



Effects of Energetic Plasticiser Impurities in the Formulation of NC-based Binders and their removal via a Thermal and Chemical Treatment.

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- Background
- Problem Statement
- Plasticiser Treatment Development
- Treated Plasticiser Ageing Trial & Results
- Conclusions
- Further Work

PBX Binder Composition

Polymer: Nitrocellulose (NC)

Energetic Plasticiser

- NC based energetic binders used as part of Polymer Bonded Explosive (PBX) formulations
- Use an energetic plasticiser to improve the NC gelatinisation and subsequent mechanical properties of the binder system

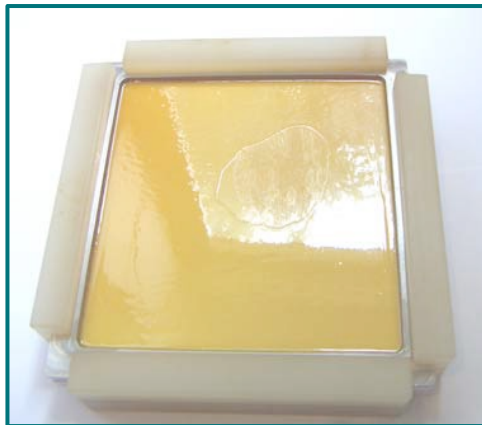
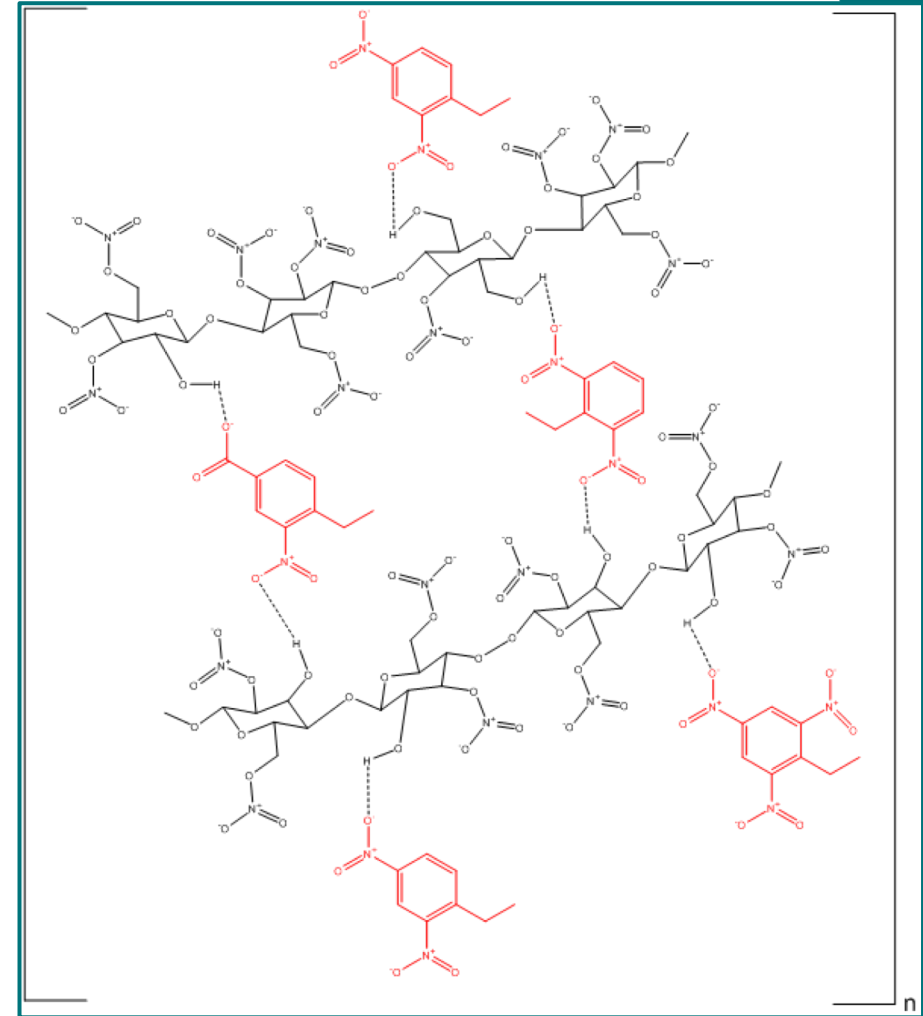


Photo of Binder System

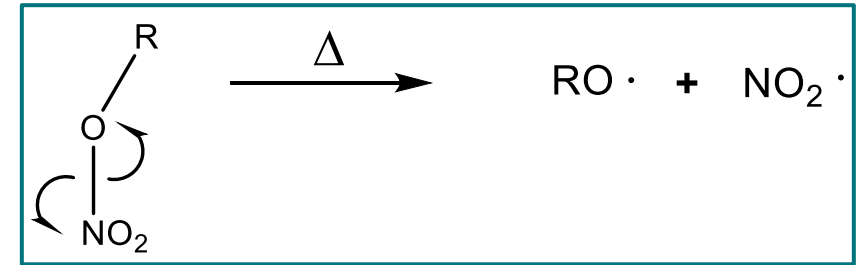


Structure of Binder System

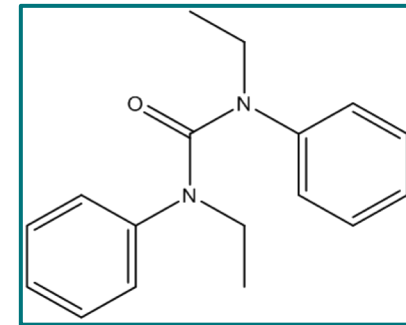
PBX Binder Composition

Stabiliser

- PBX mechanical properties related to NC polymerisation, measured by molecular mass (M_n)
- Measures taken to limit auto-catalytic degradation of NC via thermolysis, resulting in backbone scission
- Use of NO_x scavenging stabiliser to limit extent of NC thermal degradation



