Reactivity of ADN with PolyButadiene in Air

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A presentation to: Insensitive Munitions and Energetic Materials Technology Symposium
10th October 2013

QINETIQ/13/02125

Contents

1 Introduction

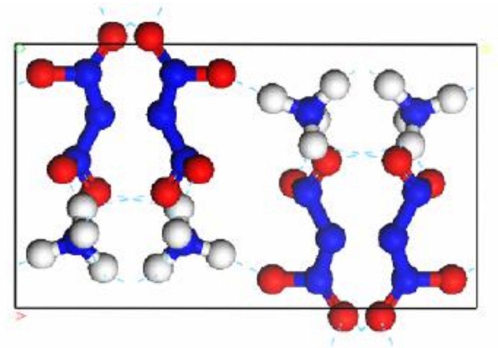
MoD (UK) is funding a Novel Propellants programme developing rocket propellants

Current composite rocket propellants usually contain ammonium perchlorate (AP)

- toxic
- stealth issues

Aim to develop rocket propellants using chlorine-free oxidisers

- ammonium dinitramide (ADN)
- 1,1-diamino-2,2-dinitro-ethylene (FOX-7)



Patrick Goede, Niklas Wingborg, ADN Solid Propellants, IVth Dinitramide & FOX 7 Seminar, 23-24 September 2009, Stockholm, Sweden.

1 Introduction

Aim to measure and understand ageing of ADN in binders

Advantageous to fill polybutadiene (HTPB) with ADN

- polymer has a proven track record as a binder system in AP composite propellants
- exhibits good mechanical properties
- low glass transition temperature

Component	Mass %
ADN	69.4
Polybutadiene	30.6

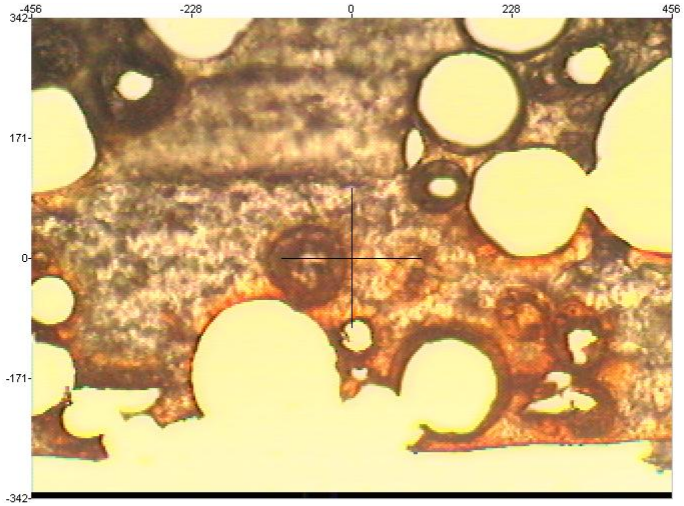
Subjected HTPB/ADN composite to a minimal ageing trial

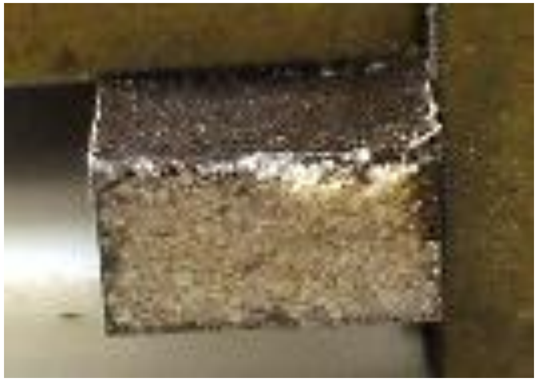
- three temperatures (60, 70 and 80°C)
- dry conditions

2 Bulk Ageing

Oxidised at a faster rate than expected in air

- darkened rapidly (within two weeks) to form a hard skin
- inhomogeneous
- brown banding at the ADN/polybutadiene interface
- downward trend in the sol fraction – oxidative crosslinking





