EURENCO

7TH NITROCELLULOSE SYMPOSIUM

MONTREAL

2016

EUROPEAN ENERGETIC MATERIALS COMPANY

MAKING PROGRESS TOWARDS "GREENER" PROPELLANTS

ALAIN DEJEAIFVE, LARA MONSEUR, NICOLE FONDER AND ROWAN DOBSON

2016

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Making progress towards “greener” propellants

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- Propellant composition and green considerations
- Current solutions and the N-NO issue
- Literature

02 Methodology and results
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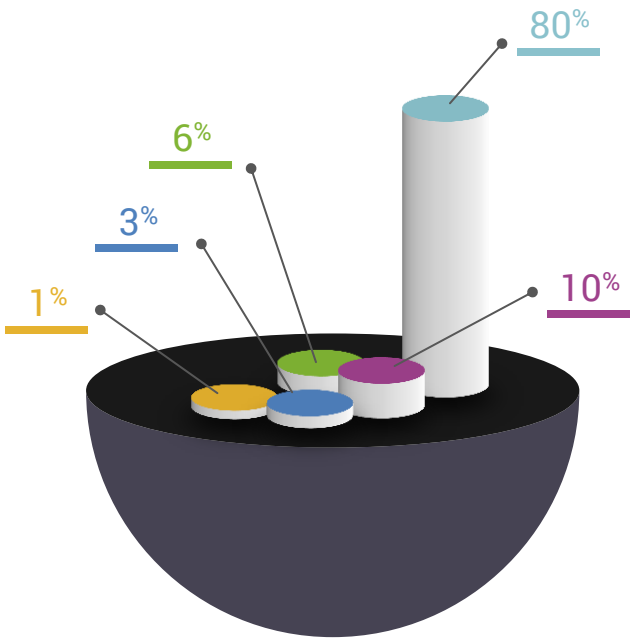
- Stability assessments of propellants
- Identification of daughter products and mechanisms

03 Conclusion and perspectives
- Conclusions

COMPOSITION and green considerations

"Green" has become a key factor in any industrial development for the protection of human health and the environment and Eurenco – PB Clermont intends to reduce the presence of harmful chemicals in their propellants.



Simplified composition of a spherical propellant

01 Nitrocellulose

02 Nitroglycerine

03 Burning rate modifier

04 Additives

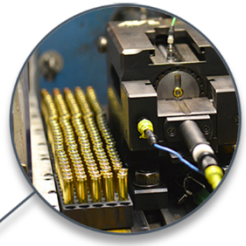
05 Stabiliser

After the successful replacement of the burning rate modifier by a green alternative, the focus is now on the replacement of the stabiliser, some considerations are:

- Readily available or easy to prepare
- Same or better efficiency than current solutions
- Less impact on the environment (synthesis, toxicity…)
- Less toxic anticipated by-products

TWO SHADES of stability

Deterrent migration



BALLISTIC STABILITY

Evolution of the pressure / velocity parameters during the propellant's lifetime

CHEMICAL STABILITY

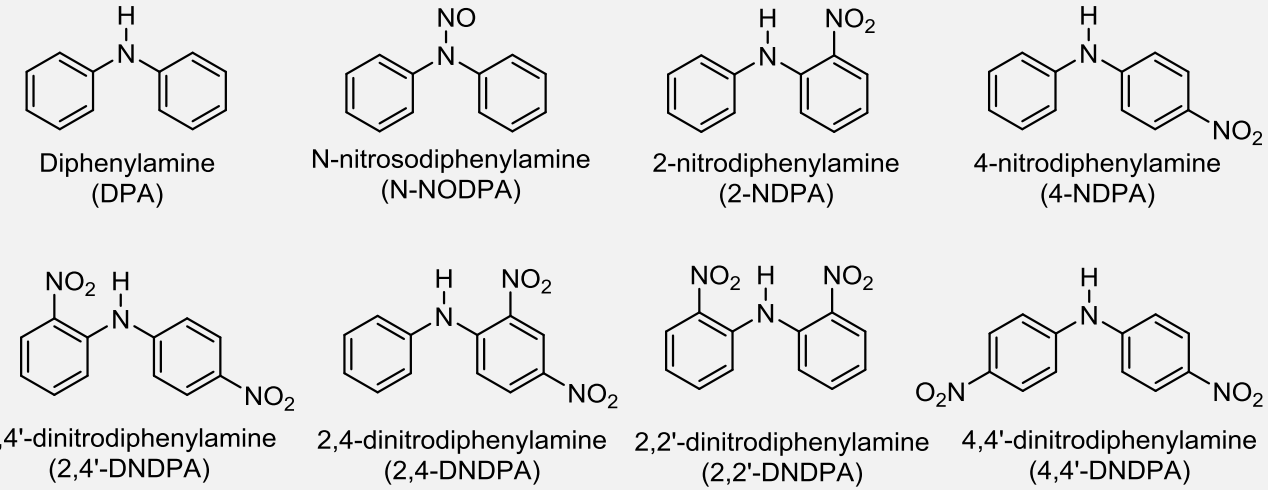
Evolution of the chemical components during the propellant's lifetime

Inherent to the degradation of nitrate esters

CONVENTIONAL stabilisers

Diphenylamine[1] has been used since 1909 as a stabiliser for nitrocellulose and at present is the most widely used smokeless powder stabiliser.

Structures and names of DPA and main degradation products



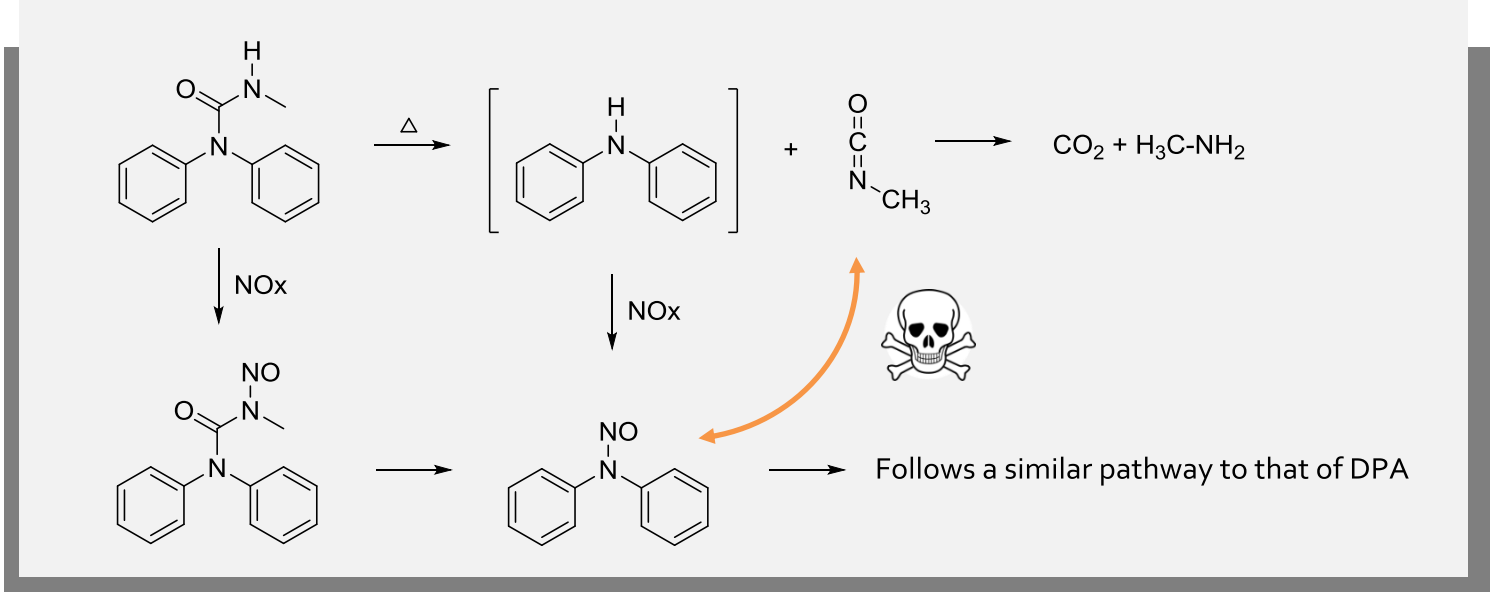
[1] Oehrle S.A.et al., Propellants, Explosives, Pyrotechnics 22, 56-60 (1998)

