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# Study of the ageing of phlegmatized Nitrocellulose in storage conditions and its sensitivity toward shock wave

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Nitrocellulose (NC) is a very specific hazardous material used for a wide range of application from military to lacquer and varnish; highly inflammable and even explosive in its dry form, NC shall be transported and stored wetted with at least 25 wt% of alcohol to inhibit its explosive properties, or at least 25 wt% of water to reduce noticeably its reactivity when burning. All NC need to pass the Bergmann-junk test to be considered as chemically stable enough to be handled (STANAG 4178 5A/5B, UN Model Regulation). Nevertheless, phlegmatized NC still requires particular safety attentions, notably regarding ageing. Indeed, at the Tianjin accident in 2015, improperly stored previously-wetted NC has been identified to be the cause of a domino effect leading to a massive sympathetic detonations of various chemicals <sup>1</sup>. A recent accident in summer 2022 at a NC manufacturer in France seems to also have involved dried previously-wetted NC, according to the released information from the officials. In both accidents, a hot weather and partial confinement seem to have created conditions for a highly sensitive NC, and due to the surroundings, sympathetic detonations between such NC may have likely occurred.

## Critical parameters

After the Tianjin accident, a wave of study emerged on the thermal stability of nitrocellulose, mainly studying the effect of the damping agent. Existing literature exhibits the strong influence of the drying rate and the type of damping agent in the thermal stability of NC, with long-term drying of water-wetted NC being the most sensitive material.

Katoh et al.<sup>2-5</sup> measured a significant drop of 45°C of the decomposition temperature between a commercially dried nitrocellulose, which decomposes at 150°C, and a nitrocellulose wetted at 2-2.5 % wt with water which decomposes at 105 °C. They also shown the influence of several minerals, present in industrial water, on the thermal stability. For Guo et al. <sup>6</sup>, the calculated SADT of gun powder drop from 117 °C dry to 100 °C water wetted.

In their study of the different damping agent used to stabilize the NC, Wei et al. <sup>7</sup> concluded that all the damping agents decrease the energy of activation of the NC, with the

water having the worst impact, and they recommend that the following temperature shall not be exceeded for storage:

<b>NC pure</b>	<b>NC + water</b>	NC + ethanol	NC + isopropanol
<b>54,5 °C</b>	<b>45,1 °C</b>	47,2 °C	50,4 °C

Figure 1: Temperature thresholds recommended for storage and transportation of humected NC according to Wei et al.

This trend is confirmed by Chai et al.<sup>8</sup> who studied the influence of the drying time and the initial water content: if the drying time increases, the calculated SADT decrease down to 43.5 °C after 45 h at 60 °C.

So while the literature is abundant in small scale calorimetric measurements, it lacks data about the influence of ageing on the NC (and its properties) in degraded storage at the scale of actual storages (such as in drums up to 140 L, UN code 1G) or for a manufacturing site. Also, the sensitivity toward shock wave, the grading of the damping agent among NC volume during time, the influence of that distribution of the damping agent needs to be thoroughly addressed to assess the actual risks of processing NC at nitration levels below of 12.6%.

## Preliminary results

In that context our work intends to answer those blind spots in the existing available scientific literature, in order to solve the practical issue of mass detonation of NC. More specifically, we are first studying the effect, on the sensitivity toward shock wave, of the percentage and the distribution of humectant in commercially available low-nitration NC's drums.

For transportation, NC is packaged in a plastic bag to retain the damping agent in a drum. A first investigation was conducted to analyse the homogeneity of solvent concentration inside a NC drum transported in normal conditions. Using a simple weighting method, a difference of 10 point has been observed between the percentage of water at the top (30%) and at the bottom of the drum (40%), to be compared to the value of 38% provided by the manufacturer. Further investigations will be performed using a Karl Fisher titration, for better accuracy, or more commercial packages.

