Nitrocellulose Characterisation:

– Survey of Standardised Testing Methods

– Stability Testing of NC

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AWE Nitrocellulose Symposium
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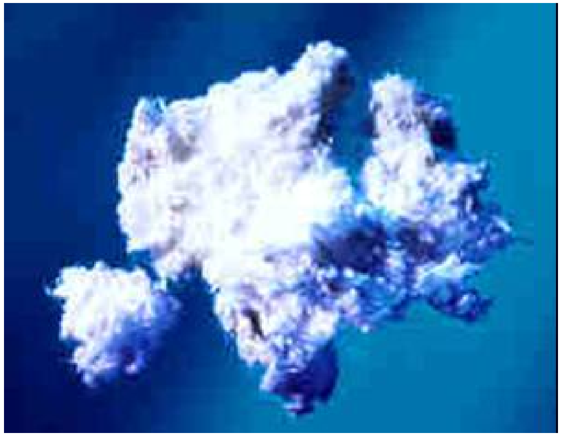

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Part 1:
Survey of Standardised Testing Methods

Standards on NC Testing

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- The following Standards for NC Testing exist:
  - DEF STD 13-175 or UK M-Methods referred therein (UK Standard; used in UK and some Commonwealth nations)
  - MIL-DTL-244B (US Standard, used in USA and in many nations worldwide)
  - STANAG 4178 (NATO Standard; bases mainly on the UK Standards except for the viscosity test which is identical to the US MIL test; not well known, rarely used !)
  - several other National Standards
- Problem: Many of the standardized test methods are very old and do no longer fit into today's production / quality management / working safety environment: Some of the tests require handling of large amount of toxic substances (e.g. mercury), produce toxic waste, are too complicated, too costly or too time consuming (up to 4 days), or they stipulate the use of material which is only available from a single source
- MIL-DTL-244B is in revision: Tests that never fail such as "Ash" might be removed, more modern tests should be added as alternative procedures
- STANAG 4178 is also under revision (done by the CASG AC/326 SG/1 CNG; UK is Custodian Nation) ⇨ Excellent chance to replace outdated test methods and to harmonize test procedures so that the STANAG can replace the national standards
- In order to assist this STANAG, Nitrochemie has performed a survey on NC testing

Contributors to International Survey

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- List of Contributors to Survey:
  - UK MoD: Neil Turner
  - QinetiQ (UK): Graham Gillies
  - EURENCO (France and Finland): Christian Spyckerelle
  - NC Mil-Spec Team (USA): Lucas Lopez, Tony Williams, Mario Paquet
  - Picatinny Arsenal (USA): Nathan Zink
  - DENEL (South Africa) Wolfgang Schimansky
  - SYNTHESIA (Czech Republic) Josef Tichý
  - ADI (Australia) John Reid, Rhonda Wheeler,
  - NCW (Switzerland) Beat Vogelsanger

The following slides represent solely the opinions of these contributors and of the author (Beat Vogelsanger)

Test Methods (1)

Sample Preparation / Drying of NC

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- Many different **drying methods** are currently used, with different methods and temperatures (e.g. in MIL-DTL-244B different drying for each subsequent test method)
- In the new Standard, **one single** and **fast drying method** should be used for all tests; or the level of moisture should be specified thereby allowing different drying methods
- This requires previous investigation of influence of drying method and remaining moisture level on results of subsequent tests

Hot Air Blower (60°C – 70°C)

Oven (40–45°C // 50°C // 60°C–70°C // 100°C–105°C)

Steam-Operated Air Bath

Drying at Room-Temperature

Test Methods (2)

Nitrogen Content

MIL-DTL-244B (USA)	DEF-STAN 13-175 (UK)	Swiss Method
Nitrometer Method Ferrous Sulphate Titration	Nitrometer Method Devarda's Alloy Method	Combustion Calorimetry Method

- The Nitrogen Content determines degree of nitrate ester substitution and thus energy content – as an intrinsic property of the NC, it can be determined in different ways
- The Nitrometer Method can no longer be used due to working safety reasons (Hg)
- The Ferrous Sulphate Titration Method is sufficiently fast and accurate but uses only small sample mass, requires cooling and produces large amounts of acid waste
- Devarda's Alloy Method is only used in the UK – automated equipment for the reduction/distillation/titration makes this method easy and quick
- Nitrochemie uses the Combustion Calorimetry Method which allows to use 10 times larger sample masses and is thus very precise; Method was calibrated using Schulze-Tiemann Method; correctness of result was confirmed by Ferrous Sulphate Titration Method
- The highly automated Nitrogen Analyzer (Combustion Elemental Analyzer) would safe working time but is only rarely used

Test Methods (2)

Nitrogen Content

Combustion Calorimetry Method

Test Methods (3)

Soluble Matter (Ether-Alcohol Solubles)

MIL-DTL-244B (USA)	DEF-STAN 13-175 / M22 (UK)	Swiss Method
Preferred Meth. (all NC) Alternate Meth. (high soluble NC)	Meth. A (low soluble NC; includes ashing / carbonating) Meth. B (high soluble NC)	Meth. 1 (low soluble NC) Meth. 2 (high soluble NC)

- **Necessary Test; measure for amount of low nitrated NC content or mixing ratio**
- **Outcome does not truly reveal the processability of the NC blend**
- **Soluble matter can be assessed in two different ways:**
  - ⇨ **Method 1) By determination of dissolved NC (direct drying of supernatant solution or precipitation of NC from supernatant solution followed by drying); this method is more accurate for low soluble NC (N ≥ 12.75%)**
  - ⇨ **Method 2) by determination of undissolved NC (filtration followed by drying); this method is more accurate for high soluble NC (N = 10.9% – 12.75%)**

- **The UK M-Method M22 Test A) is similar to Method 1) but additionally corrects for inorganic matter by subsequent ashing and carbonating steps → this adds a lot of work (= expenses and time) for little additional information and is regarded as not necessary by most NC specialists (also since the MIL-DTL-244B Test does without this additional step)**

Test Methods (4)

Insoluble Impurities (Acetone Insolubles)

MIL-DTL-244B (USA)	DEF-STAN 13-175 (UK)	Swiss Method
Assesses "Total Residuals"; Standard Meth. (Quantitative); Alternate Meth. (Semi-Quantitative)	Assesses "Insoluble Organic Matter" solely	Similar to MIL but with Centrifuging

- **Purity test, checks for unnitrated cellulose (and inorganic contaminants)**
- **All methods base on dissolution of the NC in acetone, followed by filtration and drying of the undissolved matter**
- **MIL-DTL-244B Test determines the "total residue" which consists of both organic and inorganic insoluble matter**
- **The UK-based tests (STANAG 4178 / UK M-Method M22) assess the insoluble organic matter solely which requires subsequent ashing and carbonating steps (ashing / carbonating determines the inorganic fraction which has to be subtracted from the "sum of organic + inorganic insolubles")**
  UK prefers to retain distinguishing between organic and inorganic insolubles, whereas most other NC specialists prefer the easier and faster MIL Test which does without these additional steps

Test Methods (5)

Mineral Matter (Inorganic Matter / Ash)

MIL-DTL-244B (USA)	DEF-STAN 13-175 (UK)
4.5.4 (only ashing)	M22 (ashing + carbonation)

- **Purity test**, checks for **inorganic contaminants**
- All methods base on gelatination (with paraffin / caster oil / acetone) or digestion (with nitric acid) of the NC, followed by burning and ashing / calcination at higher temp.
- Tests basing on MIL-DTL-244B directly assess this residue ("ash")
- **UK-based tests** (UK M-Method M22 / STANAG 4178 Procedure B) **add a carbonating step** ("mineral matter")
- No failures with this test have been occurred for many years – **the necessity of this test must therefore be questioned** (might be deleted from the MIL-Spec)

Ignition / burning of NC saturated with liquid paraffin

Ashing / calcination in muffle furnace at 600°C – 800°C

Test Methods (6)

Grit (Gritty Particles)

MIL-DTL-244B (USA)	DEF-STAN 13-175 (UK)
--	M22

- **Safety test, looks for gritty particles in the residue of the Mineral Matter Test**
- **Test only used in or requested by UK (UK M-Method M22 / STANAG 4178); no such test describes in MIL-DTL-244B**
- **All users of this Test (including UK) report that never any grit was found**
  ⇨ the necessity of this test must therefore be questioned

Test Methods (7)

Fineness (Settling Test)

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MIL-DTL-244B (USA)	DEF-STAN 13-175 (UK)
4.5.6	M22

- **Indirect measure for fibre length; relative fast and easy method; used for process control**
- **Correlation of test result with relevant processing properties of NC is questioned**
- **All described fineness-tests base on making aqueous NC slurry followed by settling of fibres in a graduated cylinder (recording of volume occupied by NC fibres after specified settling time)**
- **Only minor differences between test procedures described in STANAG 4178, MIL-DTL-244B and UK M-Method M22**
- **More modern direct methods basing on Fibre Quality Analyzers / Image Analysis are currently under evaluation**

settling of fibres in a graduated cylinder

Test Methods (8)

Viscosity

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MIL-DTL-244B (USA)	DEF-STAN 13-175 (UK)	Swiss Method
4.5.5; Tube Viscometer, large steel balls, 10% NC solution	M101; Tube Viscometer, small steel balls, 10% NC solution	DIN 53050; Höppler Viscometer, 1% to 4% NC solution

- Indirect measure of degree of polymerisation; outcome correlates to some extent with processability of NC
- MIL-DTL-244B / STANAG 4178 and UK M-Methods M102 / M170 use different Tube Viscometers; viscosity is determined by measuring the time duration required for steel balls to vertically fall through a highly viscous NC solution (10% NC in acetone)
- National methods use the more convenient Höppler Viscometer (DIN 53015), Brookfield Viscometer (UK AWRE Specification HR 1843), and Baume Capillary Tubes (BNC Methods) – here more dilute solutions of 1% - 4% NC are tested
- Results on the different tests cannot be converted into each other !
- Better and more modern automated methods capable of reducing both dissolution and analysis times would be welcome – dilute solution characterization techniques with capillary viscometry / rheometry are currently under evaluation
- Direct measurement of molecular size distribution using size exclusion chromatography SEC would be superior but turns out to be too expensive for routine analysis

Test Methods (8)

Viscosity

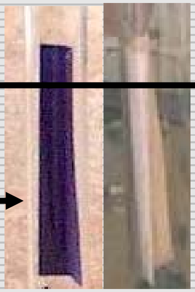
MIL-DTL-244B Tube Viscometer; measuring time duration required for medium sized steel balls to vertically fall 10 inches through a highly viscous NC solution (10% NC in acetone)