WHY do we need a *new* stabiliser?

Conventional stabilisers for nitrocellulose-based propellants belong to:

- aromatic amines (e.g., diphenylamine, 4-nitro-N-methylaniline…)
- aromatic urea derivatives (e.g., Akardite, centralite…)

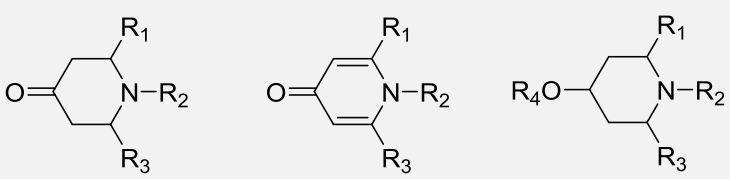
Both types produce toxic and/or potentially carcinogenic species at some point during the propellant's lifetime. As an example[2,3,4], the probable formation of harmful N-NO derivatives (and methylisocyanate[5]) during the stabilisation of nitrate esters by Ak II is presented below:



[2] WIWEB report no.99/Z0136/50019, 21.04.1999
[3] Lussier L. et al., *Propellants, Explosives and Pyrotechnics*, 31, N0.4, 2006
[4] Frys et al., *Propellants, Explosives and Pyrotechnics*, 36, 2011
[5] Chen J.P., et al., J. Mass Spectrom. Soc. Jpn., Vol. 46, No 4, 1998

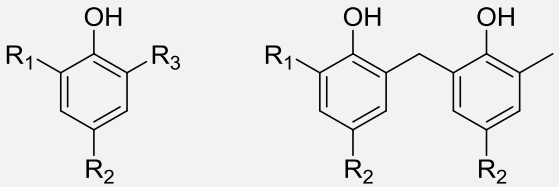
LITERATURE: the situation

Hindered amines



- Overall poor stabilising effect
- N-NO derivatives may still be produced
- TPA has been studied and discarded

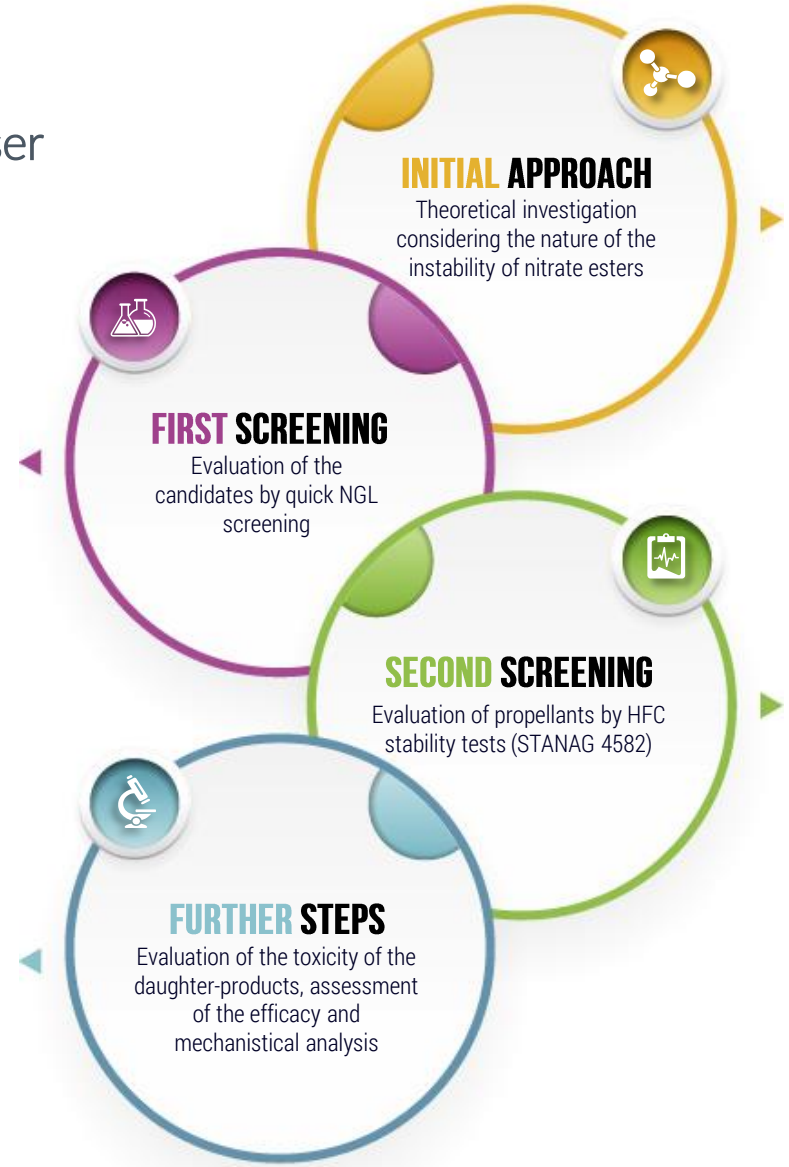
Hindered phenols



- Poor to average stabilising effect
- Slightly incompatible with NGL
- Fast depletion of the phenolic species

[6] Wilker S. et al., ICT conference **2006**, paper 84 and 85 and references within
[7] Vogelsanger B. et al., NATO presentation **2005**
[8] Katoh K., et al., *Propellants, Explosives and Pyrotechnics*, **2007**, 314

development steps
Green Stabiliser



01
IDENTIFICATION
Based on chemical reactivity, several molecules were investigated. Theoretical considerations only, no simulation involved

80 molecules proposed

02
COMPATIBILITY TESTS
NGL tests performed at 90°C, time to autocatalysis is measured and efficiency of the candidates benchmarked against DPA and AkII