2 Bulk Ageing

Understand ageing
- Quantify rate
- Nature of reaction

Identify additives
- Stabilisers
- Antioxidants

Prolong life
- Decrease costs
- Increase safety

3 Experimental

Diffuse reflectance infrared spectroscopy (DRIFTS)

- optimised for trans-flection

Coated aluminium sample holder base with thin coat

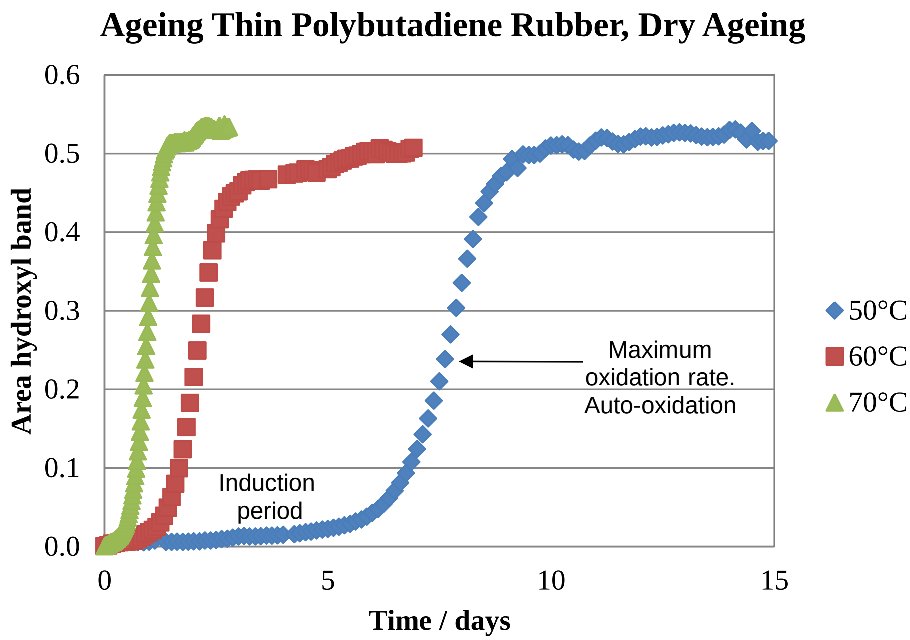
- dried in vacuum for 10 minutes prior to kinetic measurement
- ADN/HTPB (uncured) ratio 50:50
- heated in holder exposed to dry air
- collected IR spectrum every 5 minutes

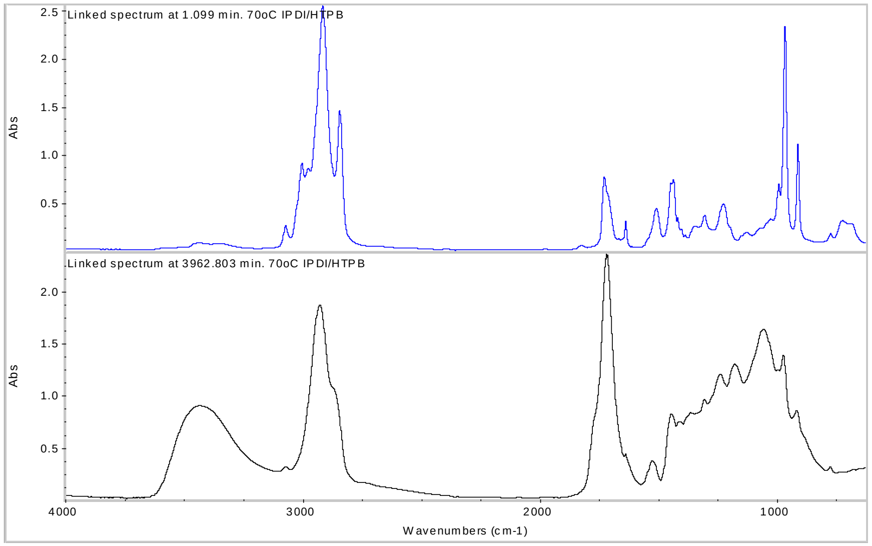
4 Aged HTPB (no stabiliser)