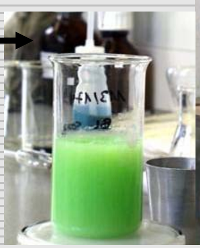
Convenient Höppler Viscometer (DIN 53015), measuring time duration required for large steel or glass balls to "roll" throug less dilute solutions of 1% - 4% NC in acetone or butyl acetate

Test Methods (9)

Stability Tests

- The following standardized NC "Stability Tests" are commonly used:
  - 65.5°C Heat Test (K.I. Starch Paper Test; 35' at 65.5°C; MIL-DTL-244B, USA)
  - 76.6°C Abel Heat Test (K.I. Starch Paper Test; 10' at 76.6°C; DEF STD 13-175 / M15 UK)
  - 132°C Bergmann-Junk Stability Test (120' at 132°C; DEF STD 13-175 / M23 UK or other)
  - 134.5°C Heat Test (Methyl Violet Paper Test; 30' at 134.5°C; MIL-DTL-244B, USA)





- The Heat Tests are cheap, easy to perform and fast; but the test results are only semi-quantitative since observation of discolouration is subjective and quality of heat test papers varies both between different suppliers and over storage time (up to factor 3 between Bishopton, Daicel, other)
- The Bergmann Junk Stability Test result is quantitative and more reliable; but the test is also more expensive and time consuming than the Heat Tests
- Heat Flow Calorimetry was proposed but found to be not suited for routine stability testing of NC (too expensive, long measurement time, autocatalysis occurs)

Test Methods (10)

Other Tests on NC which are often Performed

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- **Alkalinity (UK M-Method M22) :**
  - ⇨ Checks for presence of Calcium Carbonate (Chalk) which is often added in the final steps of NC manufacture (UK DEF-STAN 13-175 requests level 0.2 - 0.5%)
  - ⇨ Performed by adding HCl to the NC, shaking, filtration, back titration with NaOH
- **Residual Acidity :**
  - ⇨ Checks for presence of any residual acidity which would affect the results of the stability tests (UK regards Residual Acidity as an essential test)
  - ⇨ Adding water to the NC, heating until boils, cooling, titration with NaOH

- **Water + Alcohol Content :**
  - ⇨ Drying of NC in oven and weighting / IR balance / convective dryer with balance
- **Water Content :**
  - ⇨ Karl Fischer Titration
- **Alcohol Content :**
  - ⇨ Gas Chromatography (GC)
- **Sulphate Content (UK M-Method M22) :**
  - ⇨ Gravimetric method basing on precipitation as barium sulphate
- **Temperature of Ignition (UK M-Method M22) :**
  - ⇨ Standard "Temperature of Ignition Test"

Karl Fischer Titration Apparatus

Summary and Conclusions (Part 1)

- At present, there are too many standards / testing methods for nitrocellulose – many of these testing methods are clearly outdated

- The current revision of STANAG 4178 is an excellent chance
  - to eliminate no longer needed test methods from the standard,
  - to replace outdated test methods wherever possible by more modern (accurate, fast, cheap, safe) tests and
  - to harmonize test procedures so that the STANAG can replace the national (DEF and MIL) standards

- NITROCHEMIE is a member of the NATO/PfP Team responsible for the revision of STANAG 4178 and fully supports this revision

Part 2:
Stability Testing of NC

Investigation of Stability Tests (1a)

Introduction / Cause

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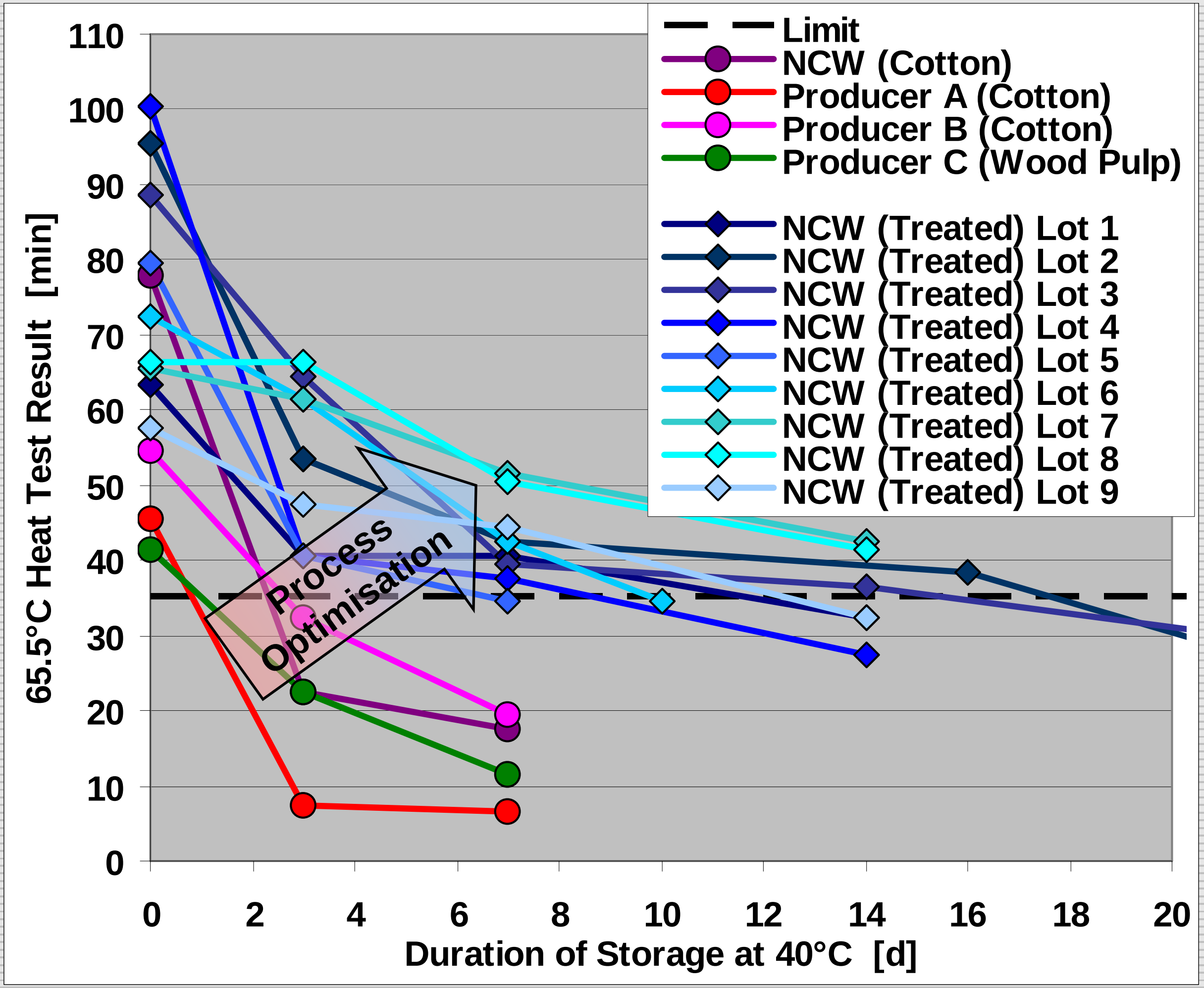
- **All four currently used test methods are based on the detection of nitrogen oxides (NO, NO_2) which have been produced / released during heating of the NC**
- **The four test methods give often totally contradictory results**
  - ⇨ **One example is the fact that slightly aged NC (several months at ambient, days to weeks at 30°C to 40°C which can occur during transportation) still has unchanged 132°C Bergmann-Junk and 134.5°C Heat Test results (and thus still excellent chemical stability), whereas the 76.6°C Abel Heat Test and 65.5°C Heat Test results deteriorate thus wrongly indicating reduced stability !**

Investigation of Stability Tests (1b)

Introduction / Cause



Deterioration of 65.5°C Heat Test results of NC artificially aged at 40°C (NC blend; N = 13.1%-13.3%; no chalk added):

- ⇨ Freshly produced NC fulfils the 65.5°C Heat Test
- ⇨ Already after 3 days of storage at 40°C, the 65.5°C Heat Test can no longer be fulfilled
- ⇨ This independent on producer and cellulose type (4 different manufacturers, NC from cotton linters and wood pulp)
- ⇨ The "short-term ageing-resistance" of NC regarding 65.5°C Heat Test result can be improved by process optimisation

Investigation of Stability Tests (1c)

Introduction / Cause

- All four currently used test methods are based on the detection of nitrogen oxides (NO, NO_2) which have been produced / released during heating of the NC

- The four test methods give often totally contradictory results
  - ⇨ One example is the fact that slightly aged NC (several months at ambient, days to weeks at 30°C to 40°C which can occur during transportation) still has unchanged 132°C Bergmann-Junk and 134.5°C Heat Test results (and thus still excellent chemical stability), whereas the 76.6°C Abel Heat Test and 65.5°C Heat Test results deteriorate thus wrongly indicating reduced stability !

- **Furthermore, not much is known about chemical / physical-chemical processes involved in theses tests, and how differences in test results can be interpreted**

➔ **A thorough investigation of the course of NO / NO_2 production of NC at the different test temperatures was therefore conducted using NO_x-Chemiluminescence Detection**

Investigation of Stability Tests (2)