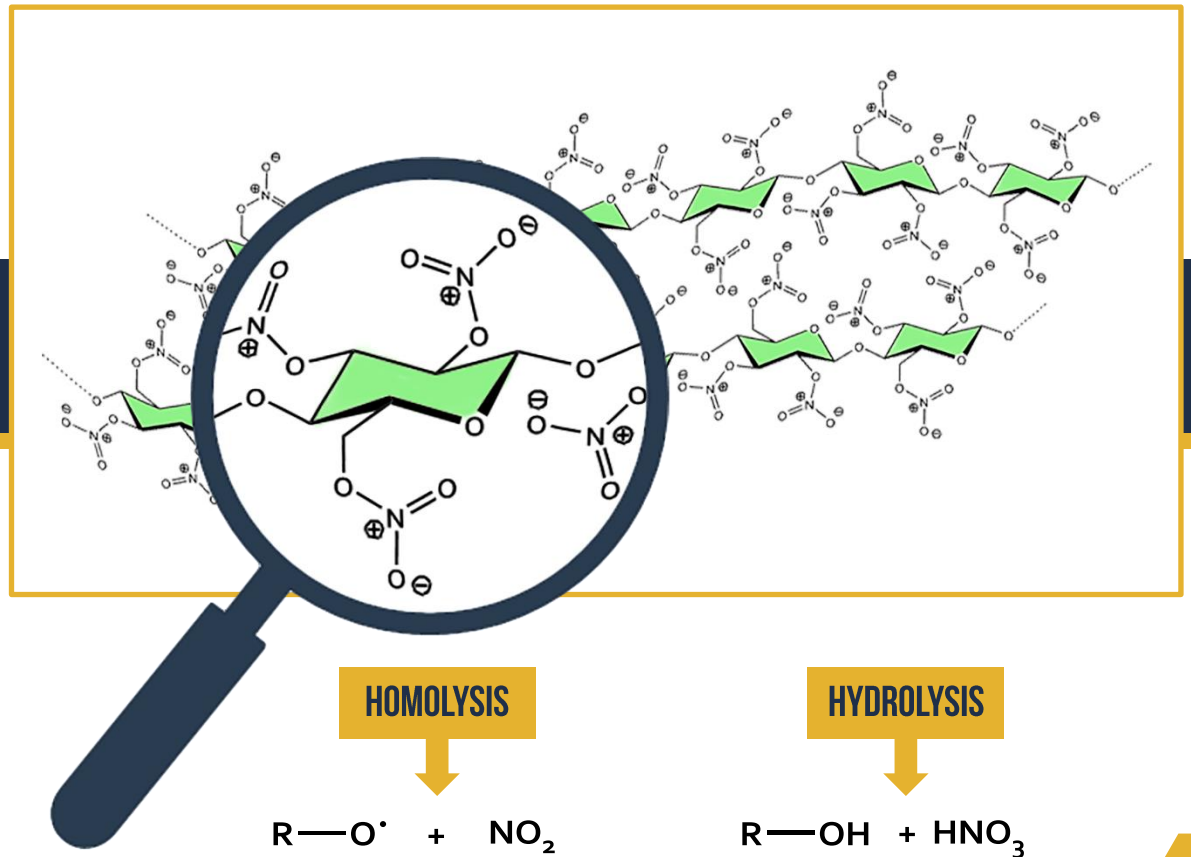
5 types of molecules passed

03
EFFICACY ASSESSMENT
Single and double base (10 to 40% NGL) propellants containing a model of the 5 selected types were prepared and evaluated using Heat Flow Calorimetry

5 families defined

04
VALIDATIONS
Identification and isolation of daughter products and subsequent toxicity evaluations. Assessment of the stability and simulations proposed

Ongoing work...



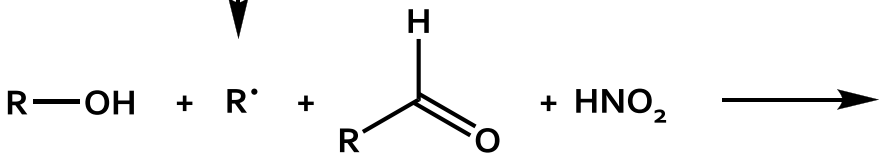
A series of compounds able to react with the alkoxy- and nitro- radicals were proposed

01 IDENTIFICATION

Nitrate esters are unstable organic functional groups that undergo homolysis and/or hydrolysis, generating more unstable species that perpetrate the degradation of the starting material

HOMOLYSIS

[H]-abstraction



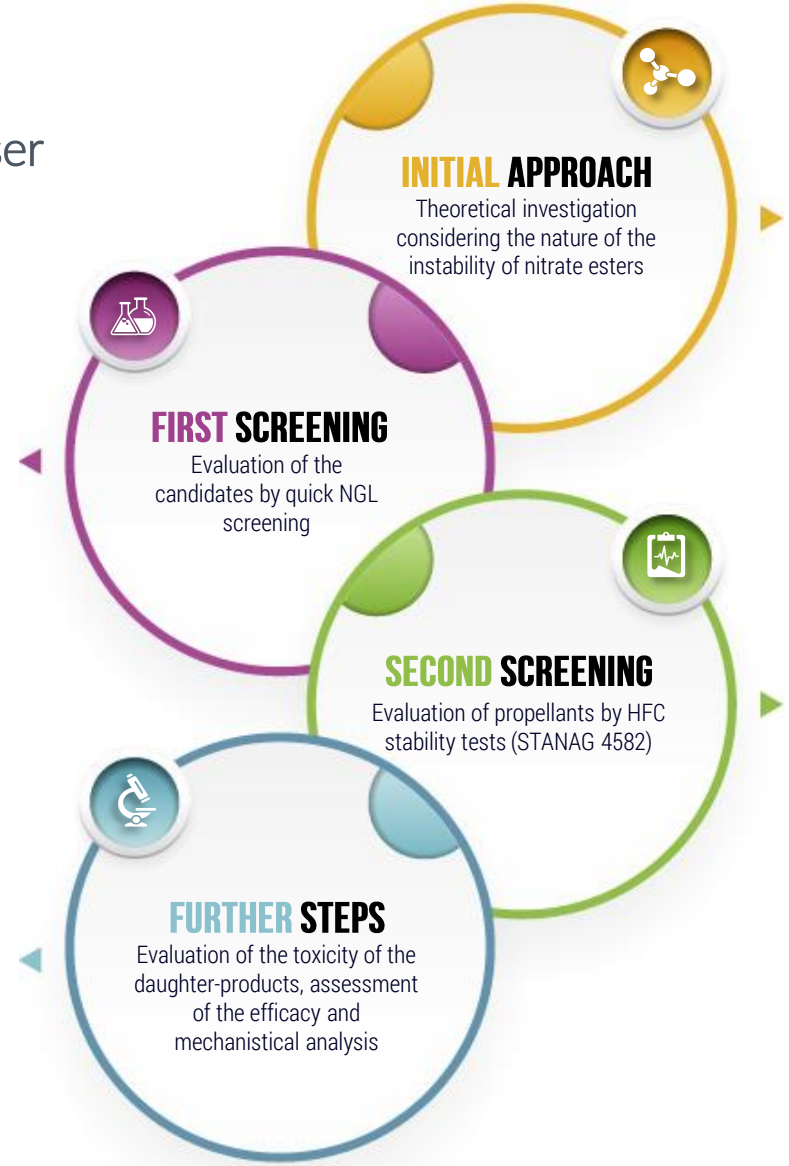
HYDROLYSIS

Action of a stabiliser

Slows down the degradation by scavenging unstable species

Further reactions (oxidations, H-abstractions…)