In our process of defining a proper wetting method, we found that homogeneity is a key parameter. From the UN recommendations on the Transportation of Dangerous Goods, the NC shall be transported with not less than 25% of water to be considered outside of the class 1 (the class of explosives); this recommendation is included as it in many regional or national regulations across the globe, such as the ADR agreement. Samples were made at

25%wt and 30%wt of water with a mechanical multiaxial mixer using the Schatz theory, where the addition of water was made in one step: the method resulted in solid mixture were NC seemed to form small aggregates, leading to a suspicion of inhomogeneity and improper dispersion. Then a second method using the same process but with several steps of addition led to less fine but more homogeneous aggregates. Those samples use the same batch of dried NC, eliminating the influence of the drying method. The nitrogen content is certified to be 12.33 %.

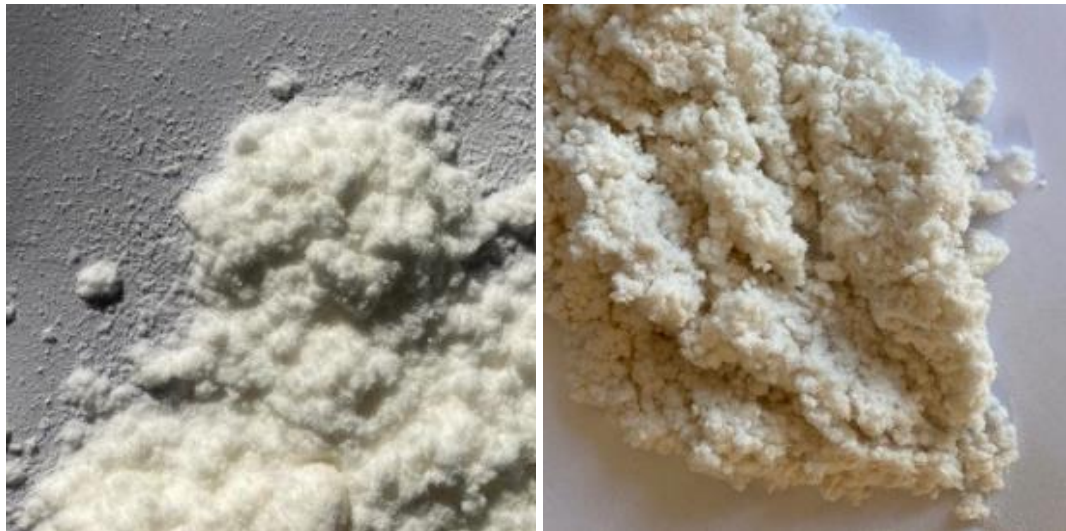


Figure 2: NC samples wetted at the desired water content after drying.  
left: one-step method; right: multi-steps method

The mix is then processed in cartridges (Ø:30mm; L:150mm) using brown (kraft) paper and initiated with a detonator with 0,6g of PETN on a witness plate.

<i>Water content</i>	30%wt	25%wt	25%wt	25%wt
<i>Method</i>	One step	One step	Multi-step	Multi-step
<i>Initiation</i>	No detonation	Detonation	No detonation	No detonation

Figure 3: initiation test

A detonation at 25%wt of water is not to be expected. The one-step mixes proved to be not reliable, therefor pointing out the quality of the mix as a critical parameter for transporting and storing NC at the legal minimum of water content.

Such lack of homogeneity at the mesoscopic scale can add up to a lack of homogeneity at the macroscopic scale of the package (drum): in that case, a packaged NC, having a low nitrogen content and the correct total amount of water, may still exhibit explosive properties while being classified as a 4.1 flammable solid only.

## Future work

In the near future, Karl Fisher titration will be used to quantify the water content and validate the drying and wetting methods. The grading over time of the water among NC in a drum will be measured from actual commercial packages and from packages placed in a controlled environment. The influence of the water content and any gradation of water content in NC will be assessed in regard of the sensitivity toward shock wave from detonator and from sympathetic detonations. As highlighted from the literature, due to the importance of the drying duration and the time before subjected to a stimuli, a strict protocol will be in place to maintain specific time intervals between each step, from drying to destructive testing.

The recently discovered impact of an uneven distribution of water at the mesoscopic scale will also be assessed. The parameters grading over time, uneven water content and total water content will be then considered in regard of the current regulations and usage to eventually suggest improvements.

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