NO_x-Chemiluminescence Test Apparatus

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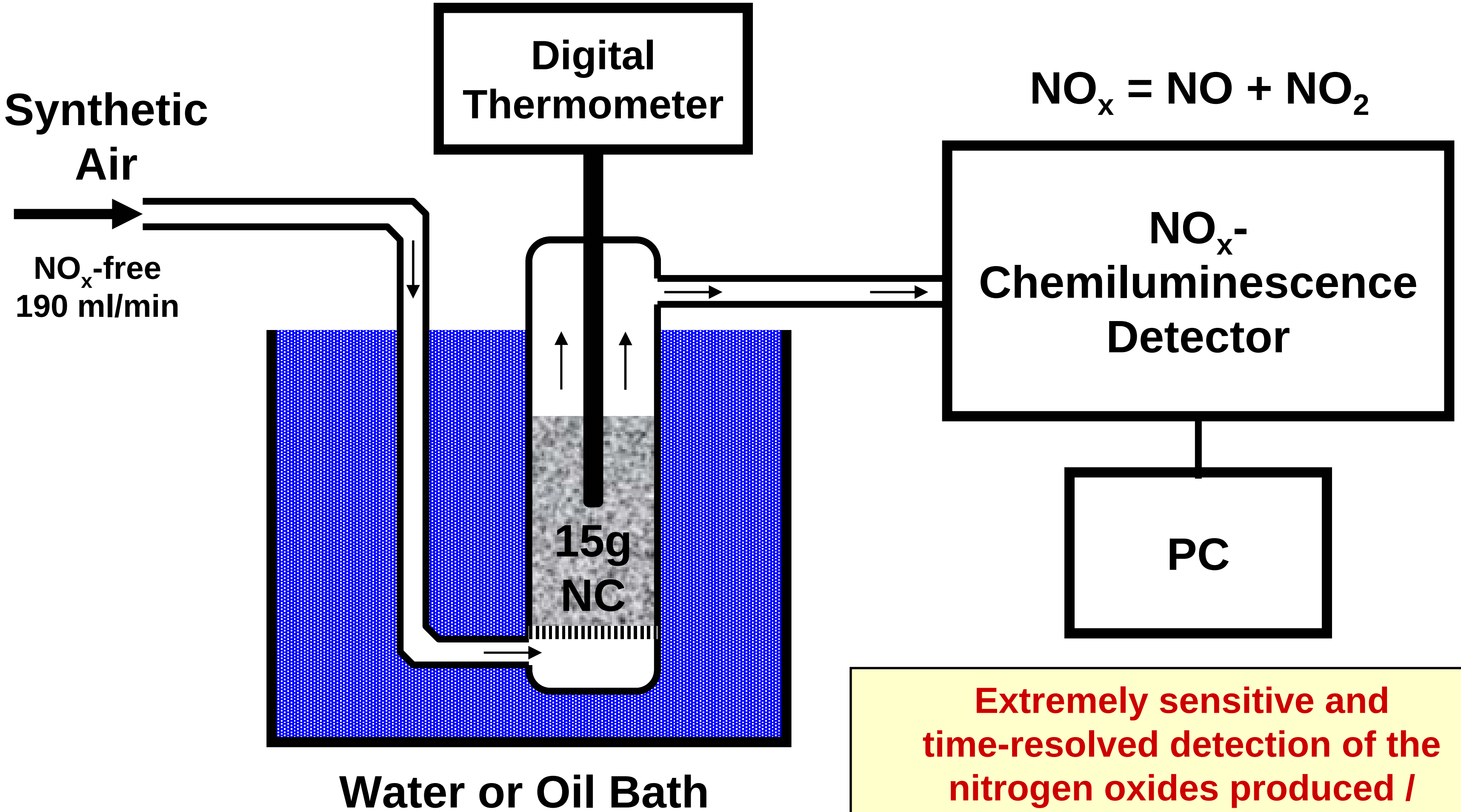

Extremely sensitive and time-resolved detection of the nitrogen oxides produced / released during heating of the NC

Investigation of Stability Tests (3)

NO_x-Production in 132°C BJ and 134.5°C MV Tests

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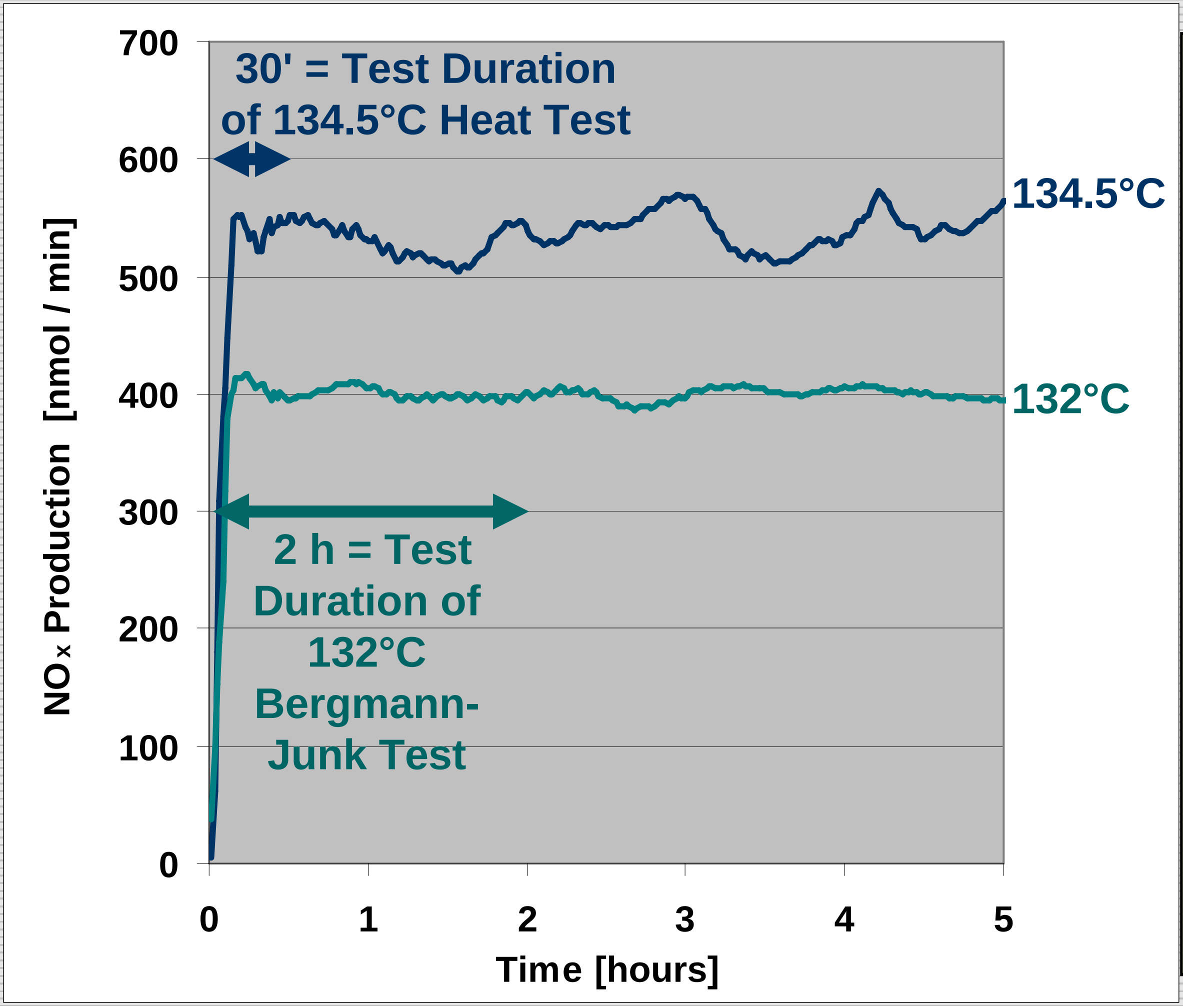

In the 132°C Bergmann-Junk and 134.5°C Heat Tests which are both conducted at relatively high temperatures, <u>high levels of constant NO_x production</u> are reached soon after start of heating

The amount of NO_x produced during the specified test durations is in the region of 0.2% to 1% of the total nitrogen content of the NC

→ a considerable amount of ageing has occurred

→ "degree of conversion" is in the typical range of stability tests of explosives

Investigation of Stability Tests (4)