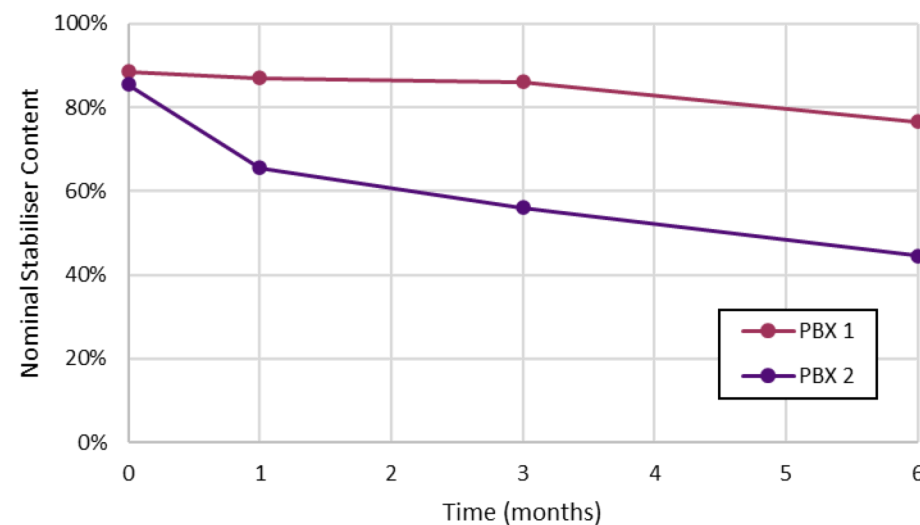
Thermolysis Reaction Mechanism



Structure of NO_x Scavenging Stabiliser

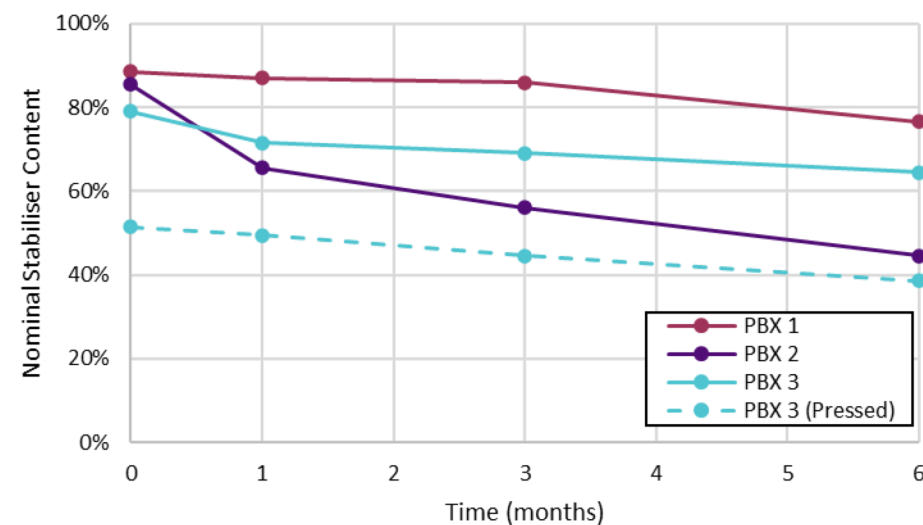
Explosive Formulation Trial

- Explosive formulation powder ageing trial (1, 3, 6 months at 60°C) with stabiliser content measured at each withdrawal
 - Compared to other batches of the same formulation, significant difference in stabiliser content after 1 month



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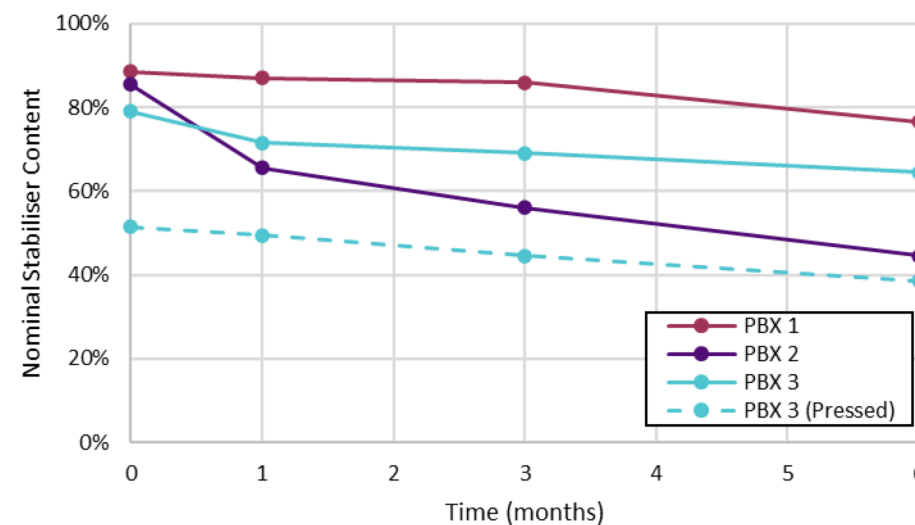
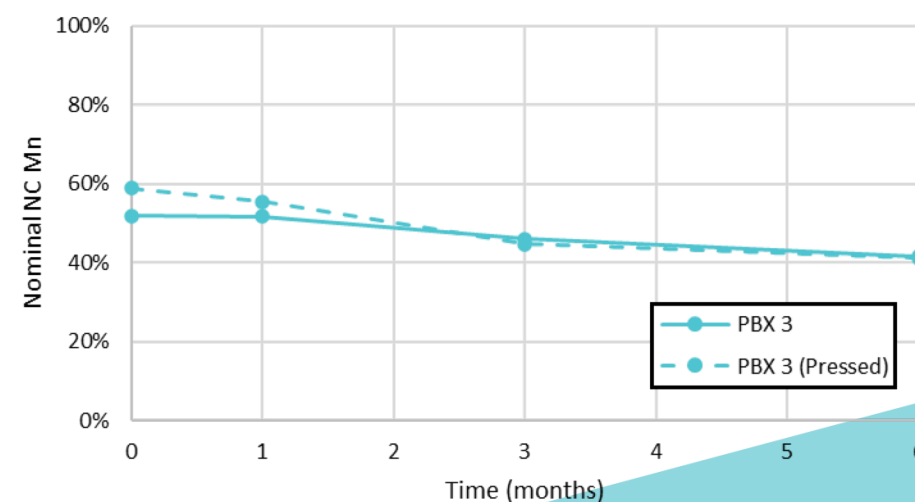
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 - Initial decrease also present in material which has been pressed