development steps
Green Stabiliser



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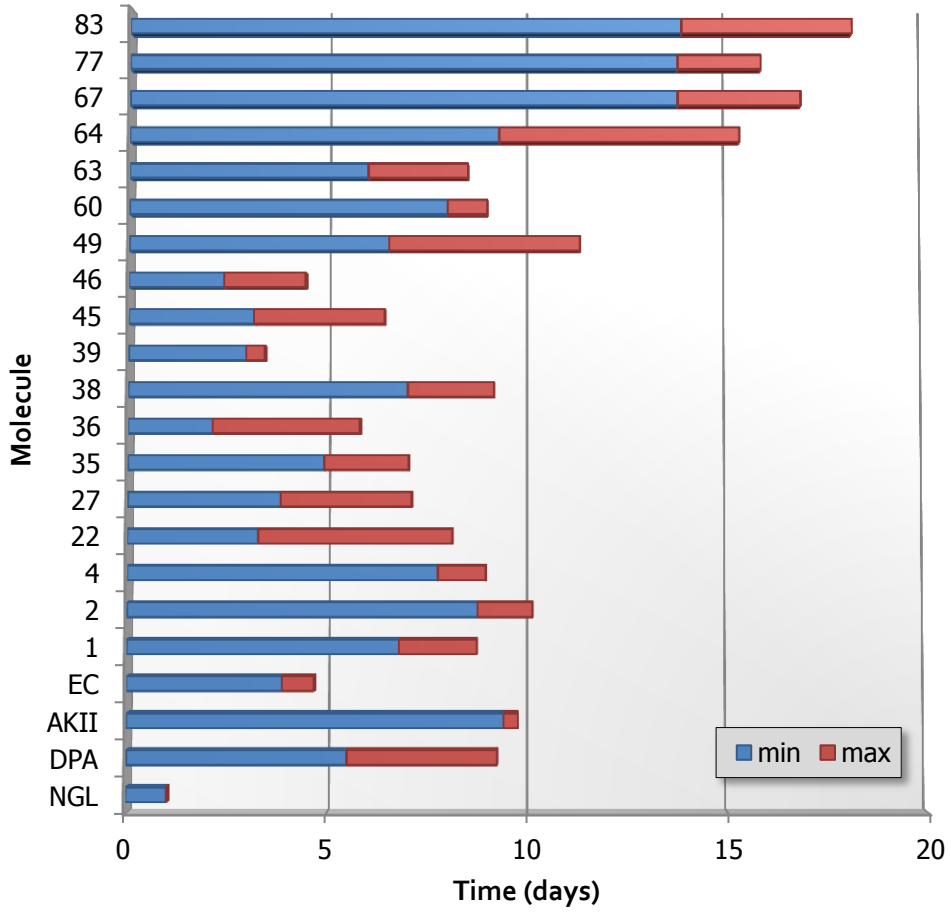
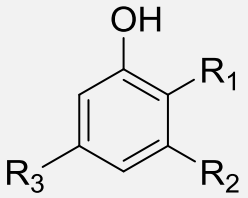
Ongoing work...

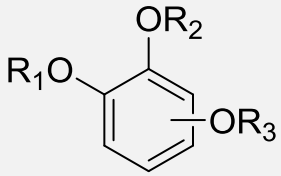
02
COMPATIBILITY TESTS

A mixture of nitroglycerine containing1% of a potential stabiliser was heated to 90°C and the times to autocatalysis were measured and benchmarked against those of DPA, Akardite II and Centralite.

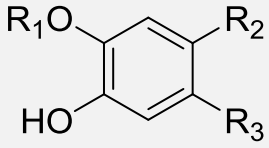




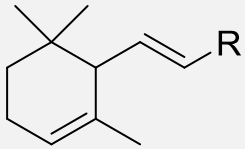
Type 0
"inverted phenols"
PCT/EP2014/071039



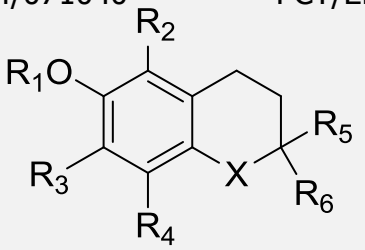
Type I
"trimethoxy-aromatic"
PCT/EP2014/071040



Type II
"guaiacol-curcumenoids"
PCT/EP2014/071041



Type V
"ionone derivatives"
PCT/EP2016/053946



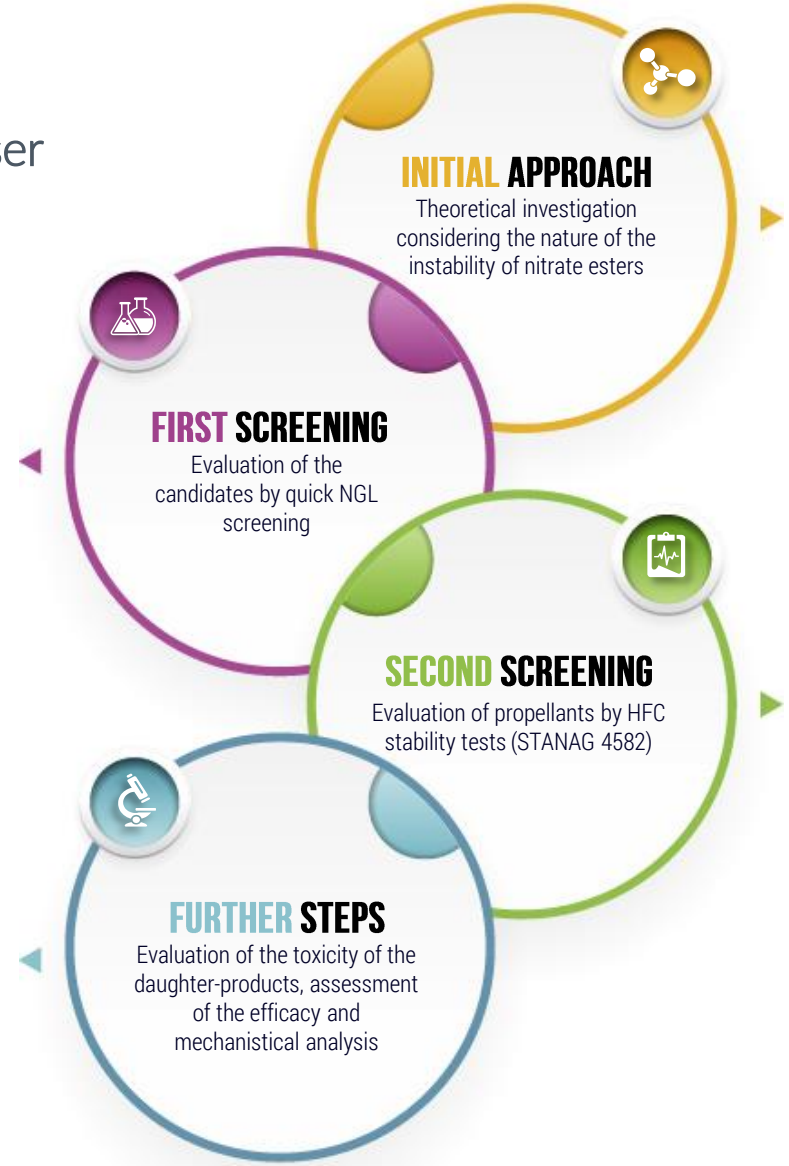
Type E
"tocopherol derivatives"
PCT/EP2016/053948

5 Patents were registered

02 COMPATIBILITY TESTS

5 types of molecules were found to stabilise nitroglycerine @90°C

development steps
Green Stabiliser



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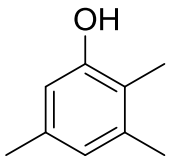
Ongoing work...