NO_x-Production in 65.5°C Heat Test

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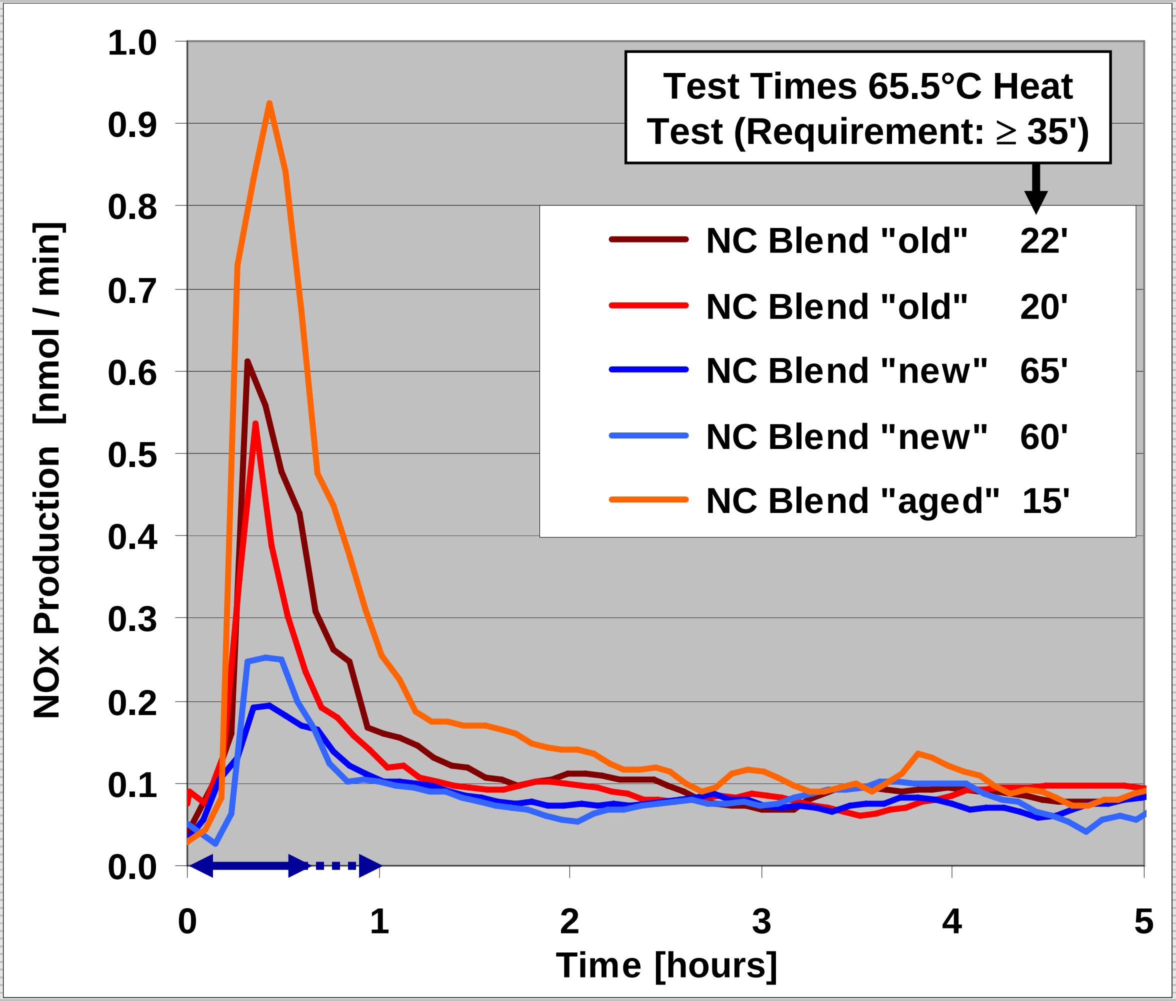
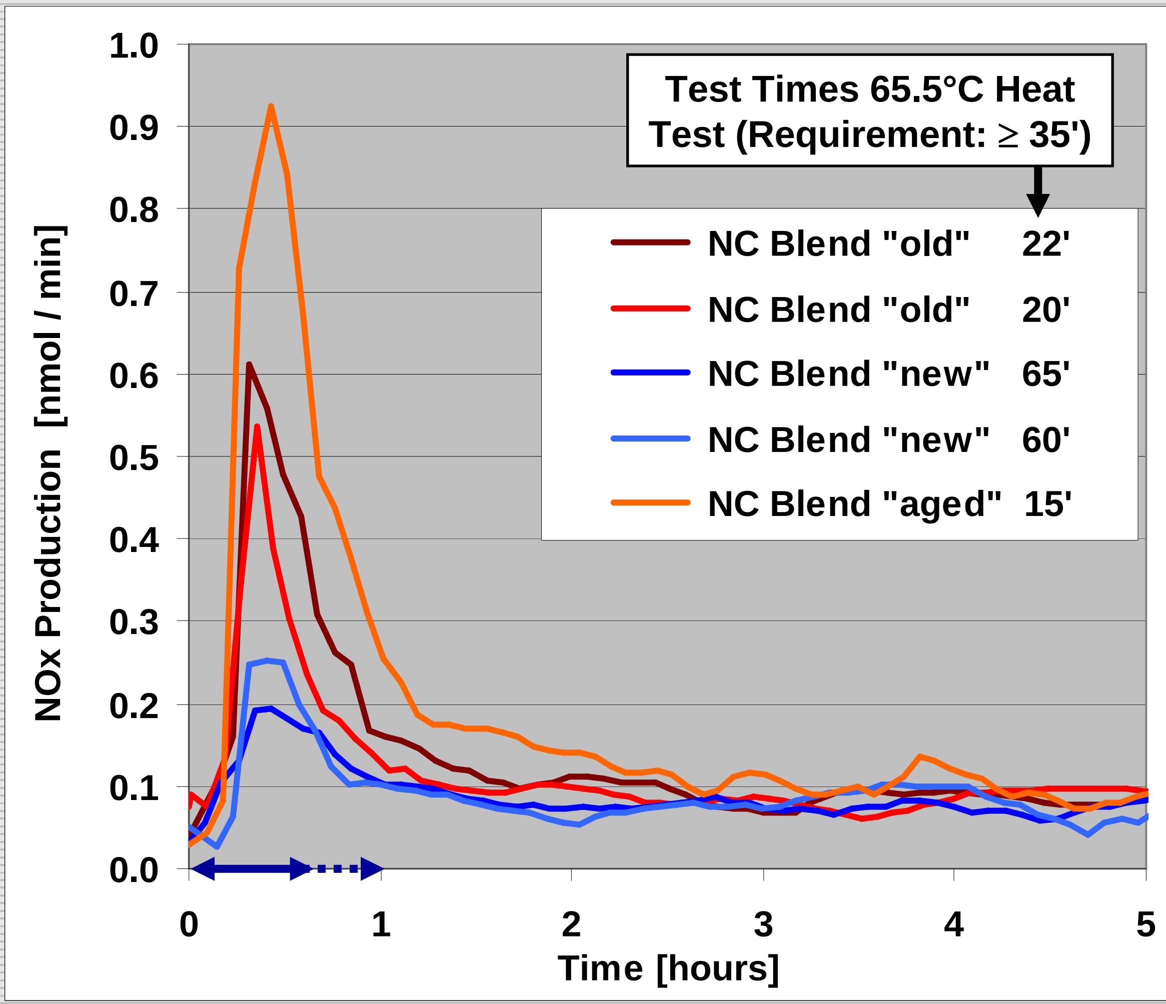


Immediately after heating to 65.5°C, a NO_x peak is produced

- **→ Peak lies within duration of 65.5°C Heat Test (typical test time = 20 min to 60 min; requirement ≥ 35 min)**
- **→ After the peak is over, NO_x production almost vanishes – this for all NC samples !**

Investigation of Stability Tests (5)

NO_x-Production in 65.5°C Heat Test



The NO_x peak height correlates with 65.5°C Heat Test results: NC which "pass" give lower peaks than NC which "fail" the Heat Test

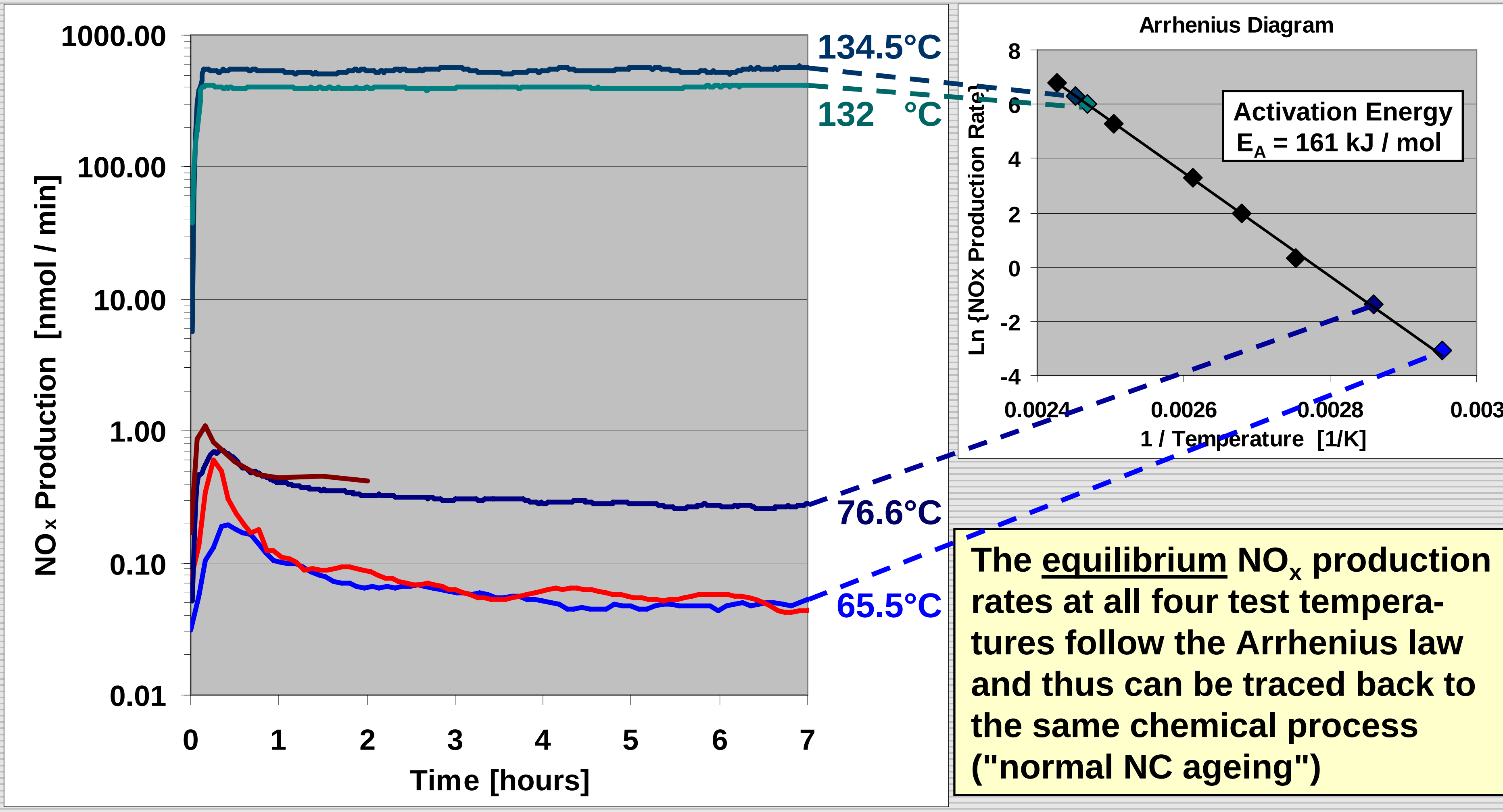
→ For "new" NC (which fulfils 65.5°C Heat Test), NO_x produced within this peak equals 0.5 – 1 / 1'000'000 of total N-content of NC

→ For "old" or "aged" NC (which do not fulfil 65.5°C Heat Test), NO_x produced equal 1 – 2 / 1'000'000 of total N-content of NC

This NO_x release is extremely small but obviously determines the result of the K.I. / Starch Paper Tests

Investigation of Stability Tests (6)

NO_x Production Rate in the different Stability Tests



The <u>equilibrium</u> NO_x production rates at all four test temperatures follow the Arrhenius law and thus can be traced back to the same chemical process ("normal NC ageing")

Investigation of Stability Tests (7)