Cured HTPB undergoes autocatalytic oxidative crosslinking (40 microns thick)

- hours to days depending on temperature

Forms new carbonyl and hydroxyl bearing species





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4 Aged HTPB (no antioxidant)

R45M

- uncured with minor amounts of antioxidant (AO)
- 80°C, dry air, ~2.4 days maximum oxidation rate
- Fits autoxidation scheme

Initial dip in the OH content

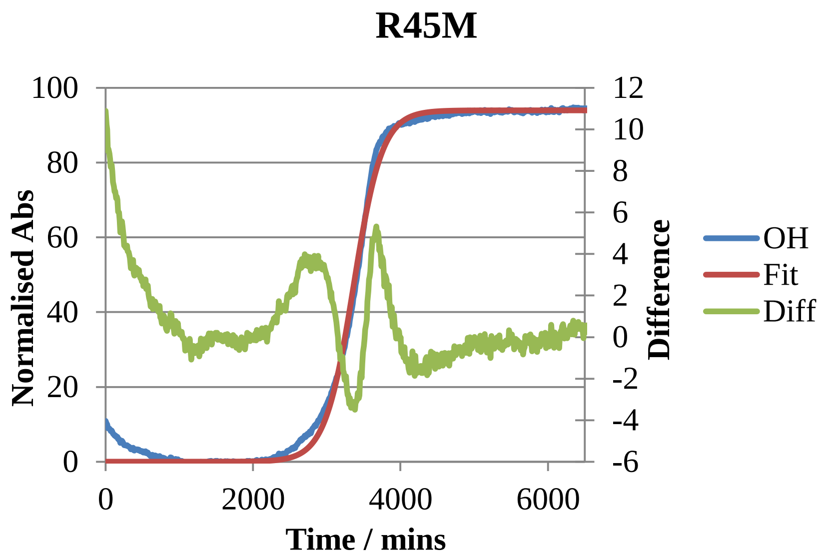
- due to hydrogen abstraction reactions of OH