PROPELLANT preparation

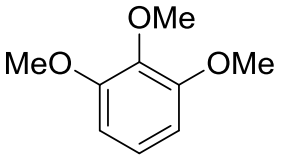
One readily commercially available model was chosen for each family of stabiliser and introduced as a stabiliser in propellants containing up to 40% of nitroglycerine.

EFFICACY ASSESSMENT 03



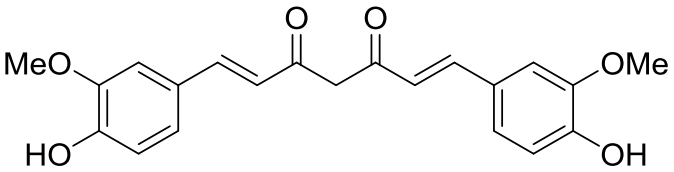
#49

2,3,5-Trimethylphenol
CAS: 697-82-5



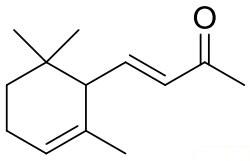
#63

1,2,3-trimethoxybenzene
CAS: 634-36-6



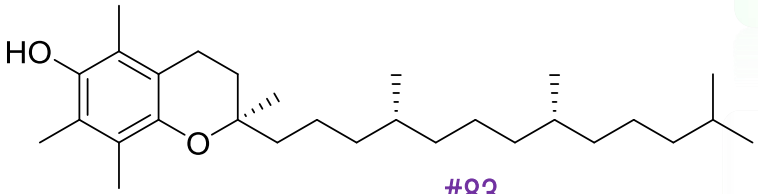
#2

Curcumin
CAS: 458-37-7



#67

α-ionone
CAS: 127-41-3



#83

α-tocopherol
CAS: 10191-41-0

Preparation of propellants
Single and double bases (up to 40% NGL)

Stability evaluation using HFC
According to STANAG4582

According to the STANAG4170 (Ed. III) concerning the use and qualification of energetic materials and following the procedure and requirements described in STANAG4582 (Ed. I) about the stability evaluated by Heat Flow Calorimetry, a propellant is considered stable and safe to store at normal conditions for a period of at least 10 years if the maximum heat flow measured between a heat release of 5 J/g and the time defined by the experiment temperature does not exceed an extrapolated limit as shown in the next table.

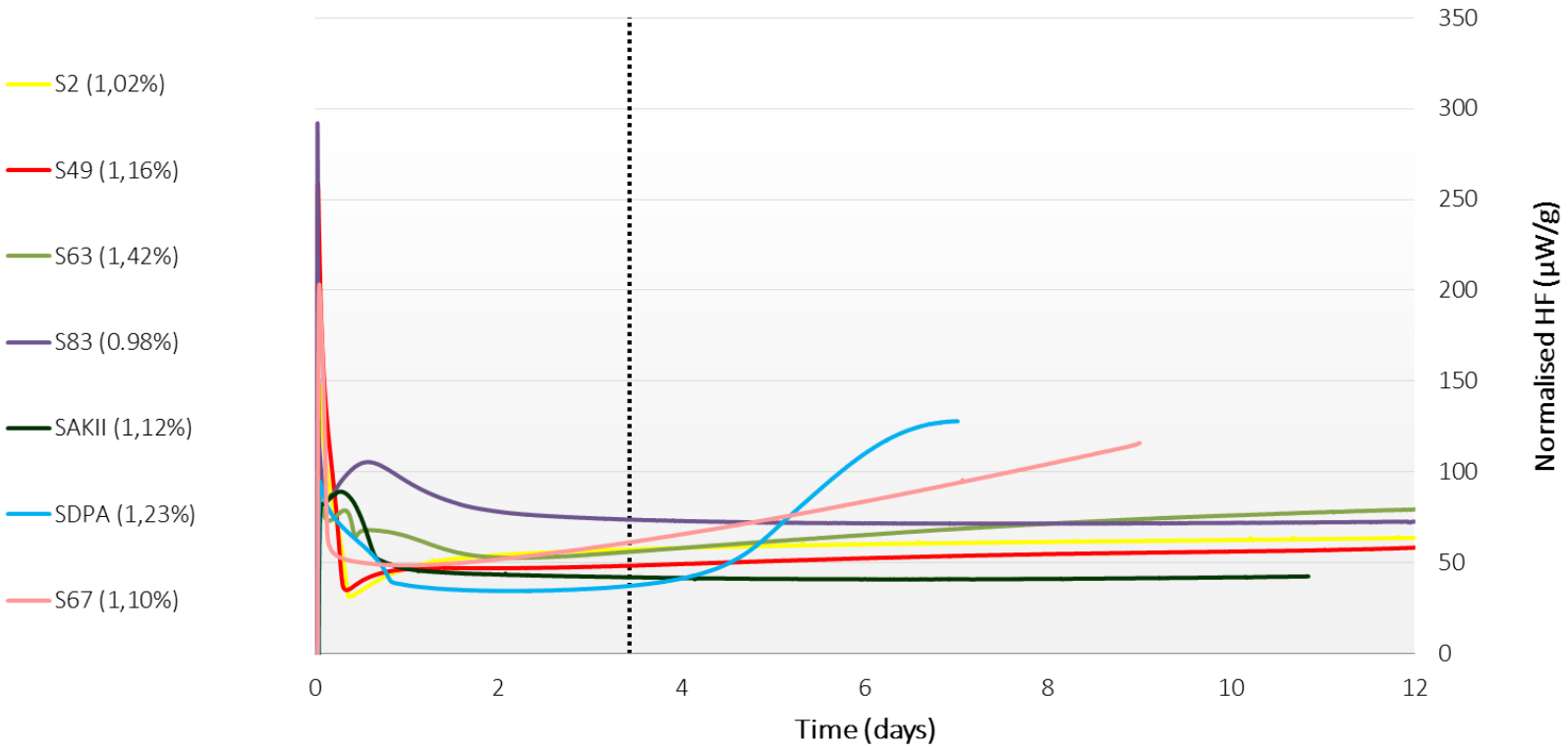
03
EFFICACY ASSESSMENT

T_m [°C]	t_m [days]	P_l [µW/g]
60	123	9.8
70	34.8	34.5
80	10.6	114
90	3.43	350

Calculations of test times (t_m) and heat flow limits (P_l) for different test temperatures (T_m)