NO_x Production Rate in the different Stability Tests

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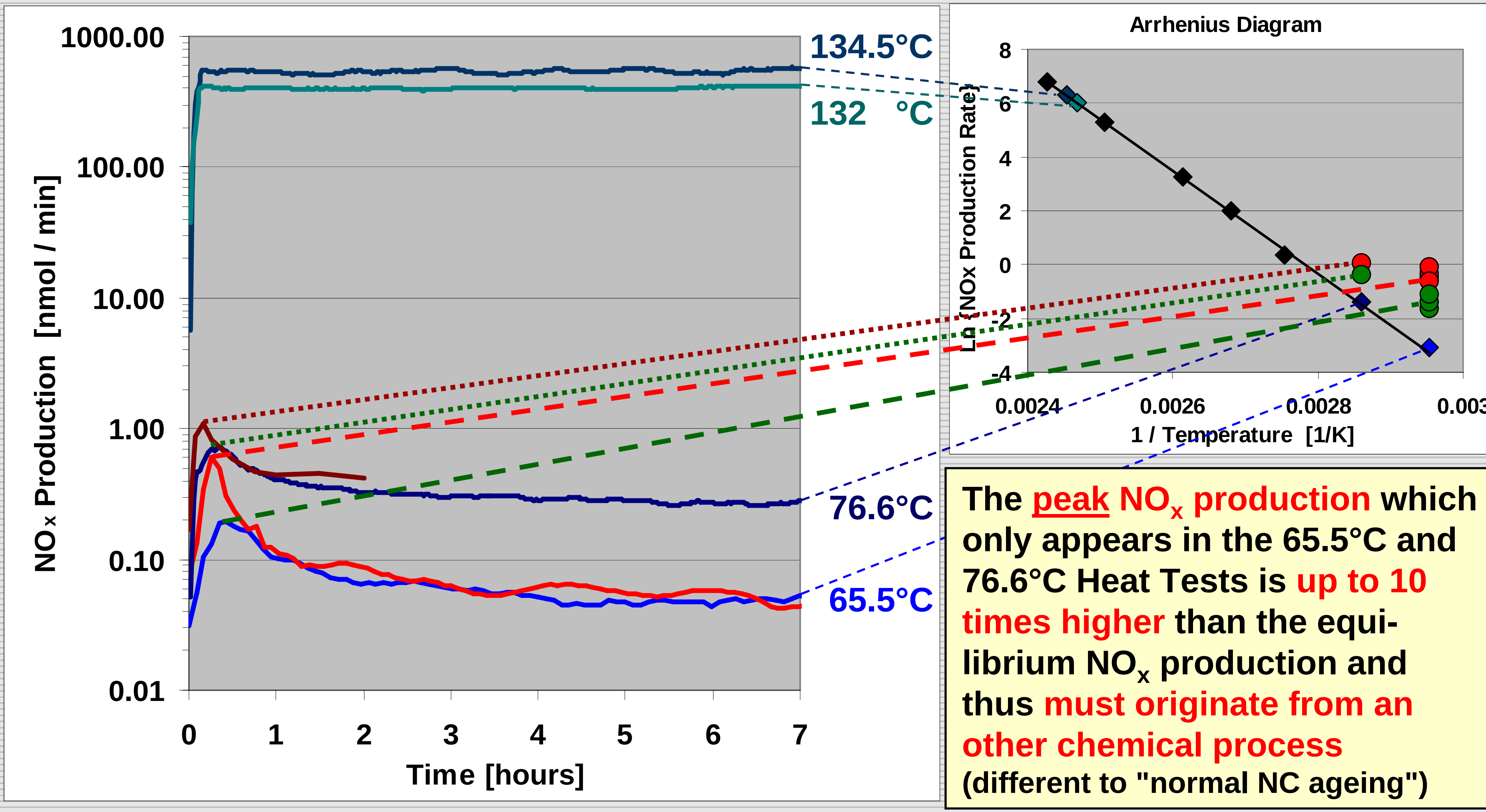


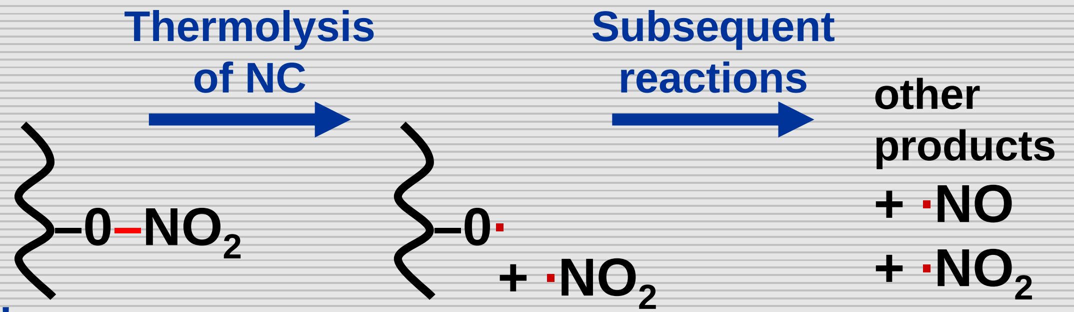
The **peak NO_x production** which only appears in the 65.5°C and 76.6°C Heat Tests is **up to 10 times higher** than the equi-librium NO_x production and thus **must originate from an other chemical process** (different to "normal NC ageing")

Investigation of Stability Tests (9)

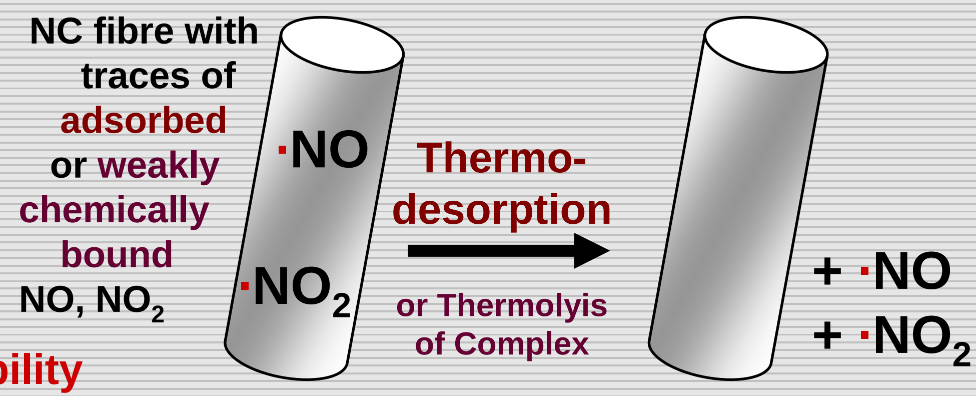
Postulated Mechanism Responsible for Test Failure

- Evidence indicates that different mechanism are responsible for NC failing the individual Stability Tests:

⇨ In 132°C Bergmann-Junk and 134.5°C Heat Test, dominating reaction obviously is "normal chemical ageing of NC" (thermolysis of nitric esters)
→ Tests show real stability of NC !



⇨ In 76.6°C Abel Heat Test and 65.5°C Heat Test, dominating initial reaction is heating-induced release of nitrogen oxides which are already present in the NC (= which have been accumulated before the test);
→ Tests do not show real chemical stability of NC but "storage history" (at least for aged NC)



Most plausible reactions are accumulation of NO_x by adsorption /// thermo-desorption or accumulation of NO_x under formation of a weakly bound complex /// thermolysis of this complex

Investigation of Stability Tests (10)

Evidence for Postulated Mechanism 65.5°C / 76.6°C Tests

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- **Evidence for postulated mechanism "thermo-desorption of nitrogen oxides which have previously been accumulated in NC":**
  - **Initial NO_x peak responsible for failing 65.5°C and 76.6°C Heat Tests is extremely small (10'000 times smaller than NO_x amount needed to fail 132°C BJ Test)**
  - **Height of initial NO_x peak directly correlates with storage temperature and time**
  - **Amount of NO_x released during initial peak is in the same range as the calculated amount of NO_x produced due to "normal ageing" during these storage conditions**
  - **Initial NO_x peak is reduced (and 65.5°C / 76.6°C Heat Test results are improved) by all processes which remove adsorbed NO_x from NC – these processes are:**
    - **washing of NC with water (more effective with hot than with cold water)**
    - **dewatering of NC with alcohol**
    - **blowing hot air through NC**
  - **All processes (ageing, washing, …) which strongly influence the results of 65.5°C / 76.6°C Heat Tests leave the 132°C BJ / 134.5°C Heat Test results unchanged**
  - **Initial NO_x peak and thus failure of 65.5°C and 76.6°C Heat Tests can be artificially generated if a small amount of NO_2 is adsorbed on new NC**
  - **Result of 65.5°C / 76.6°C Heat Tests strongly depend on sample drying method**

Investigation of Stability Tests (11)

Evidence for Postulated Mechanism 65.5°C / 76.6°C Tests
⇨ Correlation with Storage Conditions

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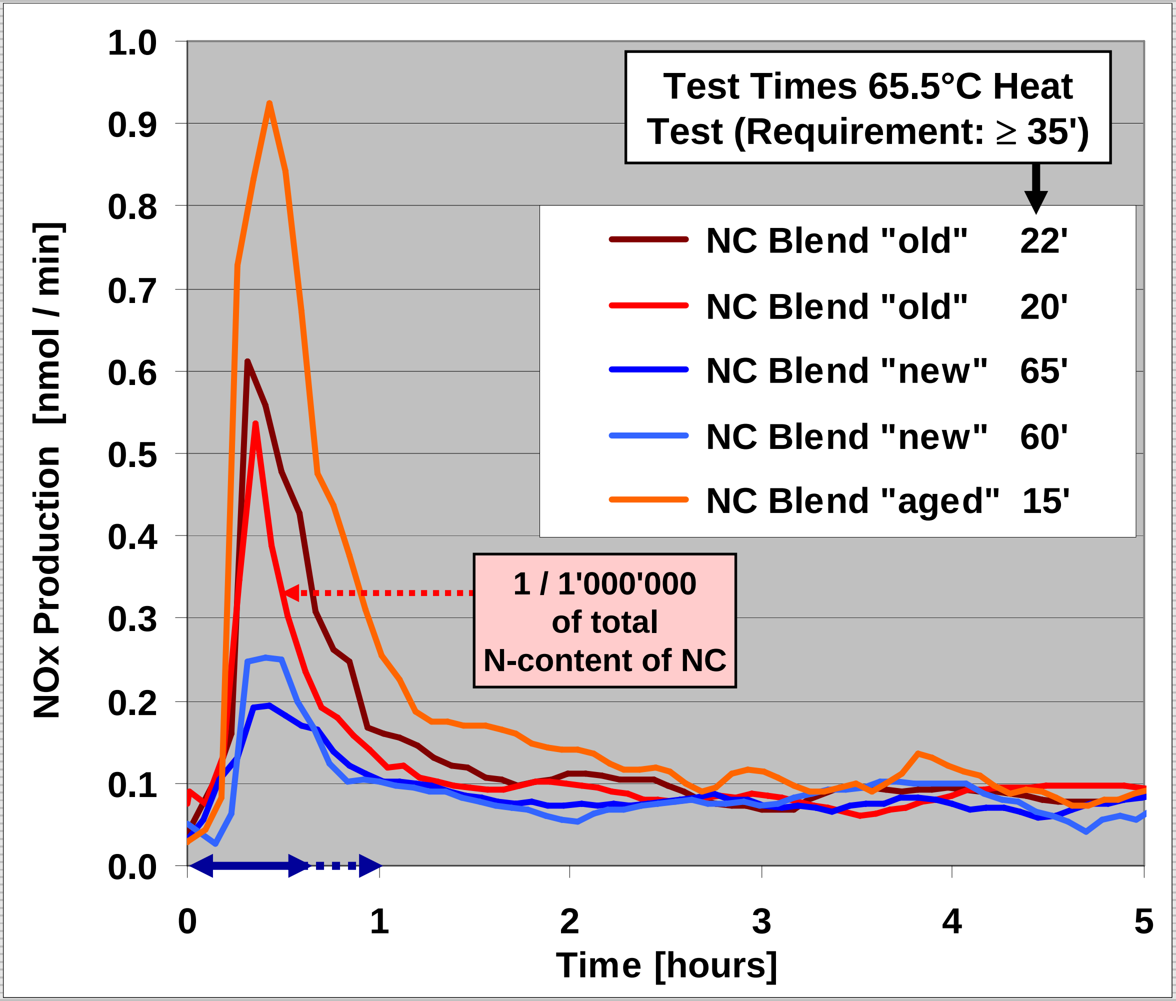