$$A \xrightarrow{k_{a1}} B + C + S$$

$$A + B \xrightarrow{k_{a2}} B + C + S$$

$$k_2 = k_{a2} \cdot [A]_o$$

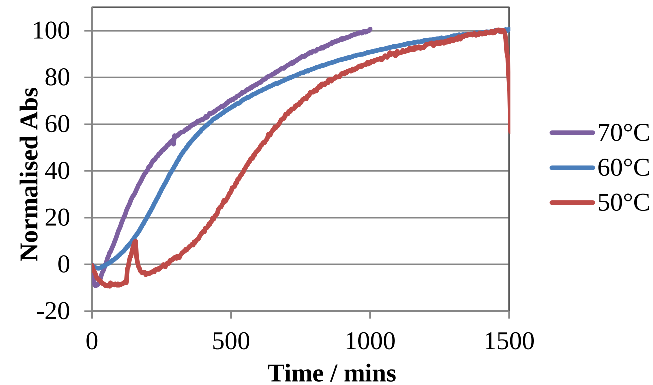
$$k_1 = k_{a1}$$



5 Aged HTPB + ADN (no stabiliser)

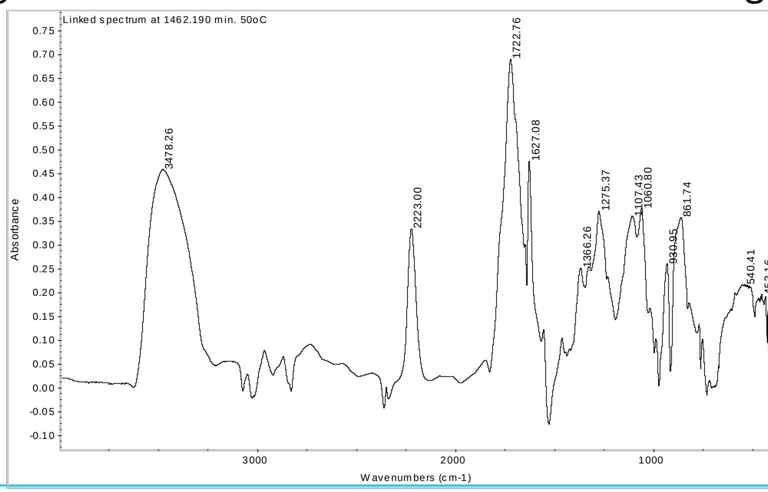
Addition of ADN

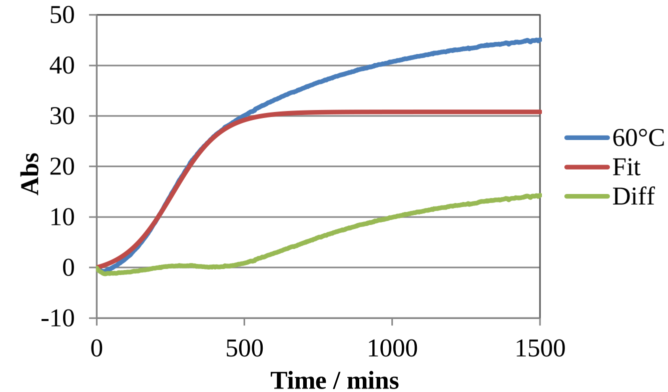
- degradation does not follow classic auto-oxidation scheme
- HTPB oxidises at a faster rate in the presence of ADN
- time to maximum auto-oxidation rate was ~ 90 minutes



Different oxidation products

- carbon-multiple bond-nitrogen species (2223cm^{-1}) – probably a conjugated nitrile – reaction of ADN with oxidising HTPB





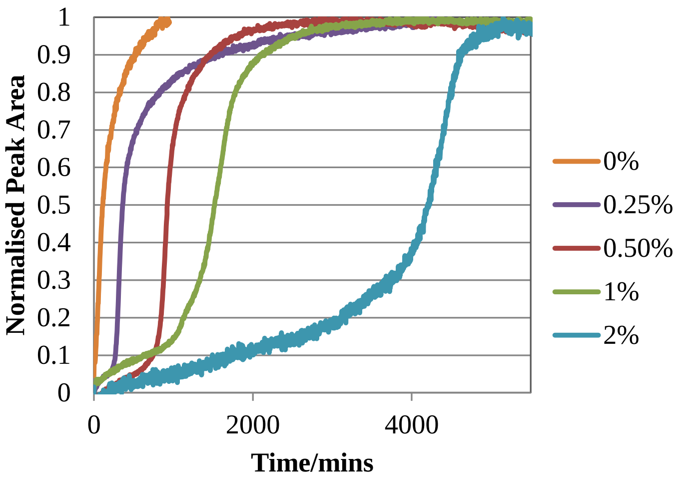
6 Effect of Antioxidant

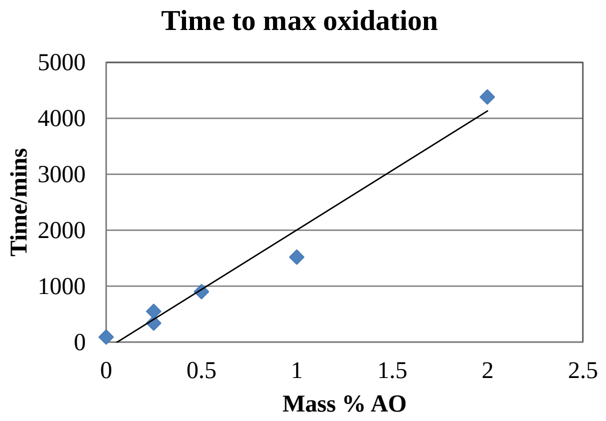
Addition of Calco2246 AO

- increased the time to maximum auto-oxidation
- linear

BUT still a fast oxidation process at 80°C

Mass % Calco2246	Time to max oxidation/days
0	0.06
0.25	0.2
0.25	0.4
0.5	0.6
1	1.1
2	3.0
3	4.4
5	7.3