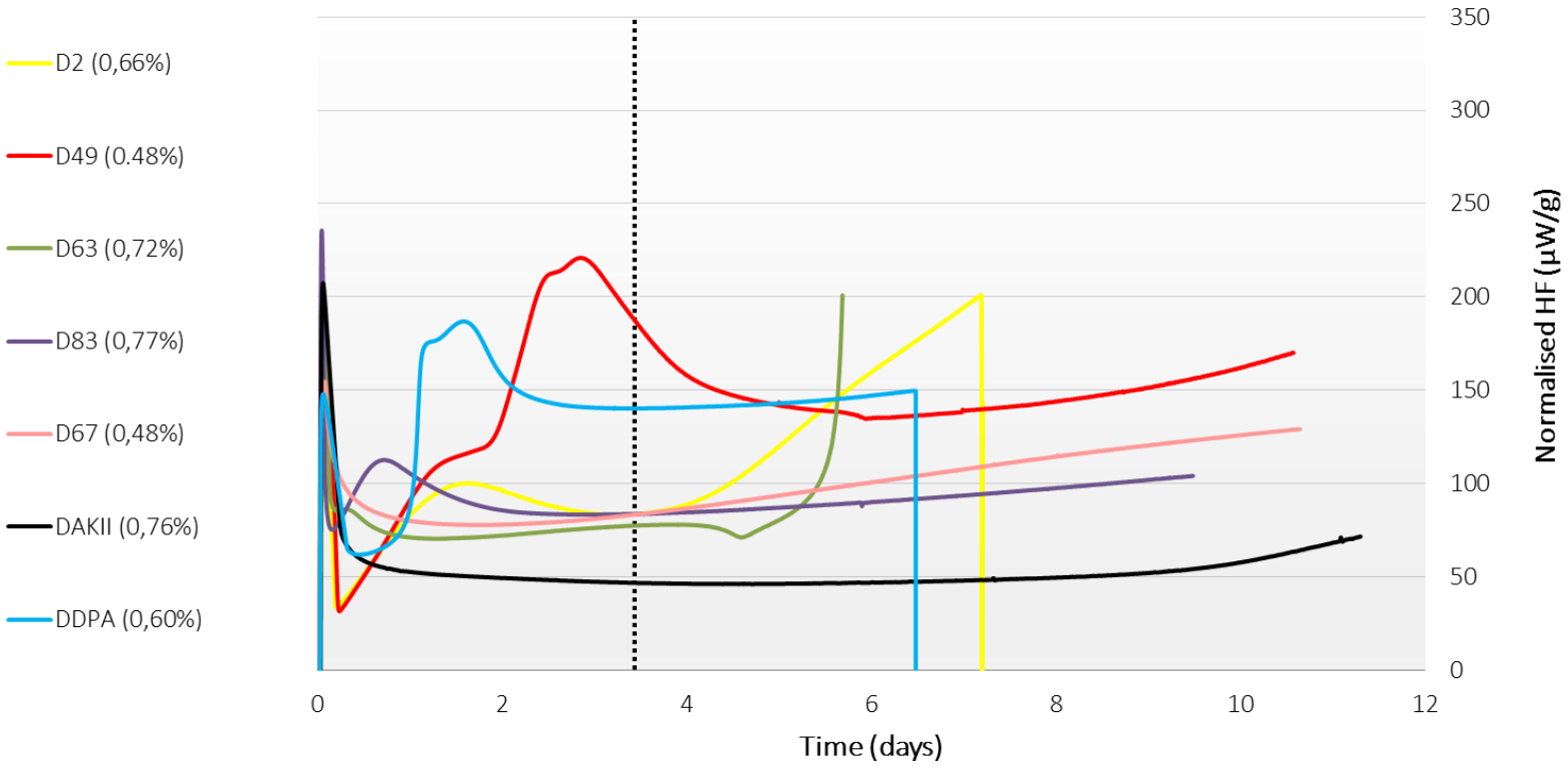
STANAG4582 stability test

Heat flow calorimetry signal of single-base propellants containing approximately 1% of stabiliser at 90°C



STANAG4582 stability test

Heat flow calorimetry signal of double-base propellants containing 40% of nitroglycerine and approximately 1% of stabiliser at 90°C



ADDITIONAL stability tests

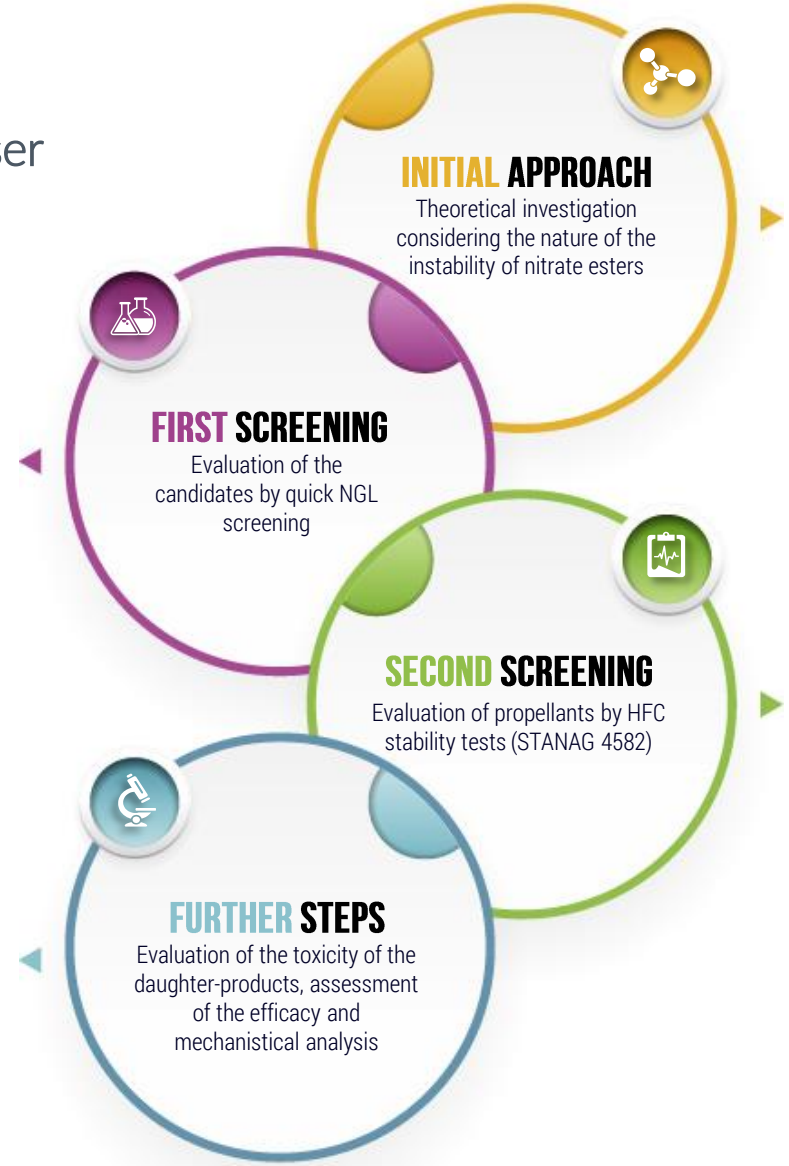
Additional stability tests were performed as well on a powder containing 10% of nitroglycerine and ~1% of the "green" stabilisers.