NO_x peak heights / 65.5°C Heat Test results correlate with storage conditions of NC:

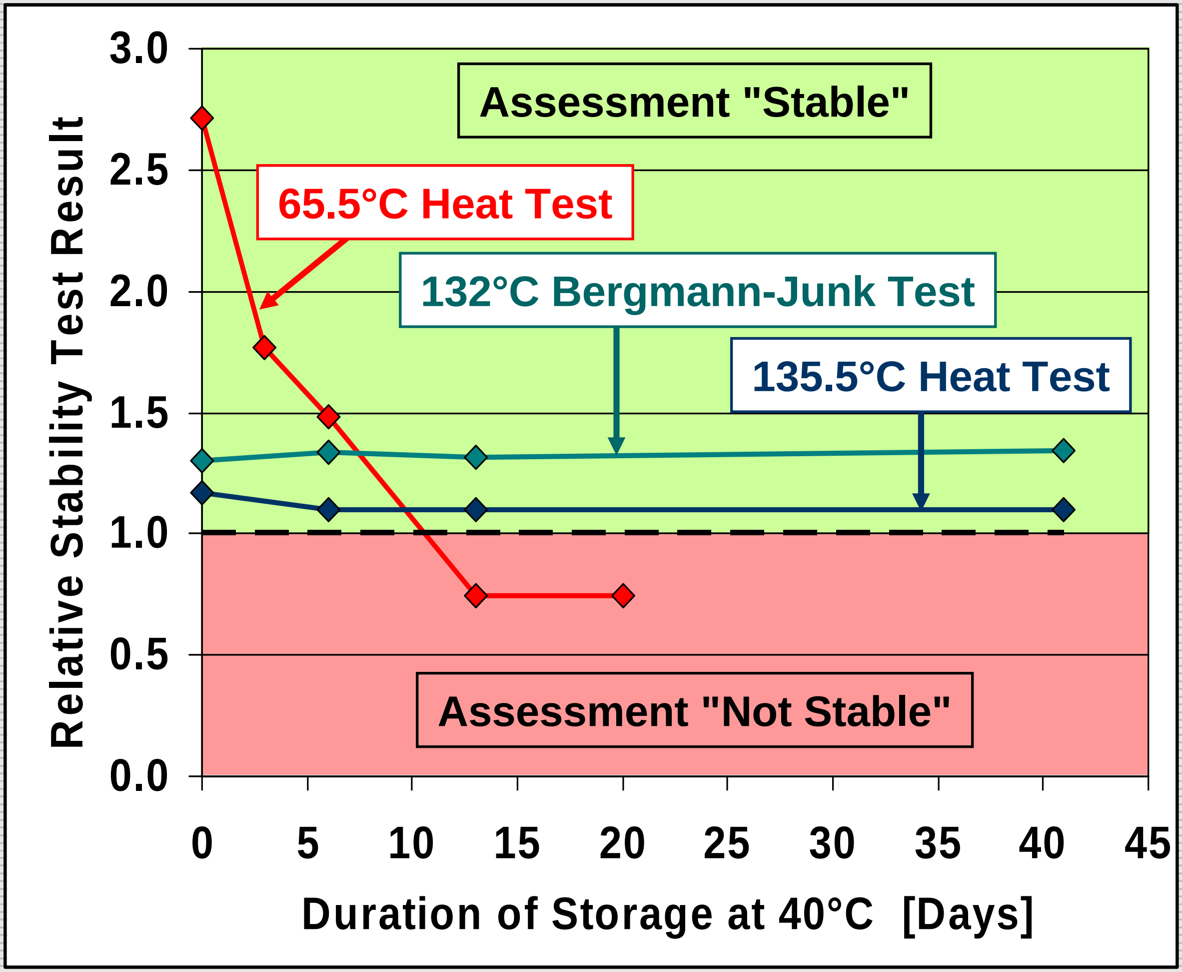
- → **"New" NC produce small peaks and fulfil 65.5°C Heat Test**
- → **"Old" or "artificially aged" NC produce large peaks and do not fulfill 65.5°C Heat Test**

This NO_x release is extremely small (0.5 to 2 millionth of total N-content of NC) but obviously determines the result of the K.I. / Starch Paper Tests

Investigation of Stability Tests (12)

Evidence for Postulated Mechanism 65.5°C / 76.6°C Tests

⇨ Influence of Storage Time at 40°C on different Tests



Influence of artificially ageing of NC at 40°C:

- ⇨ Results of the K.I. Starch Paper Tests (65.5°C / 76.6°C Heat Tests) change rapidly – after 14 days at 40°C, test requirements are no longer fulfilled
- ⇨ 132°C Bergmann-Junk and 134.5°C Heat Test clearly show that chemical stability remains essentially unchanged even after 40 days of storage at 40°C

Investigation of Stability Tests (14)

Evidence for Postulated Mechanism 65.5°C / 76.6°C Tests

⇨ Plausibility Check regarding NO_x produced during Storage

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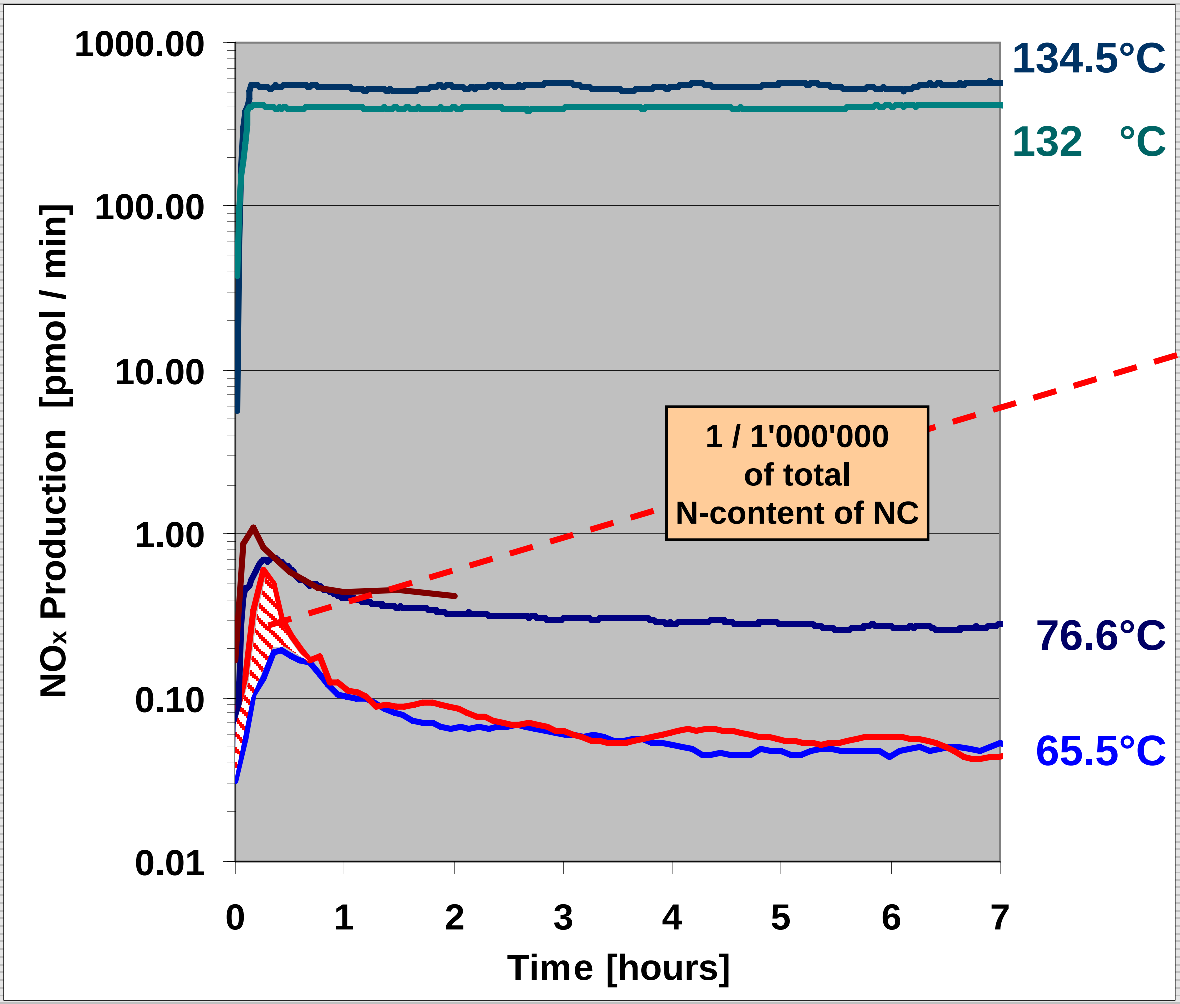
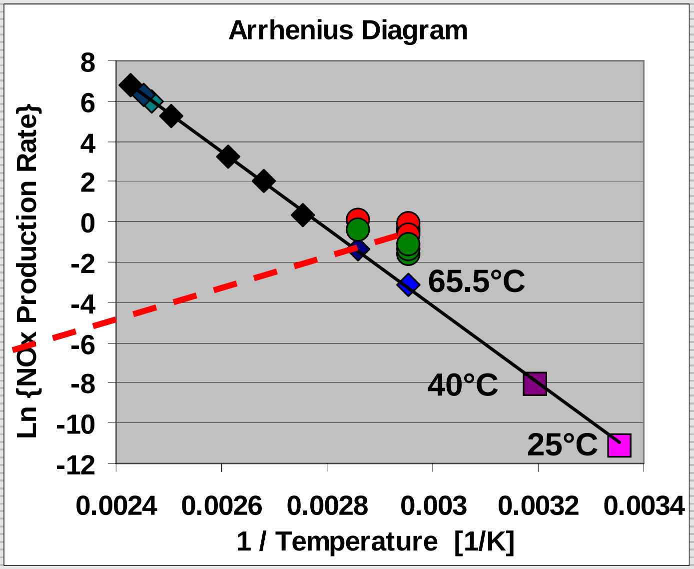


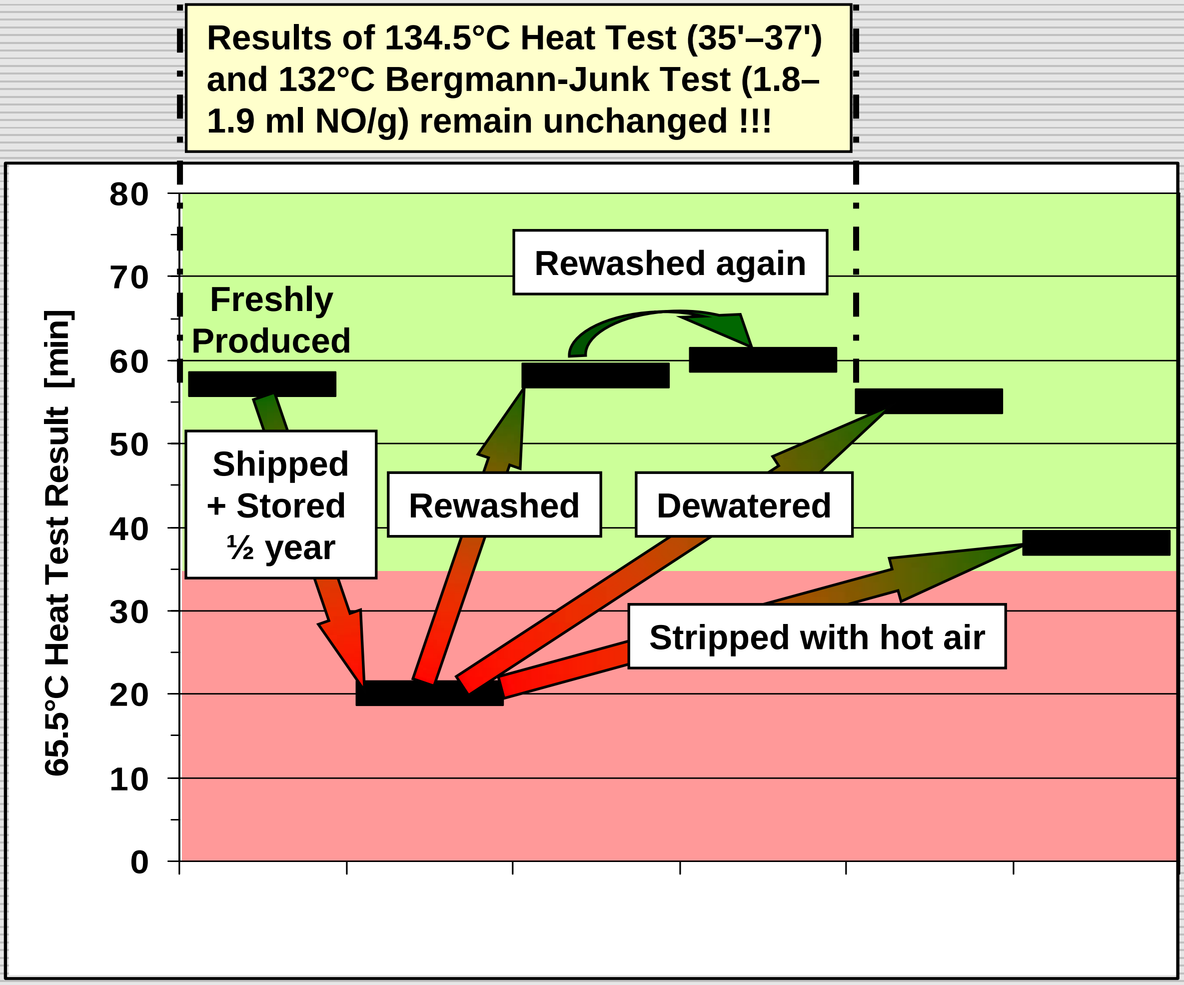


The trace amount of NO_x (approx. 5 – 10 nmol / g NC) which makes the NC fail the 65.5°C Heat Test is calculated to be produced in 1 week at 40°C, or in ½ year at 25°C ⇨ this are approx. the storage temperatures / times after which the NC fails the 65.5°C Test

Investigation of Stability Tests (15)

Evidence for Postulated Mechanism 65.5°C / 76.6°C Tests

⇨ Processes which Influence 65.5°C Heat Test Results



The 65.5°C Heat Test result of Nitrocellulose changes:

- → From 57' of freshly produced NC batch
- → Down to 20' after shipping through hot climate and ½ year of storage
- → Rewashing with hot water brings test result back to 58'; no significant further improvement by 2nd washing (60')
- → Similar improvement (to 55') by dewatering with alcohol
- → Improvement from 20' to 38' by 16 h of blowing 65.5°C hot air through NC sample
- ⇨ Test result is strongly influenced by all processes which produce or remove NO_x !!!

Investigation of Stability Tests (16)

Evidence for Postulated Mechanism 65.5°C / 76.6°C Tests

⇨ Artificial Generation of 65.5°C Heat Test Failure

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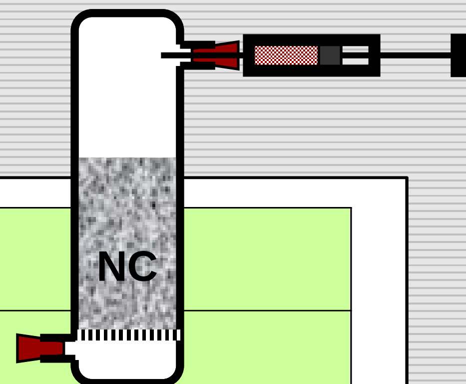
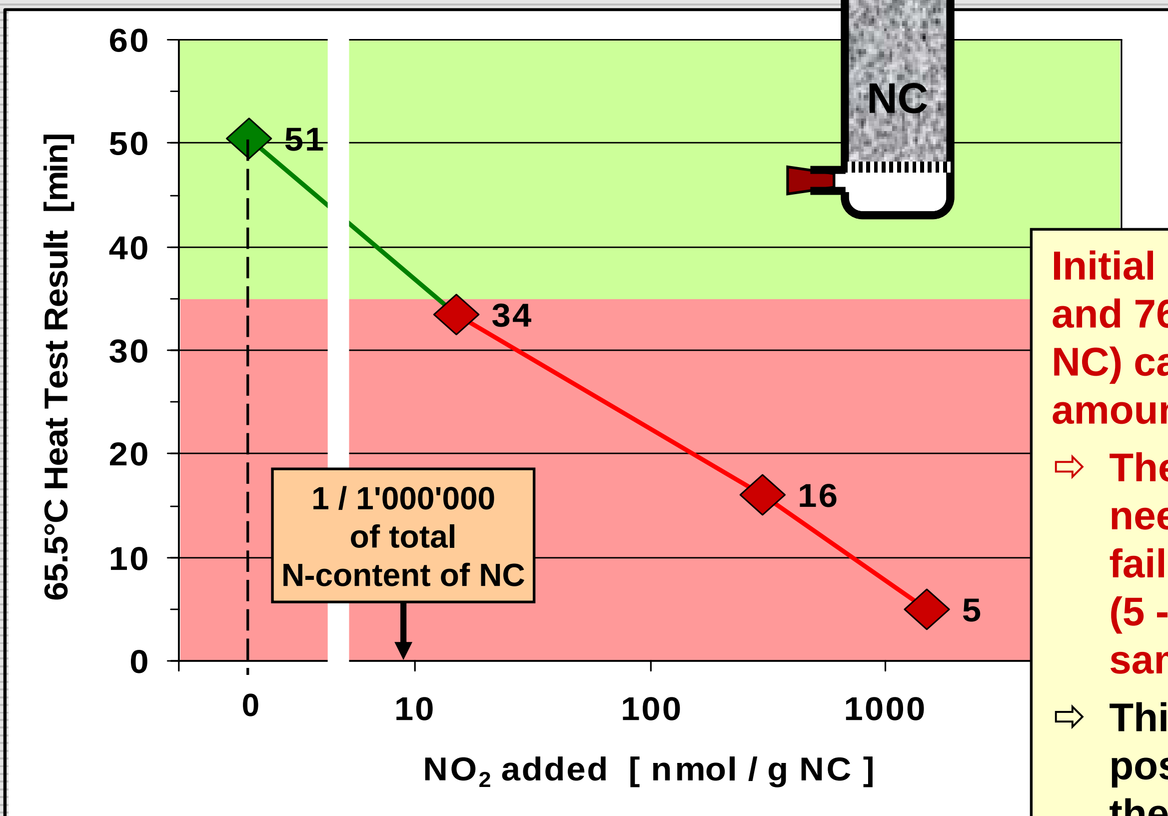
Result of 132°C Bergmann-Junk Test remains unchanged (1.8 – 2.1 ml NO/g)





Experimental:

→ NC in bottle
→ Adding NO_2 by syringe
→ Shaking, resting for 2 hours
→ Removal of excess NO_2 by blowing air through bottle
→ Stability testing of NC

Initial NO_x peak and thus failure of 65.5°C and 76.6°C Heat Tests (as seen in aged NC) can be artificially generated if a small amount of NO_2 is adsorbed on new NC

- ⇨ **The amount of NO_2 (15 nmol / g NC) needed here to reach 65.5°C Heat Test failure coincides with the NO_2 amount (5 - 10 nmol / g NC) released from aged samples during initial peak**
- ⇨ **This experiment strongly supports the postulated "NO_x accumulation / thermo-desorption" mechanism**

Summary and Conclusions (Part 2)

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- Even if all four currently used NC stability test methods are based on the detection of nitrogen oxides, they measure different processes taking place in the NC and thus often give totally contradictory results
- The 132°C Bergmann-Junk Test and 134.5°C Heat Test:
  - ⇨ Measure the "normal chemical ageing of NC" (thermolysis of nitric esters) and
  - ⇨ Are thus capable of reliably assessing the "real chemical stability" of the NC
  - ⇨ (with the Bergmann-Junk Test giving more quantitative / reproducible results)
- The 65.5°C Heat Test and 76.6°C Abel Heat Test, on the other side :
  - ⇨ Measure the initial release of traces of nitrogen oxides during heating-up
  - ⇨ Whereas the released nitrogen oxides often had been accumulated during previous storage
  - ⇨ In such cases (e.g. for aged NC), these tests do not show the "real chemical stability" of the NC but its "storage history"
  - ⇨ 65.5°C Heat Test and 76.6°C Abel Heat Test thus might be well suited for in-process control (check for impurities) and stability testing of freshly produced NC but definitively fail (give wrongly-negative results) when applied to aged NC

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- Manfred Bohn (ICT): Review and Discussion
- Contributors to Survey on NC Testing:
  Neil Turner (UK MoD); Graham Gillies (QinetiQ); Christian Spyckerelle (EURENCO); Lucas Lopez, Tony Williams, Mario Paquet (NC Mil-Spec Team USA); Nathan Zink (ARDEC); Wolfgang Schimansky (DENEL); Josef Tichý (SYNTHESIA); John Reid, Rhonda Wheeler (ADI Australia).