6 Effect of Antioxidant

Extrapolation to lower temperatures (Arrhenius) – still fast oxidation process

Mass % AO	Temperature/°C	Time to max oxidation / days	Time to max oxidation / years
0.5	80	0.3	0.001
0.5	60	1.5	0.004
0.5	20	105	0.29
1	80	0.5	0.001
1	60	2.6	0.01
1	20	177	0.48
2	80	1.3	0.004
2	60	7.5	0.02
2	20	509	1.4
5	80	3.1	0.01
5	60	18	0.05
5	20	1224	3.4

Roxel Propulsion systems

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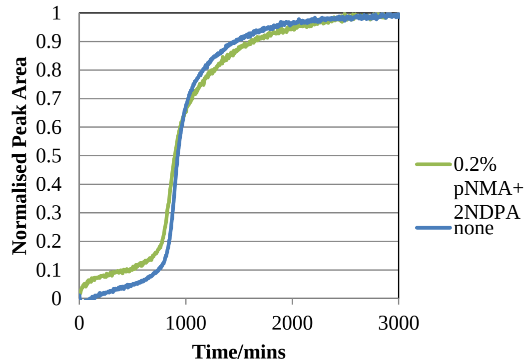
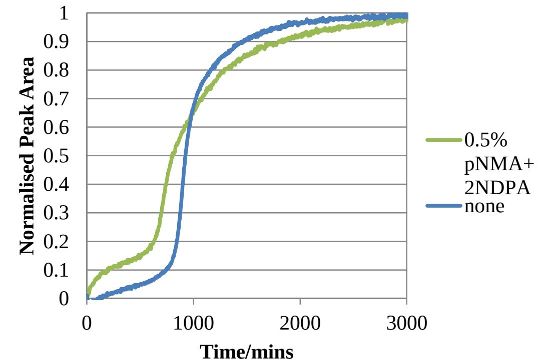
7 Effect of Stabiliser and Antioxidant Type

Addition of stabiliser pNMA at 80°C

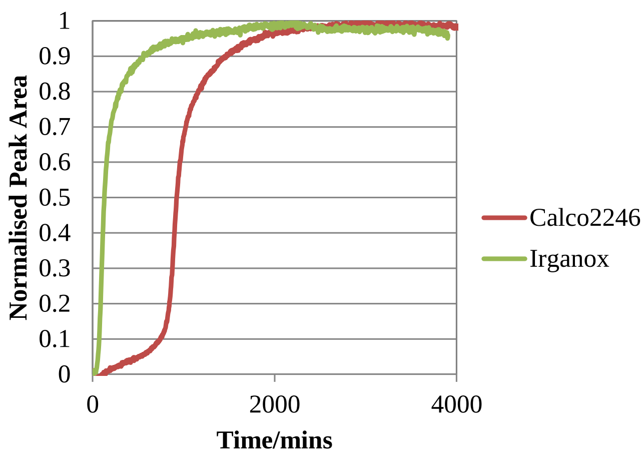
- 0.2% - no affect
- 0.5% appears to accelerate oxidation





Change antioxidant to

- Irganox 1520 - (4,6-bis (octylthiomethyl)-o-cresol)
- less efficient antioxidant than Calco2246



8 Effect of Polybutadiene Type

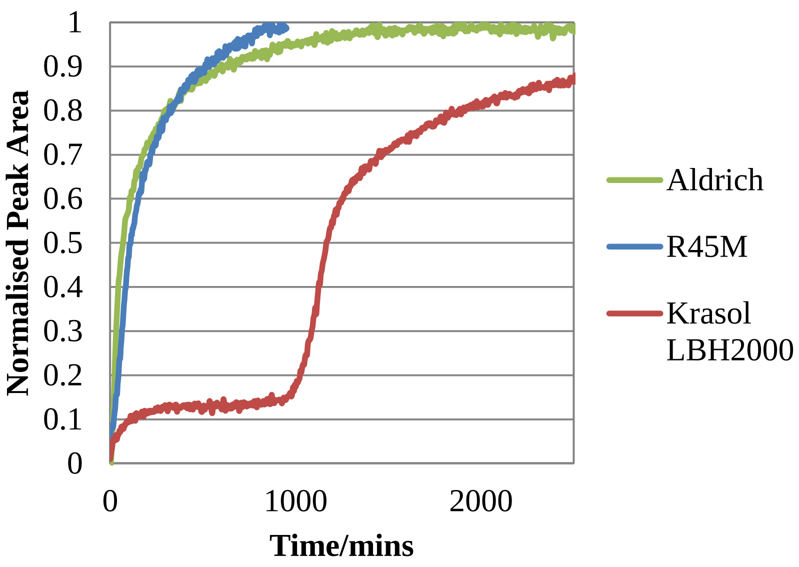
R45M – 20% vinyl, 60% trans, 20% cis (minor antioxidant)

Krasol LBH2000 (vinyl-HTPB) – 65% vinyl, 22.5% trans, 12.5% cis (minor antioxidant)

Aldrich HTPB (cis-HTPB) – 1% vinyl, 27% trans, 72% cis (no observable antioxidant)

Reactivity

Vinyl HTPB<<R45M<cis-HTPB



8 Effect of Polybutadiene Type

Vinyl HTPB + minor AO - extrapolated oxidative ageing to room temperature

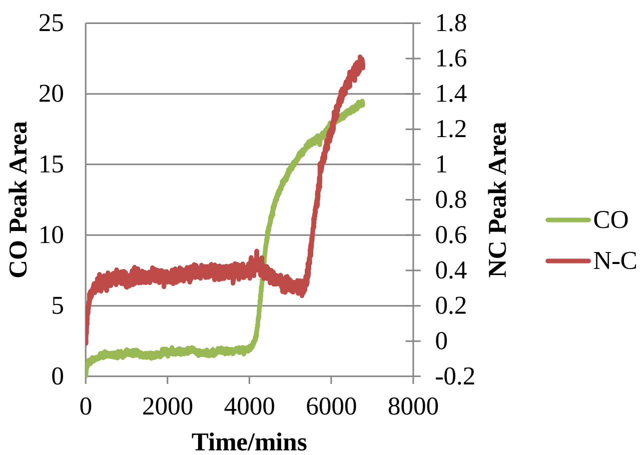
- longer life

Disadvantage Vinyl HTPB

- higher glass transition temperature (-46°C versus -75°C for R45M)

Formation of the conjugated nitrile after maximum oxidation rate

Temperature/°C	Time to max oxidation / days	Time to max oxidation / years
80	0.8	0.002
70	3	0.008
60	~13	~0.04
50	~64	~0.2
40	~339	~0.9
30	~2010	~5.5
20	~13441	~36.8



9 Conclusions

HTPB/ADN propellant, with small amounts of antioxidant, ages rapidly

- highly inhomogeneous process

Followed oxidation of thin ADN/HTPB R45M samples using IR spectroscopy

- does not follow the classic autoxidation kinetic scheme
- much faster than pure HTPB R45M
- evidence of ADN reaction with oxidising HTPB - formation of a conjugated nitrile species

Addition of antioxidants mitigates degradation

- inefficient additives

Stabiliser pNMA does not improve oxidation rate

Oxidation depends on polymer backbone

- vinyl HTPB<<R45M<cis HTPB

The authors thank the DSTL's Programme and Delivery Directorate (MoD, UK) for funding this work.

Thank you for your attention!