

Diffusion Coefficient of Nitrocellulose in Propellants

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Introduction

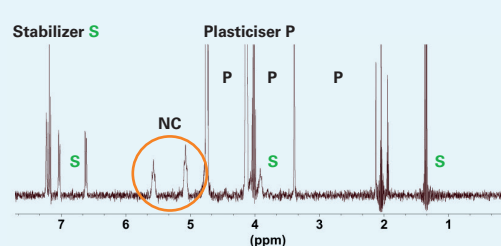
Nitrocellulose **NC** in propellants degrades slowly by an autocatalytic process in which nitrous fumes **NO_x** are produced. These nitrous fumes **NO_x**, mainly radicals, attack the **NC** chain and the energetic plasticizer. A stabilizer is added to trap this **NO_x**. In this process, nitrated reaction products of the stabilizer are formed.

In investigations the efficiency of new chemical compounds as stabilizer is studied by artificial aging through hot storage at 89°C for 18 days. The treated propellants are assessed by visual observation as colour change and deformation. The weight loss is determined as well as the stabilizer content.

The degree of degradation of the **NC** chain during the hot storage was not quantified in these studies. In order to find a method to characterize **NC**, experiments in NMR have been performed for the determination of the diffusion coefficient – this parameter depends on the molecular weight.

Sample Preparation and DOSY-experiments

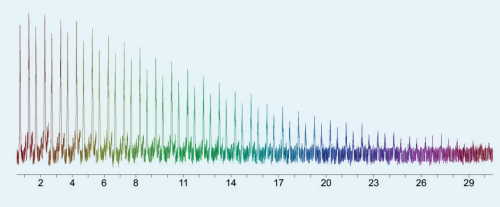
Dissolution of propellant without pre-treatment:
22-24 mg in 0.5 ml CD₃CN or Acetone



¹H -Protone spectra of a propellant in CD₃CN



Diffusion through Brownian motion



Signal depletion of **NC** in an arrayed gradient field in NMR **DOSY**-Experiments

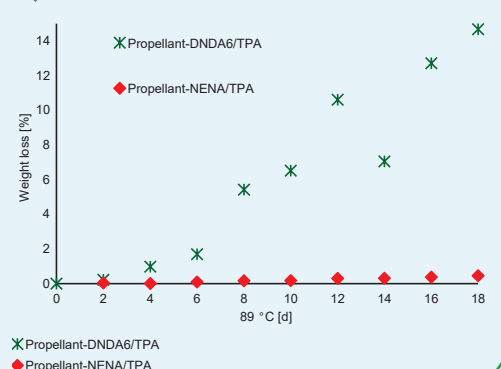
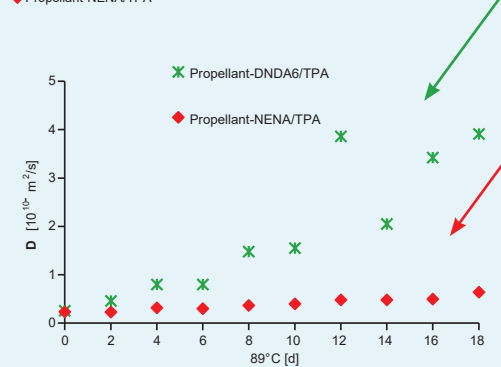
AIM of the study

- ♦ Quantification of the nitrocellulose chain length reduction during hot storage/ simulating ageing
- ♦ Determination of the diffusion coefficient of nitrocellulose in propellants by **DOSY**-Experiments (**D**iffusion-**O**rded-**S**pectroscop**Y**) in NMR → Diffusion coefficient is dependent on the **molecular weight**, structure, temperature, solvent, viscosity etc.
- ♦ Development of an alternative method to Gel Permeation Chromatography (GPC)



Main question:
what state is the
NC chain in???

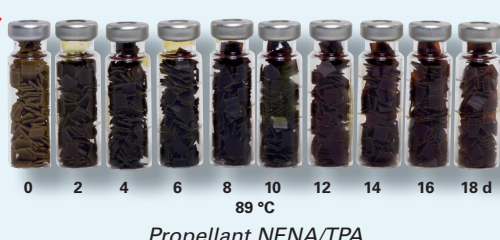
Scission of Nitrocellulose Chain



The effect of the stabilizer Triphenylamine (TPA) in **NC** propellants gelatinized with two different plasticizers NENA and DNDA6 showed a strong difference in the appearance of the flakes and their weight loss during hot storage at 89 °C.

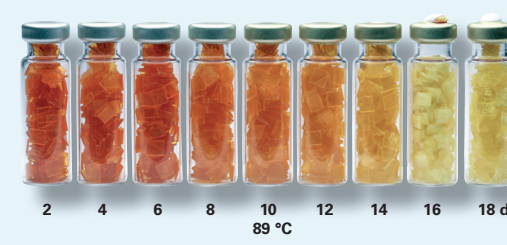


Propellant DNDA6/TPA

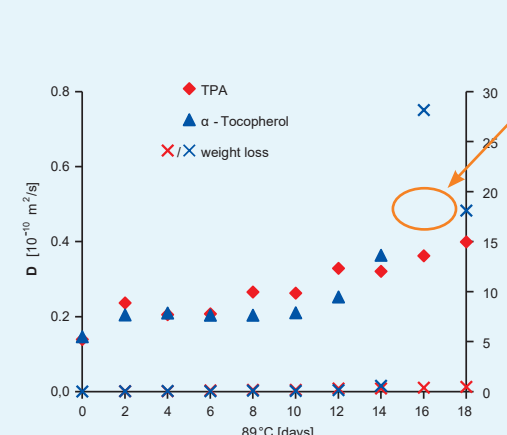
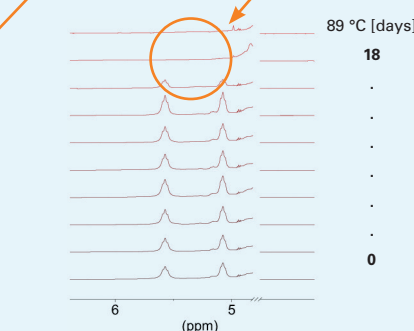


Propellant NENA/TPA

A second mechanism of **NC** degradation is shown for the hot stored propellants NENA/ α -Tocopherol. Propellant did not dissolve after 16 and 18 days of hot storage → mainly low nitrated cellulose chains remained.



Propellant NENA/ α -Tocopherol



Superposed ¹H-spectra of different NENA propellant samples/ α -Tocopherol after hot storage

Diffusion coefficient **D** shows:
Propellant DNDA6/TPA → strong scission of **NC** chain
Propellant NENA/TPA → weak scission of **NC** chain

Conclusions

The diffusion coefficient **D** determined in NMR **DOSY** experiments:

- ♦ Is a useful tool in quantifying the scission of the **NC** chain
- ♦ Allows to evaluate the efficiency of a stabilizer, which is an important parameter besides stabilizer content and weight loss

The analytical method delivers no absolute values but only relative results
→ comparable under same conditions
NMR **DOSY** experiments could be used as an alternative to GPC.

References

S. BRAUN, F. CISZEK, B. WANDERS, K.-T. HAN
Influence of different plasticizers on the efficiency of a stabilizer in propellants, ICT-Conference 2016