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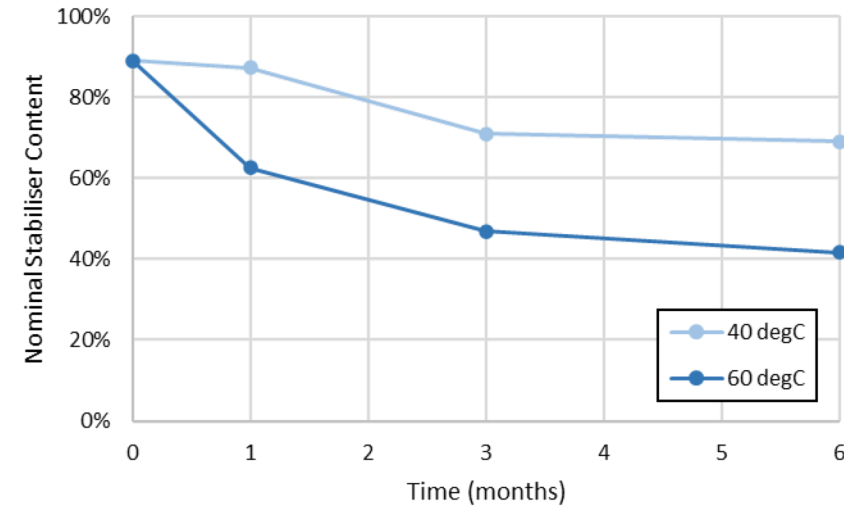
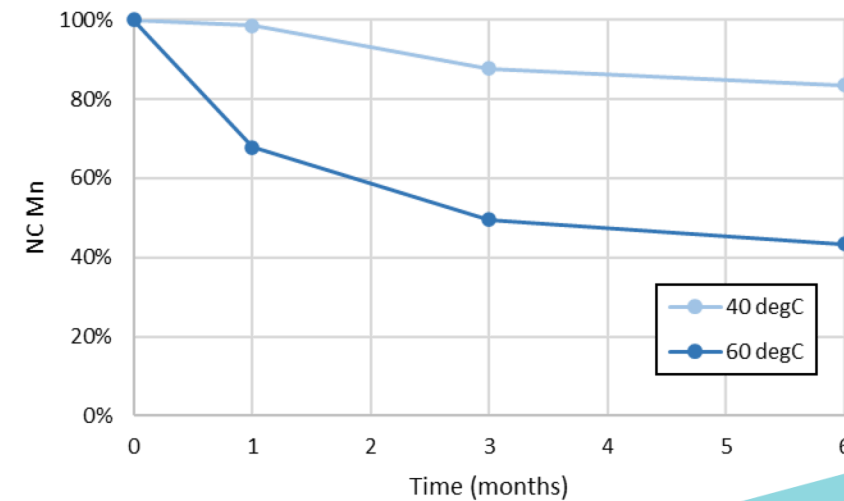


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 - Associated NC Mn degradation and onward impact to PBX mechanical properties



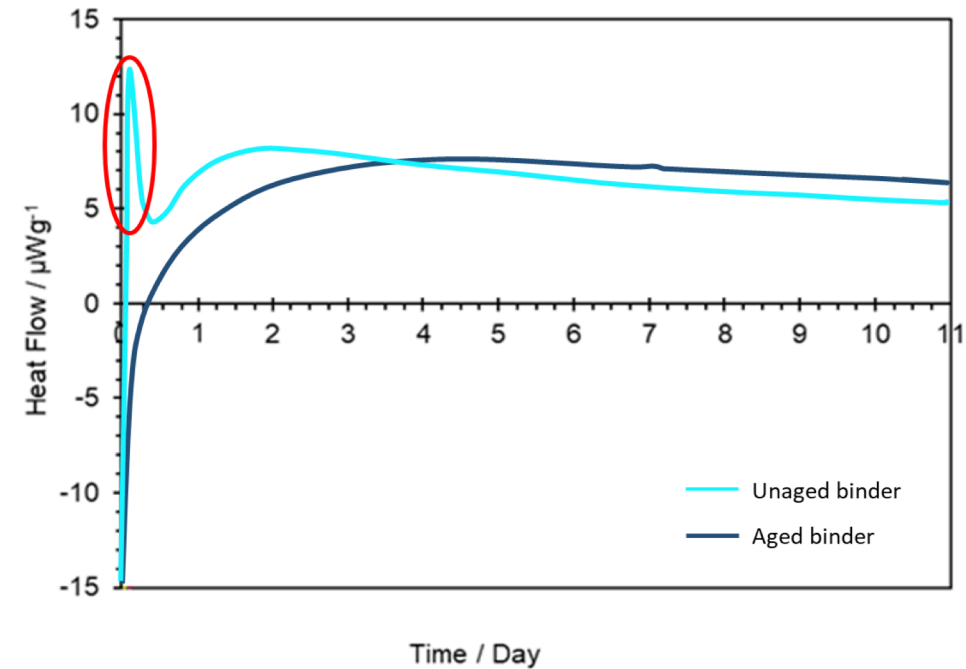
Binder Ageing Trial

- Removal of HE filler from PBX to leave binder, consisting of a polymer (NC), a plasticiser and a stabiliser
- Binder underwent identical ageing trial as powder, with stabiliser and NC Mn measured at each withdrawal
- Similar pattern for stabiliser reduction and NC Mn degradation observed in aged binder samples



