RECHARGE
The Advanced Rechargeable & Lithium Batteries Association

EUROBAT
ASSOCIATION OF EUROPEAN AUTOMOTIVE AND INDUSTRIAL BATTERY MANUFACTURERS

Position Paper | May 2017

Recommendation about n-methyl-pyrrolidone (NMP; CAS no. 872-50-4) proposal for inclusion in Annex XIV for authorization.

About the usage of NMP in the lithium-ion battery industry.

Most lithium-ion batteries manufacturing processes are using NMP as a solvent of the electrodes binder , due to stringent solvation and dry atmosphere requirements.

Lithium batteries do not contain NMP. But high performance products are based on the usage of this solvent, totally removed during the manufacturing process.

The NMP used as a solvent is essentially collected after the drying process, reused for cleaning of equipment and finally sent for proper recycling.

The usage of NMP is key for the European battery industry's competitiveness and future development.

The proposal for inclusion in Annex XIV contradicts the opinion given by RAC (Risk Assessment Committee) and SEAC (Socio-Economic Assessment Committee) from ECHA in November 2014 to the EU Commission to opt for restriction for NMP as the best risk management option.

Key recommendations

✓ Do not propose NMP for authorisation

- Usage of NMP for batteries is rather limited in Europe, compared to the rest of the world, as most of the lithium batteries manufacturing is located in Asia.
  This represents less than 4% of the total usage of NMP in EU (as recycling/re-use rates are not published). See data in annex 1.
- **No alternatives are available today for the battery industry use**, as stated in the table C.01 of the background document to RAC/SEAC opinions on NMP (see Annex 3). Indeed, other substances have already been assessed:
  - the usage of NEP as a substitute has not been useful, as it was proven reprotoxic as well (see summary in annex 2).
  - Alternative solvents, including water, have been tested, but are less efficient or still requiring long testing for the manufacturing of high performance batteries.
  - The couple (NMP/PVDF) was replaced successfully by (water/elastomers) for the manufacturing of graphite cathodes for Li-ion batteries, but the physical properties of materials used for the anodes are not compatible with the use of a water based binder: for example, an efficient coating on aluminium collector without corrosion was not achievable.

✓ End the period of regulatory uncertainty by including NMP restriction into Annex XVII.

- The battery as a final product doesn't contain any NMP and it cannot be detected when NMP has been used as a solvent. The NMP hazards are kept under strict controlled industrial use.This was recognized during the RAC /SEAC assessment of NMP in Sept 2014 (see summary annex 3). **The advice given by RAC/SEAC in November 2014 to the EU Commission to opt for restriction for NMP (reduced occupational limit) as the best risk management option, is perfectly suitable for the batteries manufacturing.**
- Investment in Europe for battery manufacturing is uncertain. Many questions are raised about the investment in the EU for battery manufacturing, in particular for electric mobility and energy storage for renewable energy. This uncertainty about the future is even increased when a proposal for authorization is supported. **It is contradictory with the Commission DG GROWTH incentives to develop the batteries manufacturing in Europe as an essential part of the decarbonization program.**

✓ Implement harmonized OHS requirements

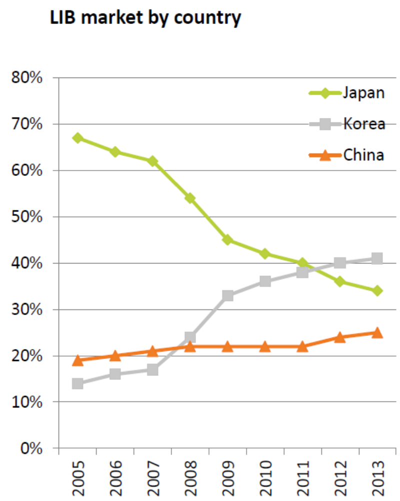
- The valid OEL-value for NMP of 40 mg/m³ as derived by SCOEL is the appropriate protection measure for industrial use. The industry already implemented this limit on a voluntary basis.
- Even if RAC and SCOEL were unable to reach a compromise on a common DNEL for the restriction during the earlier discussions, **there is a need to achieve a harmonized effective new occupational limit for the fair industry competitiveness in Europe**. **Authorization is seen as disproportionate and in contradiction with the restriction, identified as the best RMO for NMP.**

Annex:

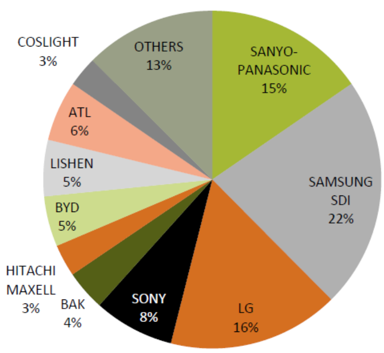
1. Data about the Li batteries manufacturing in EU and the usage of NMP.

- Usage of NMP for batteries is rather limited in Europe, compared to the rest of the world, as most of the lithium batteries manufacturing is located in Asia (data from Avicenne). 2% is manufactured in EU.
  This quantity represents less than 4% of the total usage of NMP in EU (as recycling/resuse % are not known).

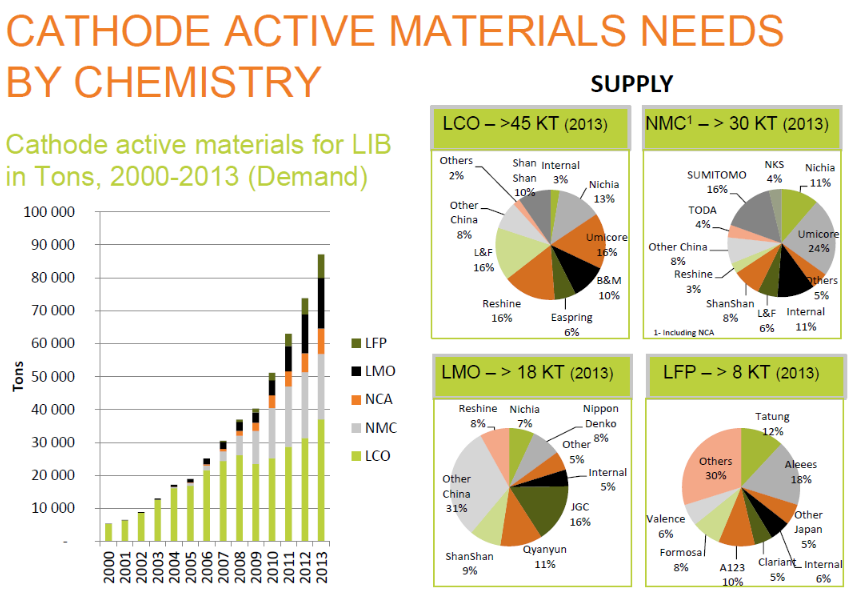
Avicenne 2014



The worldwide Li-ion battery market Company market share in 2013 in volume: 5000 M cells



Less than 2% in total Wh of Li-ion batteries are manufactured in EU.



NMP solvent is needed in order to manufacture high performance Li-ion batteries.

The usage of NMP is in the range of 1 g of solvent per Wh of Lihtium-ion battery produced (reference Batteries PEF bill of material – Commission website).

As a result, the NMP usage in EU for the battery application represents less than 4% of the total usage on NMP in EU (in the range of 30 ktons/year).

2. Data about the substitution of NMP as a solvent for Li-ion battery electrodes manufacturing.

- Substitution with water: as previously stated, (NMP/PVDF) was only successfully replaced by (water/elastomers) for the manufacturing of graphite-based negative electrodes coated on copper foil but it was impossible until today to achieve the same substitution for the positive electrodes Several testings are still in progress because replacing NMP by water, in addition to the replacement of an hazardous substance by a non-hazardous one, would represent a significant cost reduction at the level of the cell manufacturing cost.

- Substitution with other organic solvents: no improvement of the toxicity.

  Test of NEP as a substitute (a chemical manufacturer mentioned that several companies use NEP instead of NMP).

  This practice started when NEP was not classified while NMP was classified as C1b.It was then allowed to transport NEP without hazard label and it was authorized for use in several industries that were banning the use of Carcinogenic substances. From October 22, 2013, NEP has been officially classified as Repr. 1B.

  It will most probably be added to the Candidate List and become de facto a potential candidate for Authorization as NMP became.

3. BACKGROUND DOCUMENT TO RAC AND SEAC OPINIONS ON 1-methylpyrrolidin-2-one (NMP) – Several extracts concerning the battery industry -

25 November 2014

"A.1.2 Scope and conditions of restriction(s)

Proposed restriction:

NMP may only be manufactured and used if it can be guaranteed that under normal operating conditions the exposure (as 8-hr TWA (time-weighted average) will remain below 5 mg/m3. Peak exposures (15 min. STEL (short-term exposure limit)) must remain below 10 mg/m3 and must be compensated by lower exposures during the same day in order to remain below the 8-hr TWA value. To give industry sufficient time to adjust their equipment, the restriction entries into force 60 months after inclusion in Annex XVII.

Further NMP may only be manufactured and used if dermal exposure is avoided with protective clothing and gloves, which comply with the requirements of Council Directive 89/686/ECC or other measures.

The exposure level (both inhalation and dermal) must be guaranteed by the use of preventative measures that are applied in the order of the so-called "hierarchy of control", an established concept referred to in the Chemical Agents Directive (Directive 98/24/EC), i.e. substitution, enclosure, increased local exhaust ventilation, increased general ventilation, change in operational conditions and if needed personal protective equipment.

The proposed exposure limits takes into account the use of respiratory and dermal protective equipment, other preventative measures are however preferred (as indicated in the Chemical Agents Directive).

Manufacturers and industrial and professional users of NMP must be able to demonstrate at the request of the local authorities that they comply with the above restrictions. This can be done by maintaining an exposure monitoring program in accordance with the BOHS / NVAA1 Standard or national equivalent."

Usage of NMP in the Battery industries

Information on use of NMP for manufacture of lithium ion batteries was obtained from industry (public consultation Annex SVHC dossier, SVHC-RCOM 10052011) and from the literature. NMP is used both in lithium ion batteries as in other hybrid batteries using nickel, magnesium, or cobalt. In lithium battery production it is applied as a solvent for the binder resins for both the carbon anode and the lithium cobalt oxide cathode, it may be used in gel-polymer lithium ion battery separators/electrolytes, and it may be used in coatings on the outside of the batteries.

In the manufacturing process of the electrode, NMP is used as a solvent for binder resins between a metal foil and an active material for positive/negative electrode agents. From the point of view of proper performance of the electrode, it is essential for a solvent to dissolve PolyVinylidene diFluoride (PVDF) of the binder sufficiently. The solvent with the active material need to be dispersed uniformly on the metal foil with the binder resin. PVDF is often used as a binder to hold the active material particles (e.g. lithium) together and bind them to the cathode. For the anode graphite is mixed with similar binder material. The slurry, made of solvent, binder, active material and additives, needs to disperse the binder uniformly on both sides of the cathode, often made of aluminum foil, and the anode, often made of copper foil. In addition, it is indispensable for the solvent to be vaporized and completely removed from the electrode after coating.

Various electrolytes may be used in lithium batteries. One of the electrolytes that may be applied are polymer gel electrolytes, which are produced by casting solutions of PVDF in acetone, MEK, NMP, or THF into an electrolyte solution (Arora & Zhang, 2004; Yang & Hou, 2012; Michot et al 1999). Arora & Zhang (2004) describe that the originally used supported-liquid membranes made from polypropylene, polysulfone, poly(tetrafluoroethylene), or cellulose acetate, which use relative softer solvents will In contrast, Orendorff (2012) indicate that polyethylene and polypropylene are much more common in commercial non-aqueous lithium ion separators than separators in which PVDF is being used. Also for other hybrid batteries using nickel, magnesium, or cobalt NMP is used in the slurry to bind the active material to the electrodes. A description of the developments in the US battery production is provided by Lowe et al (2010).

The production of lithium and other hybrid batteries needs large amounts of NMP. Because of the high price, NMP is recovered from the exhaust gasses after drying the electrodes and is re-used. Several specialized companies are active in this field.

In addition, NMP is used in this industry for cleaning all apparatus before coating (public consultation 2013/2014).

Substitution of NMP

"As described in part B.2.2, NMP may have various applications in lithium batteries production and is also used for other hybrid batteries using nickel, magnesium, or cobalt. Looking at alternatives for NMP in the battery application, Zackrisson (2010) carried out experiments in which water replaced NMP as a solvent for the PVDF binder of the cathode. As water was used, another binder was applied. The experiments showed that technically it is possible to replace NMP by water, although the commercial application still has to be proved. There are already commercial binders based on styrene butadiene rubber for application as a binder in lithium batteries that do not need NMP (Targray, 2013). There are also several other efforts to replace PVDF by water soluble binders. To conclude, the development on NMP free lithium ion and other hybrid batteries is ongoing, however, at this moment no alternatives have been proven on a commercial scale. Some supporting confidential information has been provided during the public consultation of the Annex XV restriction dossier (public consultation 2013/2014)"

Impacts on the battery sector

"In the battery sector, NMP is used for production of electrodes for lithium batteries. Information from one company suggests that the originally proposed limit of 5 mg/m3 for inhalation is not proportional, as fundamental modifications of dryers are said to be necessary. Costs related to re-engineering of the process

are said to be €1-9 M , and even then the comment (REF PC COM290) indicates that it is uncertain if the desired emission target is achieved. The comment indicated that an inhalation value limit of 20 mg/m³ with a short term exposure level (STEL) of 40 mg/m³ could be realized reliably and on a reasonable economic basis. There is no information on the need to modify the machines if the inhalation exposure limit value is established at 10 mg/m³.

Another comment from this industry suggested that the proposed by the DS limits are already complied with (REF PC COM301).

SEAC therefore concludes that for the battery sector would not be impacted.**"**

"*Turnover and jobs in the battery industries that can be connected to the use of NMP are not known, although signs have been received in the public consultation that these effects will occur for some of the actors in this sector. One actor indicated in the public consultation that besides effects to the sector itself, also supply chain effects might occur, causing additional turnover effects and losses in jobs to down stream users of batteries (e.g. automotive industry)".*

Overview of the availability of alternatives for different uses

BACKGROUND DOCUMENT TO RAC AND SEAC OPINIONS ON
1-METHYLPYRROLIDIN-2-ONE (NMP)

Table C.01: Overview of the availability of alternatives for different uses.

Use category	Alternative available	Comment
Petrochemical industries	Possibly	Exchangeability will differ per use, technical and economic feasibility not shown
Non-wire coaters	Yes	Alternatives already available
Wire coaters	Possibly	Technical and economic feasibility not shown
Cleaners	Yes	Alternatives already available
Electronics and semiconductor industries	Possibly	Technical and economic feasibility not shown
Battery industries	No	Development ongoing
Membrane manufacturers	Possibly	Technical and economic feasibility not shown
High performance polymer manufacturing	No	Production already > 30 years through similar patented process
Agricultural chemical industries (synthesis and formulation)	Yes (formulation) Unknown (synthesis)	Replacement already ongoing
Pharmaceutical industry	Likely	Information very limited. Replacement recommended by the International Conference on Harmonisation of technical requirements for registration of pharmaceuticals for human use
Laboratory	Possibly	Exchangeability will differ per use
Functional fluids	Unknown	
Construction chemicals	Yes	Based on signals that the use of NMP is stopped in this application