The results are in line with the values obtained from conventional propellants:

03
EFFICACY ASSESSMENT

		DPA	AKII	Mol. #02	Mol. #49	Mol. #63	Mol. #67	Mol. #83
Stability tests	**Units**							
Bergmann-Junk	[mL]	6.65	2.70	5.40	7.80	7.80	5.40	6.40
Holland test	[%]	0.66	0.47	0.87	**3.89**	**2.93**	1.07	1.30
Ignition temperature	[°C]	169	172	169	172	170	169	169
Methyl violet	[min]	95	105	90	90	75	120	65

development steps
Green Stabiliser



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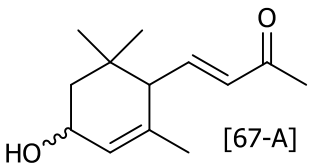
Ongoing work...

Daughter-products of α-ionone

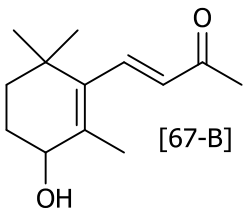
04
VALIDATIONS

Propellants containing α-ionone were artificially aged at 90°C for a period of 5 days in order to produce a wide range of degradation products

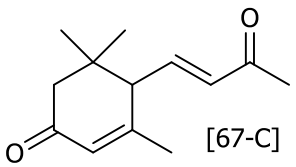
- Extraction
- Separation
- Structural analysis (GC-MS)
- Synthesis
- Validation



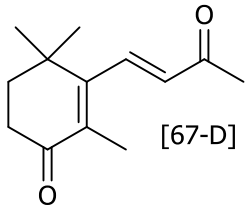
[67-A]



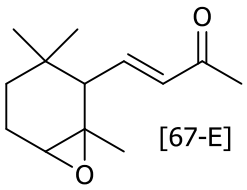
[67-B]



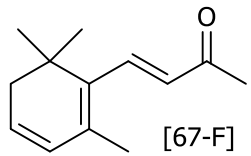
[67-C]



[67-D]



[67-E]

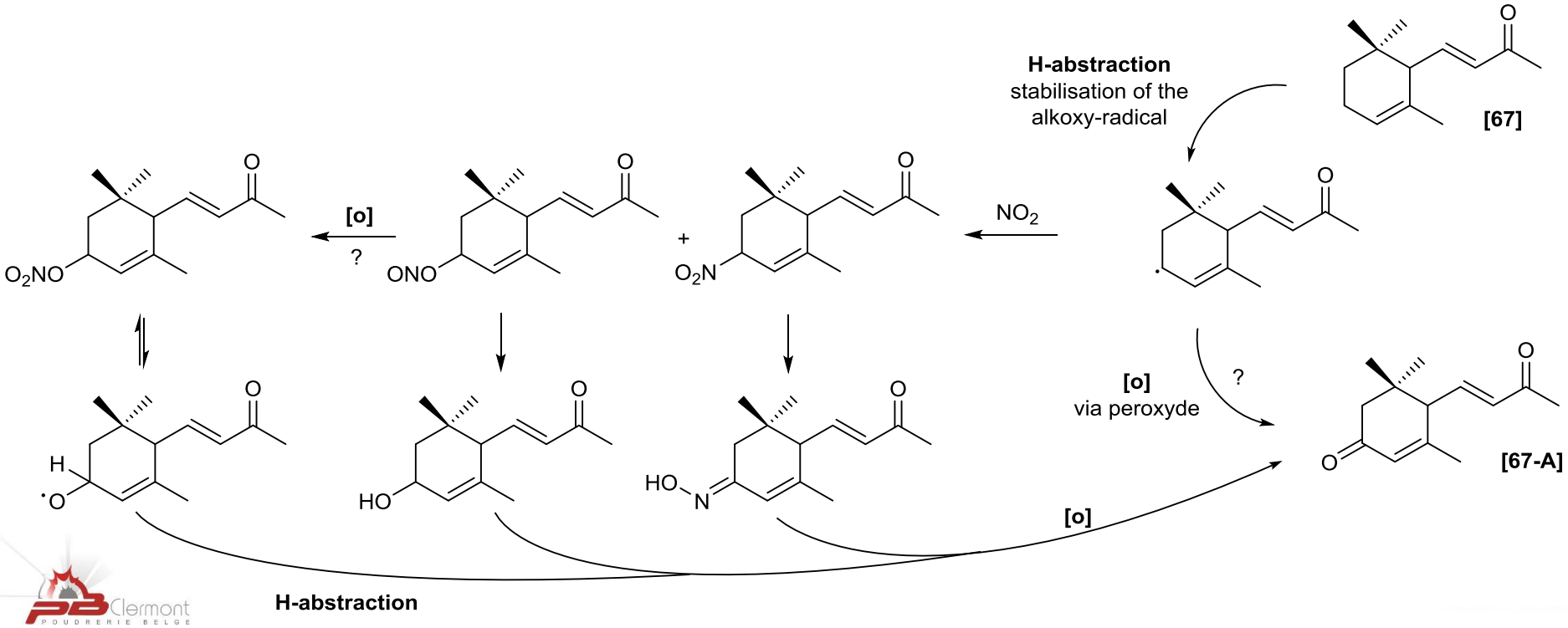


[67-F]