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Additional Results to Stability Testing of NC

Investigation of Stability Tests (8)

NO_x Production Rate in the different Stability Tests

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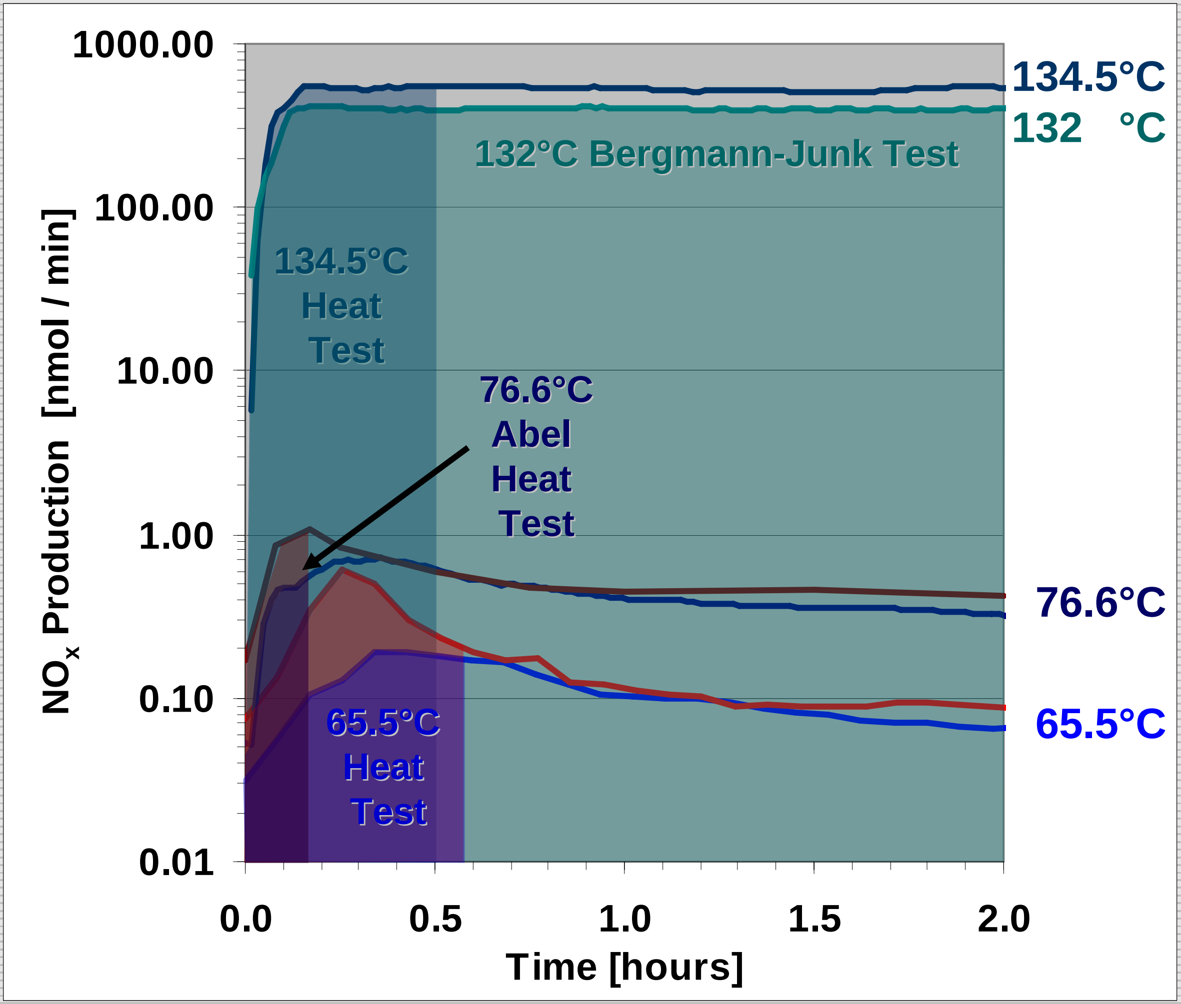

The amount of NO_x produced during test duration (= integral) of 134.5°C Heat Test (30') and 132°C Bergmann-Junk (2 h) is

more than factor 1'000 larger

than in 76.6°C Abel Heat Test (10') and 65.5°C Heat Test (35')

Investigation of Stability Tests (13)

Evidence for Postulated Mechanism 65.5°C / 76.6°C Tests

⇨ Influence of Storage Temperature on 65.5°C Heat Test

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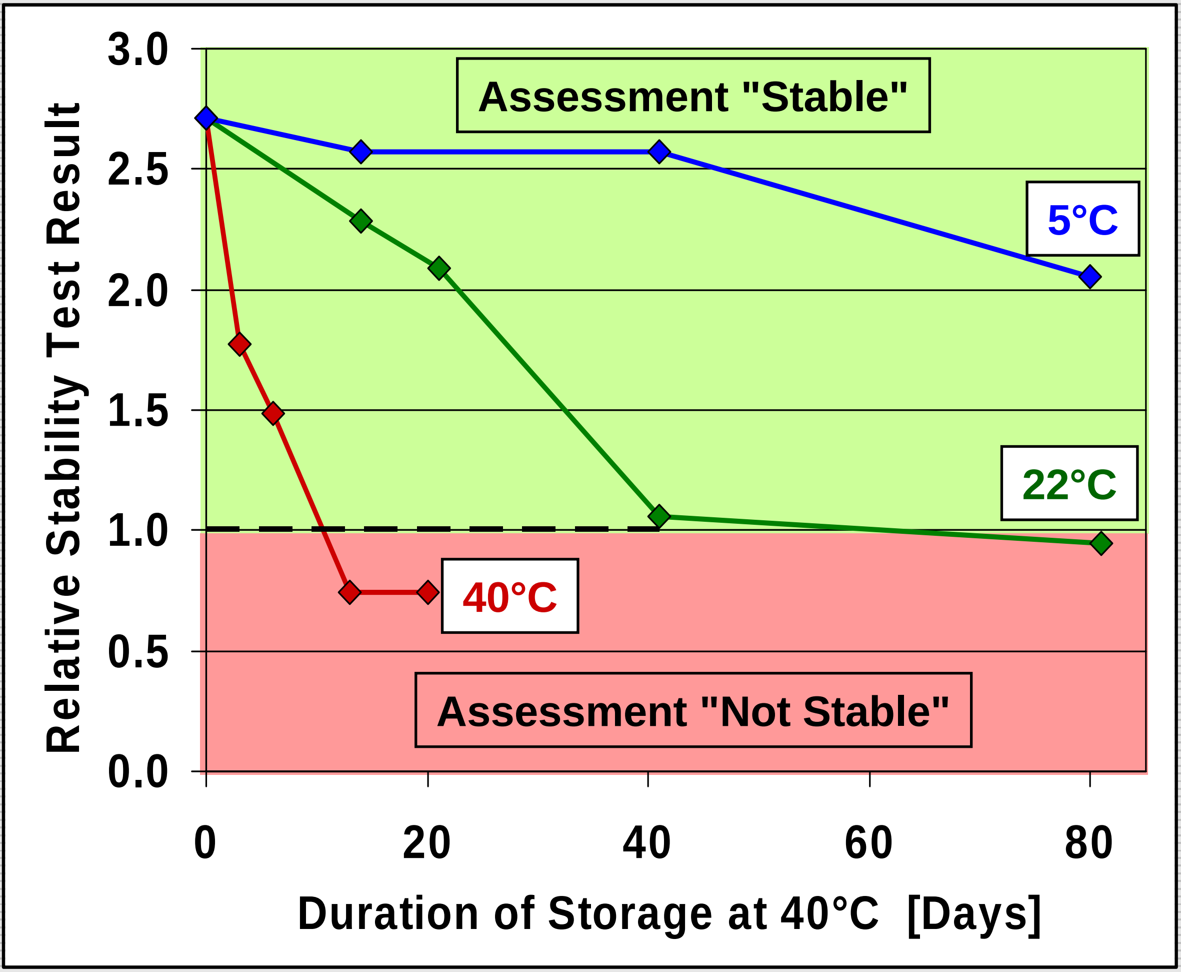

The 65.5°C Heat Test result of Nitrocellulose changes during storage !!!

- ⇨ **At 40°C deterioration of 65.5°C Heat Test result is very fast – after 14 days, test requirements are no longer fulfilled**
- ⇨ **At 22°C, deterioration of 65.5°C Heat Test result is much slower – after approx. 60 days, test requirements are no longer fulfilled**
- ⇨ **At 5°C, 65.5°C Heat Test result changes very slowly**

Investigation of Stability Tests

Evidence for Postulated Mechanism 65.5°C / 76.6°C Tests

⇨ Exclusion of Hydroperoxide Decomposition

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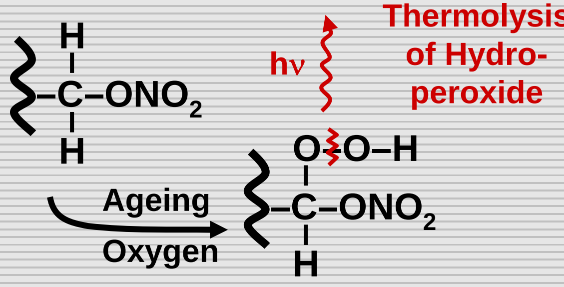
- J. Kimura (Japan Defence Agency) has shown than nitrate esters such as NC can form hydroperoxides during ageing under presence of oxygen (autoxidation) – these hydroxyperoxides decompose if the nitrate ester is heated to 80°C-110°C under emission of chemi-luminescence light – intensity of chemiluminescence correlates with age of nitric ester (and thus hydroperoxide content)



- The ageing related deterioration of 65.5°C / 76.6°C Heat Test results was found to be not connected with this autoxidation / thermolysis of hydroperoxides:
  - NC was aged at 40°C under air, oxygen and nitrogen → deterioration of 65.5°C Heat Test results of air and nitrogen samples was comparable, and that of oxygen sample even slower (if autoxidation would be involved, deterioration of Heat Test results would have to be fasted in the oxygen sample and lowest in the nitrogen sample)
  - New and aged NC was investigated by direct chemiluminescence at the Technical University Bern – both samples showed similar chemi-luminescence signals which presumably arise from excited NO_x states (will be confirmed later) – no signals which could arise from hydro-peroxide decomposition were found
    (Diagram shows CL-results of "old" NC which fails 65.5°C Heat Test with test time of 20 min)