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- Similar pattern for stabiliser reduction and NC Mn degradation observed in aged binder samples
- Heat Flow Calorimetry on unaged binder sample shows a clear interaction between materials



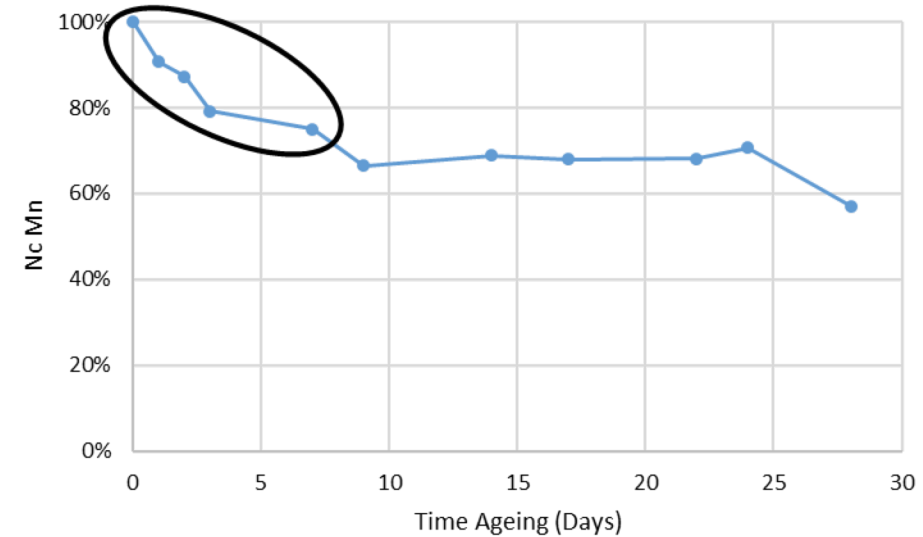
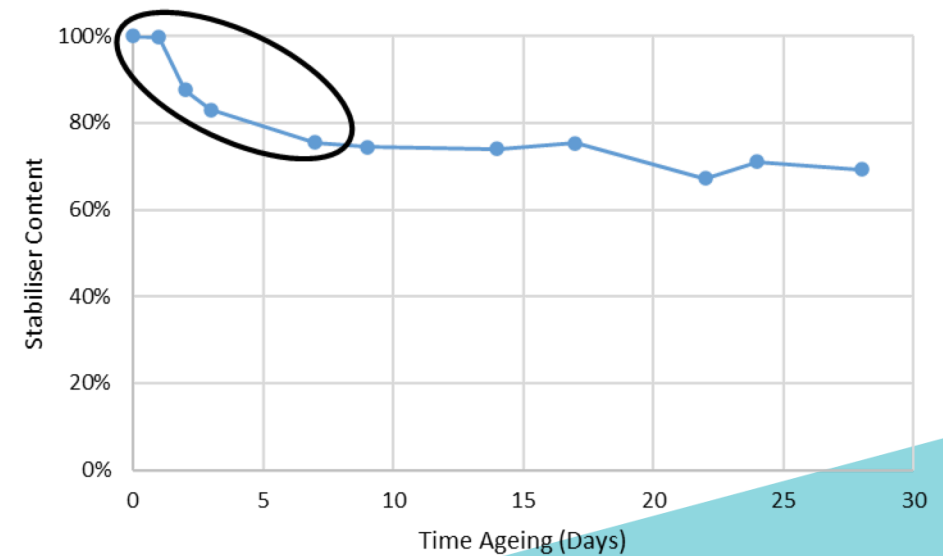


<1 month Binder Ageing Trial

- Binder samples aged at 60°C for ≤ 6 months displayed stabiliser content and NC Mn reduced by 30% from original within first month
- Short term ageing trial conducted to understand binder behaviour within the first month of ageing

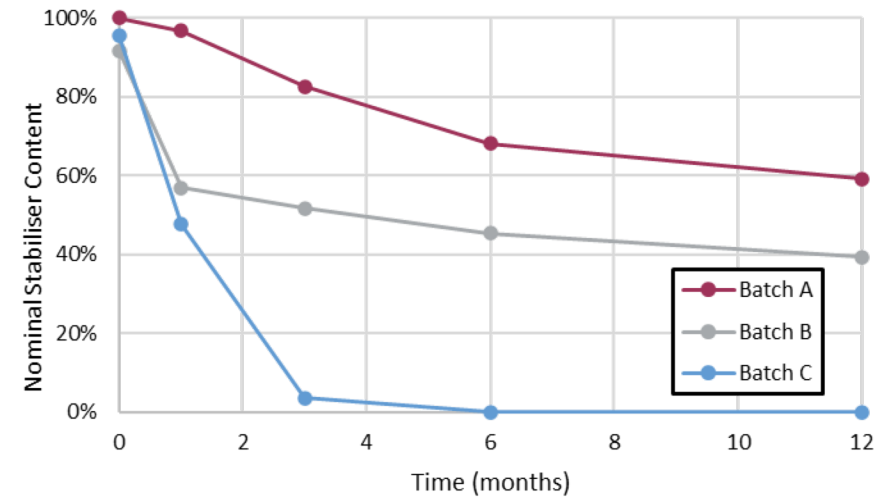
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- Samples withdrawn every few days and analysed shows an initial consumption within the first week of ageing (supporting HFC results)