MECHANISTICAL approach

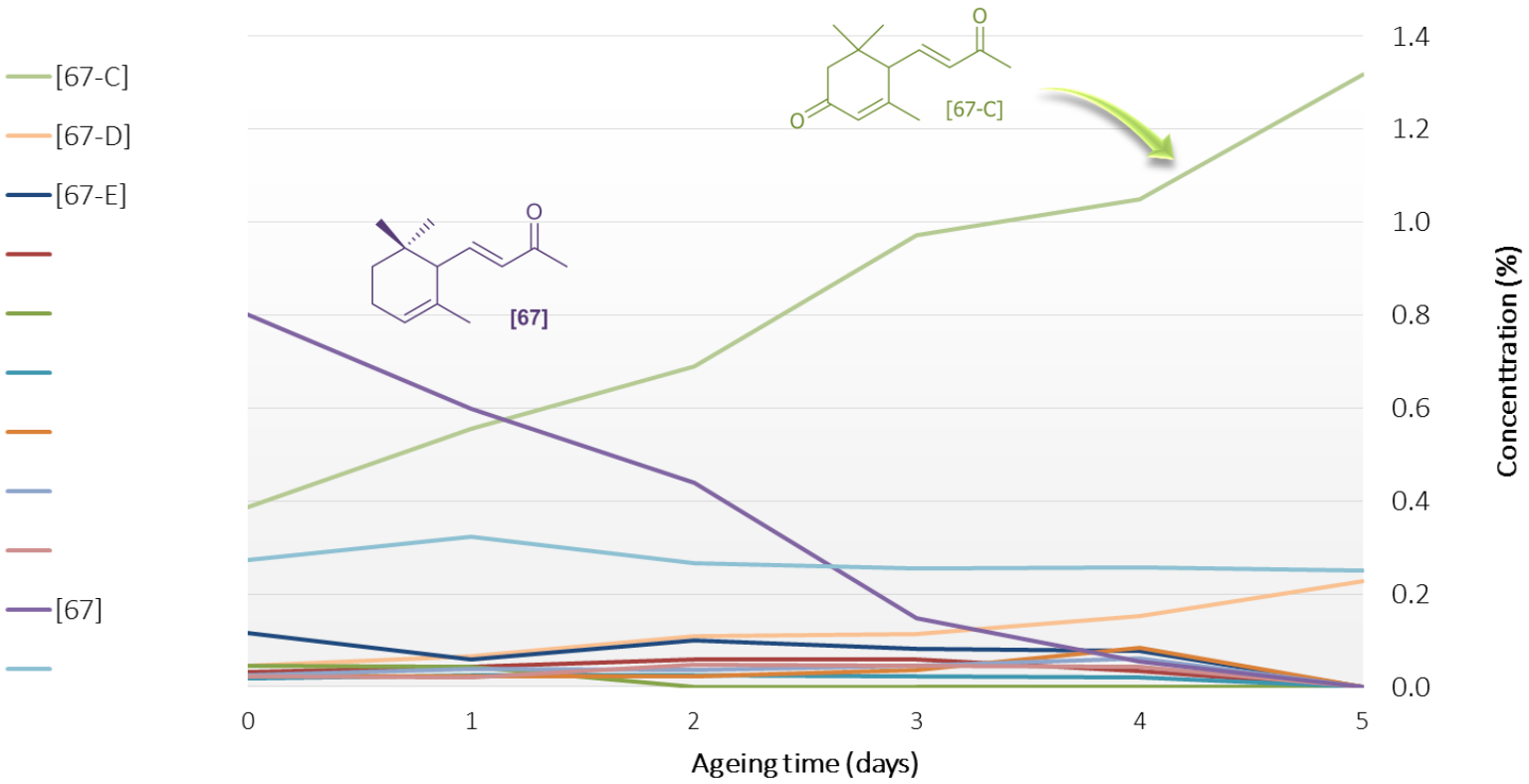
The observed daughter-products probably arise from a series of oxidations, a mechanism is proposed below:

04
VALIDATIONS



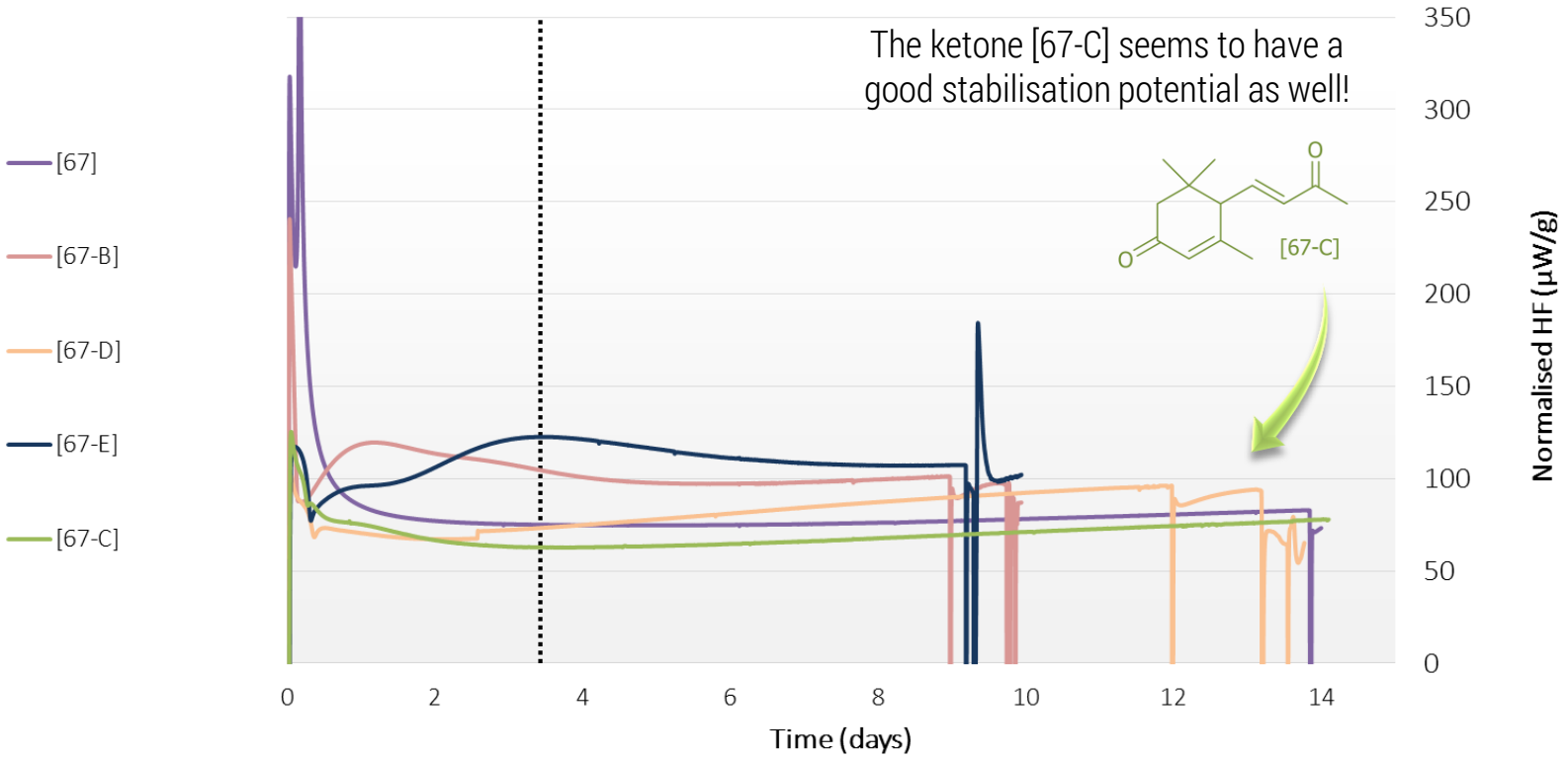
EVOLUTION of daughter-products @90°C

Evolution of the consumption of α-ionone and apparition of different reaction products



STABILISATION potency of the daughter products

Heat flow calorimetry signal of double-base propellants containing 10% of nitroglycerine and approximately 1% of the daughter-products of α-ionone at 90°C



PROGRESS Towards greener propellants

Five types of molecules were found to stabilise nitrate esters, with efficiencies similar to or better than the conventional solutions currently used in industry.

Stability assessments were successfully performed by HFC at 70°C, 80°C and 90°C for propellants containing up to 40% of NGL.
Old school tests passed as well.

Identification of the daughter-products is ongoing for the best candidates. Derivatives of α-ionone show promising stabilisation potentials and a friendly toxicity profile should be expected.

Further identification and synthesis of daughter products and in-silico evaluations of the toxicity risks of these new solutions with a toxicity / environmental impact study. Assessment of the stabilisation mechanisms and upcoming kinetic studies (determination of activation energies) and simulations using the AKTS software.

7TH NITROCELLULOSE SYMPOSIUM

MONTREAL

2016

Acknowledgements:

AKTS

DRDC | RDDC

UCL Université catholique de Louvain

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra