions, it is noticeable that in accordance to packing instruction P408 applicable to sodium batteries (UN 3292), they can be transported as well in packaging that do not need to satisfy PG I but only PG II, or even unpacked or simply in protective enclosures which do not need to satisfy the approval requirements of 4.1.1.3. This differences in treatment of the risks between metallic sodium and sodium in batteries demonstrates alone that the regulations already have considered that the risk presented by transports of metallic sodium are not comparable to the risks of transports of sodium in batteries. If, as it is the case, it can in addition be established that a specific kind and construction of batteries brings even more safety, this should be taken in consideration by the experts in order to allow more relaxation.
- 9. Sodium/nickel chloride batteries have overcome drop tests from much higher heights, as documented in informal document INF.8, the batteries have passed the following tests:
- 10. Test No. 1 was intended to simulate the effects of a side impact from a height of 9.8 meters onto the end of a 1 meter long section of Arm coTM crash barrier so that the barrier impacted the center of the battery's side;
- 11. Test No. 3 was intended to simulate the effects of a side impact into a pole or tree, dropping the battery from a height of 10 meters onto a rigid 150-mm radius half-cylinder
- 12. In addition, cells and batteries pass Impact (Test No. 11), Shock (Tests No. 9, No. 14), Crush (Tests No. 7, No. 10, No. 15) tests provided by other standards on "hot" batteries, thus under more critical conditions.

Immersion in water

- 13. The cells and the intact batteries are sealed in a stainless steel container and do not present problems in contact with water and pass immersion tests for 3 hours in salt water (Tests No. 5, 17)
- 14. Damaged batteries have shown not to react with an aqueous foam fire fighting agent on a fully charged battery by piercing it with a hydraulic ram with drawing the pike, and applying the contents of two 'Chubb" handheld fire extinguishers—dispensing a total of 18 kg of aqueous foam, the entire contents of the extinguishers—at 3-minute intervals over a 30-minute duration (Test No. 2)

Resistance to Fire

15. Fully charged, fully operational batteries passed the test No. 4, suspended 400 mm above a tray containing burning gasoline, and maintained there for 30 minutes. The battery case vacuum was also released to include the loss of its insulating effect. Same positive result in test No. 16.

Vibration

16. Many tests have been conducted on sodium/nickel chloride batteries (Tests Nos. 6, 8, 12, 12, 13) following different standards, and all exceed the requirements, a test in particular has the same parameters as expected from special provision (SP) 238 to classify "non spillable" batteries. "Non spillable" batteries are excluded from the regulation of the transport of dangerous goods if they pass the vibration and differential pressure tests and if no liquid escapes from the broken container.

Comparisons with other batteries

Non-spillable batteries

17. Making a comparison with the vibration test for "non-spillable" batteries, the sodium/nickel chloride battery pass the test and does not present any leakage, as shown in the following table:

SP 238	test No. 8, test reference is UL1973, section B.2.2.2.	Note
simple harmonic motion having an amplitude of 0.8 mm (1.6 mm maximum total excursion) is applied. The frequency is varied at the rate of 1 Hz/min between the limits of 10 Hz and 55 Hz. The entire range of frequencies and return is traversed in 95 ± 5 minutes for each mounting position (direction of vibration) of the battery. The battery is tested in three mutually perpendicular positions		passed
Differential pressure	n/a	no valves, the cell is sealed
Leakage at 55°C	n/a	all solid state, no liquid

18. It should be inferred that, as for "Non-spillable" batteries, the absence of liquid leakage in the event of case breakage after vibration test, could exclude sodium/nickel chloride batteries from the transport regulation.

Sodium-sulfur-chloride vs Sodium-nickel-chloride

- 19. Even if both technologies appear under the same UN entry (UN 3292), the sodium-sulfur-chloride and the sodium-nickel-chloride batteries are quite different regarding chemical reactivity and safety issues which should be considered for a decision to allow an exemption in particular conditions. In comparison sodium-sulfur technology the sodium-nickel-cloride technology offers the following advantages in relation to safety issues:
 - (a) Safer product of reaction. The exothermic heats of reaction are lower and the vapour pressure of the reactants less than atmospheric up to a temperature level of 900°C;
 - (b) Less metallic components corrosion. The chemistry of the positive electrode is non-aggressive compared to molten Na2Sx;
 - (c) Assembly in the fully discharged state without the handling of metallic sodium;
 - (d) Reliable failure mode. If the ceramic electrolyte fails, sodium will react with the secondary electrolyte to short circuit the cell.

Lithium vs Sodium

- 20. From a chemical point of view metallic lithium and metallic sodium have similar behaviours but, as discussed above, the accidentology in relation with lithium metal batteries and sodium/nickel chloride batteries reveals the higher safety level of the latter and we therefore believe that with regard to the transport of sodium/nickel chloride batteries, we must take into consideration the real risk.
- 21. The experience gained with sodium-nickel-chloride batteries, of a length comparable to that of lithium batteries and under extreme operating conditions that lithium batteries can not withstand, shows that no accidents involving sodium/nickel chloride batteries are recorded.
- 22. Packing instructions also reflect these differences. Sodium batteries are considered sufficiently strong no matter the size so that when transported unpacked it is not necessary that the packaging must satisfy the provisions of 4.1.1.3 (P408 (2)). For lithium batteries instead this level of robustness appears to be sufficient only for lithium batteries exceeding 12 kg (P903 (2)).

Proposal

- 23. Based on the mentioned long experience, the characteristics of the cold battery described above and the test done in the recent past it is proposed to review the current classification of Sodium Metal Chloride battery (UN3292, last discussed document: ST/SG/AC.10/C.3/2010/30) in order to apply less restrictive transportation conditions than those required by the current classification.
- 24. Add the following sentence at the end of special provision 239:

"Cells and batteries containing sodium tetrachloroaluminate when carried in cold state below 98°C are not subject to these Regulations".

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