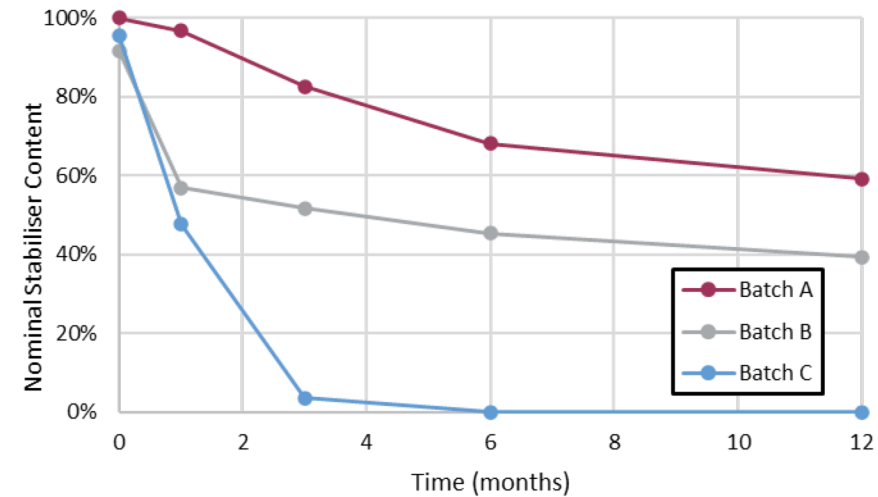
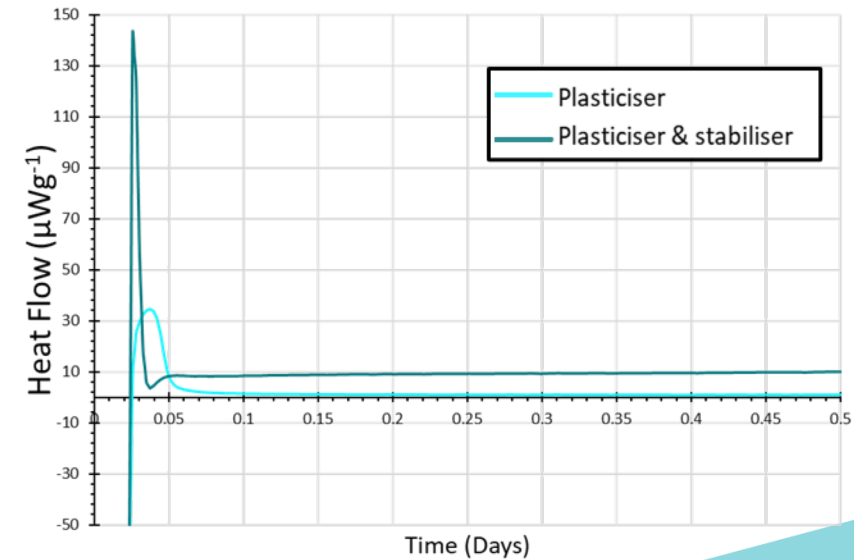
Plasticiser & Stabiliser Ageing

- Plasticiser & stabiliser mixes underwent same ageing trial temperatures as powder and binders
- Range of plasticiser batches aged to assess batch to batch variation



Plasticiser & Stabiliser Ageing

- Plasticiser & stabiliser mixes underwent same ageing trial temperatures as powder and binders
- Range of plasticiser batches aged to assess batch to batch variation
- HFC of samples show direct interaction between plasticiser and stabiliser
- Characterisation of plasticiser batches via NMR showed varying impurity profiles
- Plasticiser identified as a contributor to increased stabiliser consumption and NC Mn reduction



Plasticiser Treatment Development

- Plasticiser identified as a contributor to increased stabiliser consumption and NC Mn reduction, due to an increased impurity profile
- Chemical wash matrix established to isolate specific washes and heating stages to reduce the impurity profile to an acceptable level
- Ageing trials conducted on treated plasticiser and stabiliser sample mixes to evaluate effectiveness of chemical and thermal treatments



Pre treatment



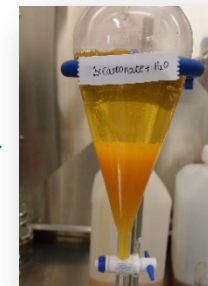
Post heat treatment



During sodium carbonate washing



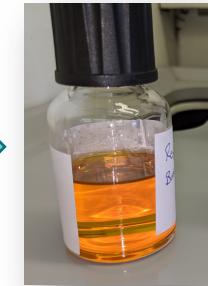
Post sodium carbonate washing



During water washing



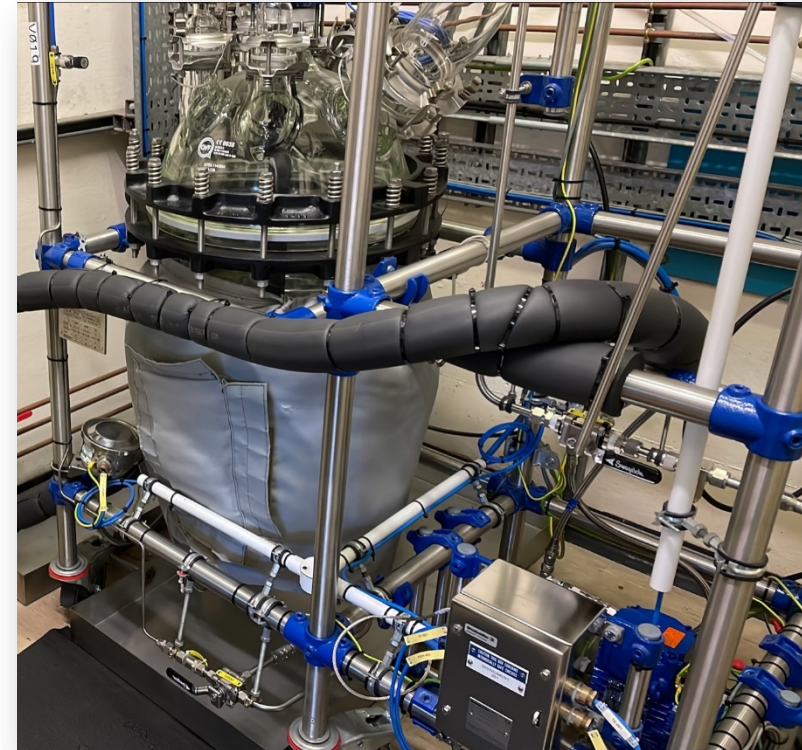
Post water washing



Post drying
'Treated'

Plasticiser Treatment Development

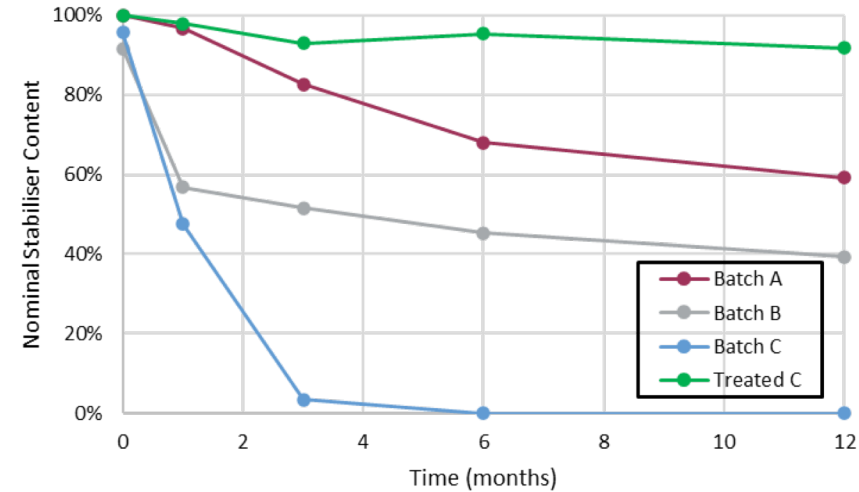
- Process reactor rig established to conduct:
 - Heat Treatment;
 - Thermally degrade and solubilise potential NO_x producing molecules
 - Carbonate Wash;
 - React with unsymmetrical isomers (less thermally stable and more susceptible to hydrolysis to release nitrous acid)
 - Water Wash;
 - Remove highly coloured reaction products formed by sodium carbonate washes
 - Dry
 - Remove water in the product



Reactor Vessel Set-Up

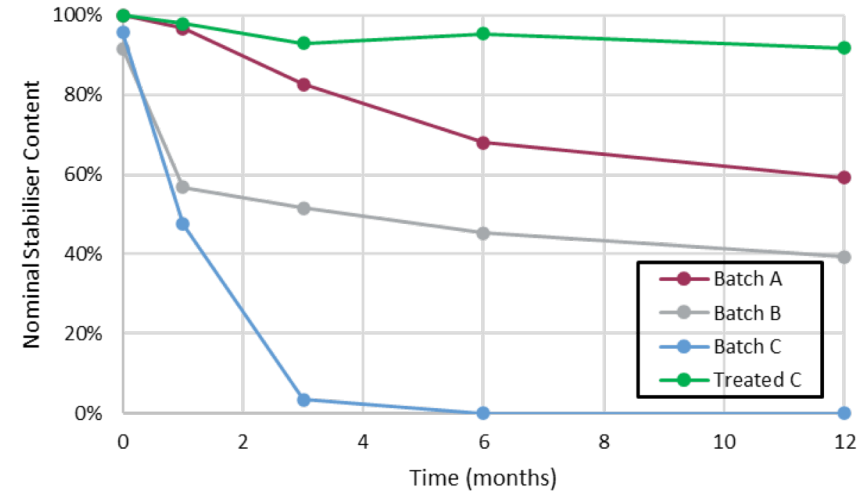
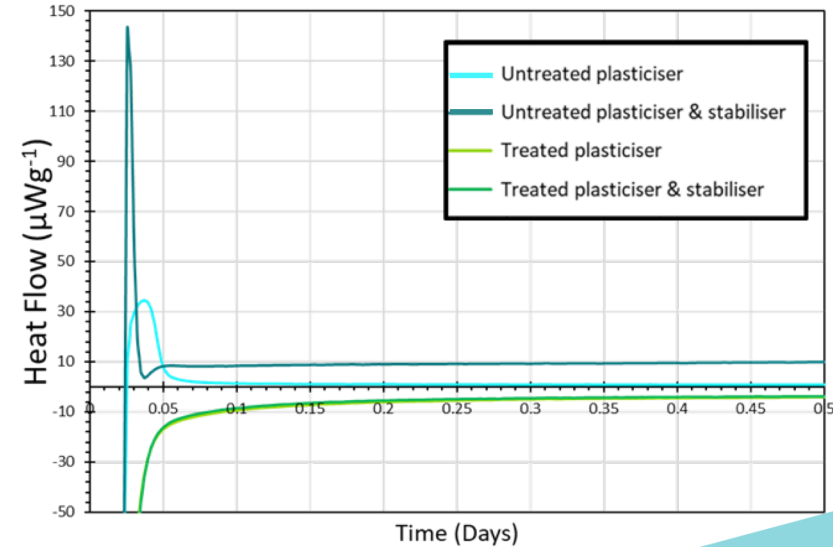
Treated Plasticiser Results

- Treated plasticiser and stabiliser underwent thermally accelerated ageing trials to assess depletion rates
- Significant difference in stabiliser consumption rates between untreated and treated plasticiser mixes



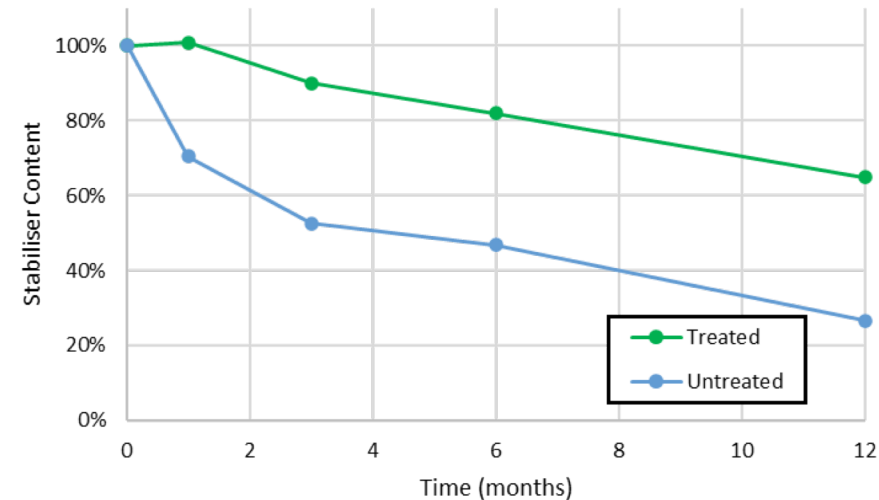
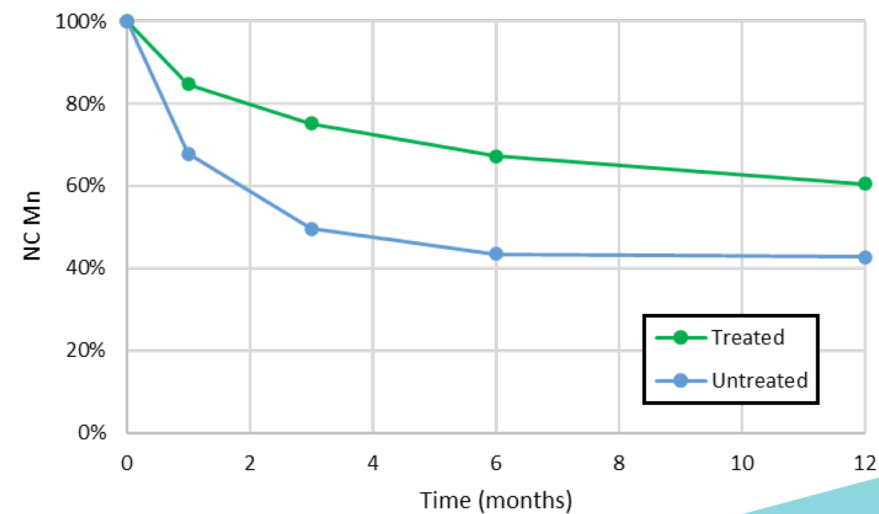
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- Absence of exotherm in treated plasticiser and stabiliser HFC trace



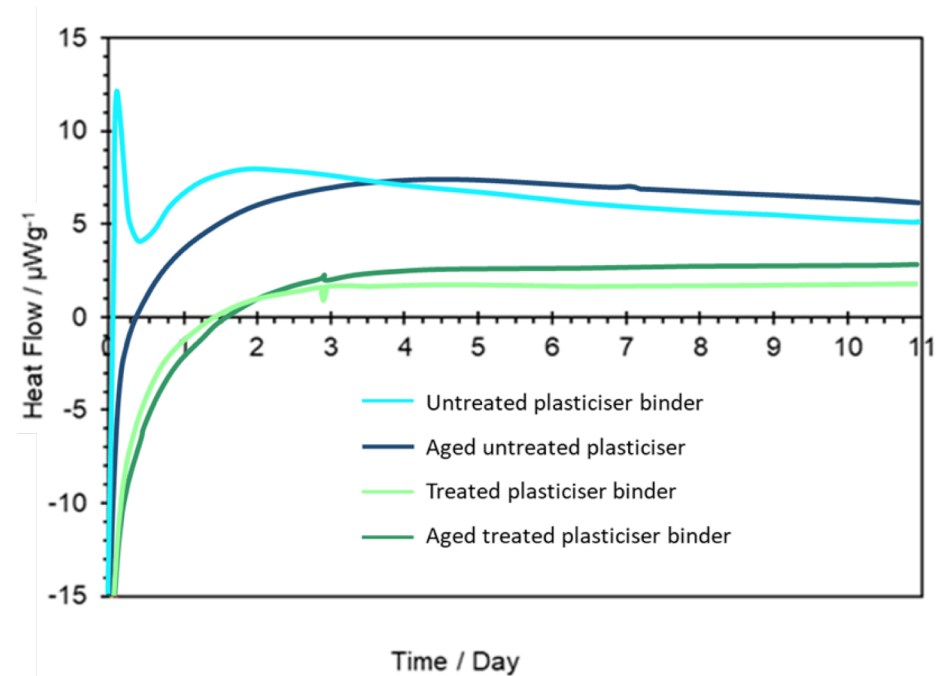
Treated Plasticiser Binders

- Binder sheets containing treated plasticiser thermally aged with stabiliser and NC Mn measured at each withdrawal
- Significant difference in stabiliser consumption rates and NC Mn between untreated and treated plasticiser mixes



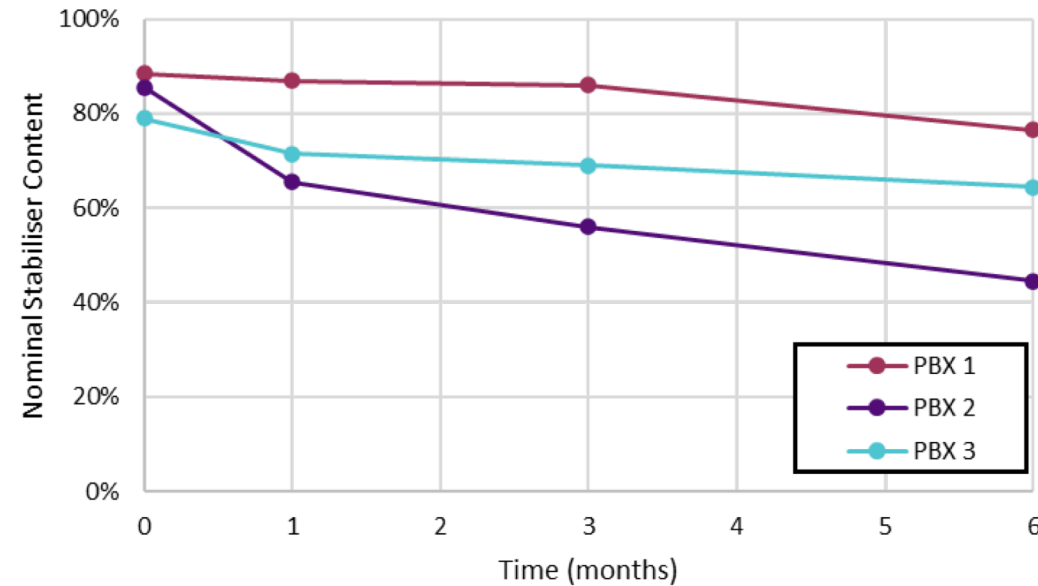
Treated Plasticiser Binders

- Binder sheets containing treated plasticiser thermally aged with stabiliser and NC Mn measured at each withdrawal
- Significant difference in stabiliser consumption rates and NC Mn between untreated and treated plasticiser mixes
- Absence of exotherm in unaged reprocessed plasticiser binder HFC trace



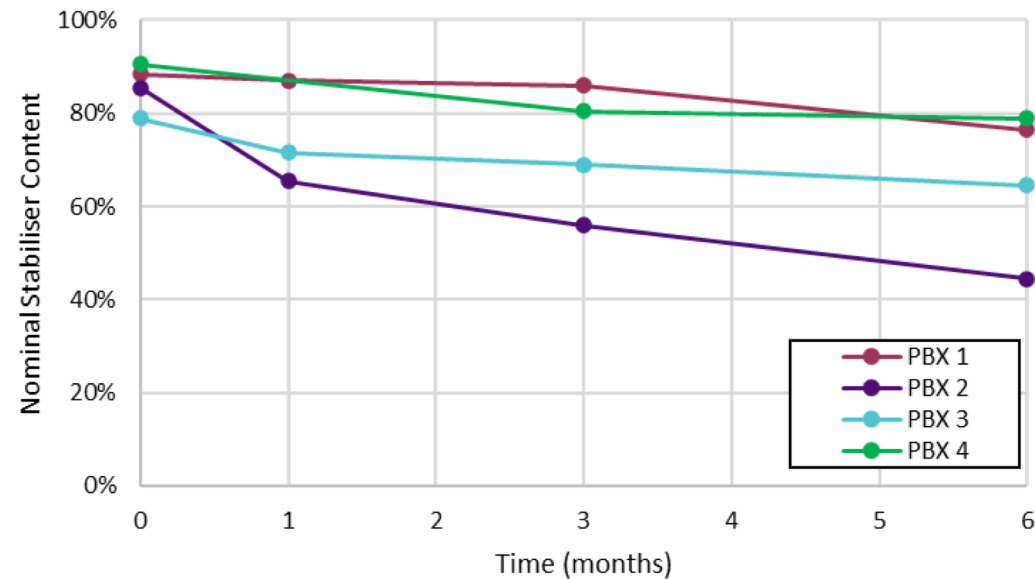
Treated Plasticiser Explosive Formulation

- Treated plasticiser formulated into PBX composition
- Underwent thermally accelerated ageing trial with stabiliser measured at each withdrawal



Treated Plasticiser Explosive Formulation

- Treated plasticiser formulated into PBX composition
- Underwent thermally accelerated ageing trial with stabiliser measured at each withdrawal
- Reduced stabiliser consumption when compared to untreated plasticiser based PBXs





Conclusions

- **NC-based formulations** (PBXs, binders) made with differing batches of plasticiser and **artificially aged**
- **Varied rate** of stabiliser depletion and NC depolymerisation observed
- **Plasticiser impurities** identified as a cause and a treatment process developed
- Analysis of NC-based binder systems and formulations using **treated plasticiser shows reduced rates** of stabiliser depletion and NC depolymerisation
- Heat Flow Calorimetry data supports understanding that there is an interaction between untreated plasticiser and other binder materials



Further Work

- Increased characterisation of impurity profile of treated and untreated plasticiser batches
- Further understanding of specific reaction mechanisms related to interactions of the plasticiser, stabiliser and NC
- Continuing work to understand the onward ageing behaviours of the NC in the PBX system



Acknowledgements

- Life & Assessment Team for reporting and data analysis
- Materials Development Team for binder manufacture and plasticiser treatment development
- Characterisation & Compatibility Team for analytical testing

Thank you & any questions?