
# 5th International Nitrocellulose Symposium

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## Qualitiy Aspects and Testing of Industrial NC

Dr.Herbert Nagorski

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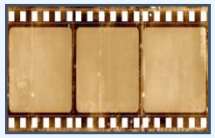
History

# Industrial NC

- Nitrocellulose in industrial applications is known since more than 100 years.
- Nitrocellulose has been used to produce Celluloid for

  Photographic media (film) 

  Toys, tennistable balls  

  Devices for household applications 

- Binder component in lacquers and inks 


- While Celluloid more or less disappeared - Nitrocellulose is still well regarded for binder systems in lacquers and printing inks.

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Applications for Industrial NC

# Protective surface coatings

## Lacquers

## Decorative coatings

(wood lacquer)

## Car repair systems


## Corrosion protection

Electrical varnish

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Applications for Industrial NC

# Minor Applications

Adhesives


Membranes

Diagnostic stics

Nail Varnish

Fireworks

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# Main applications

## Printing Inks


Printing Inks is the major application in Europe

## Lacquers

# NC Products







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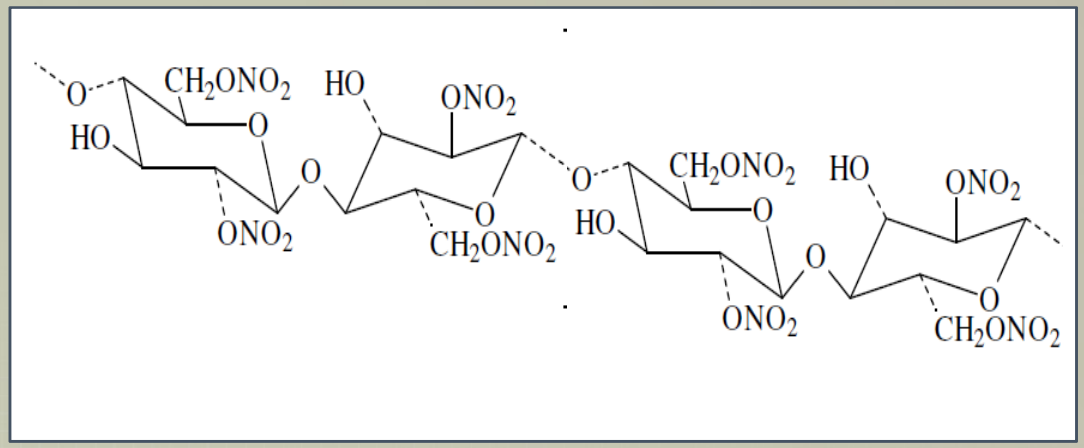
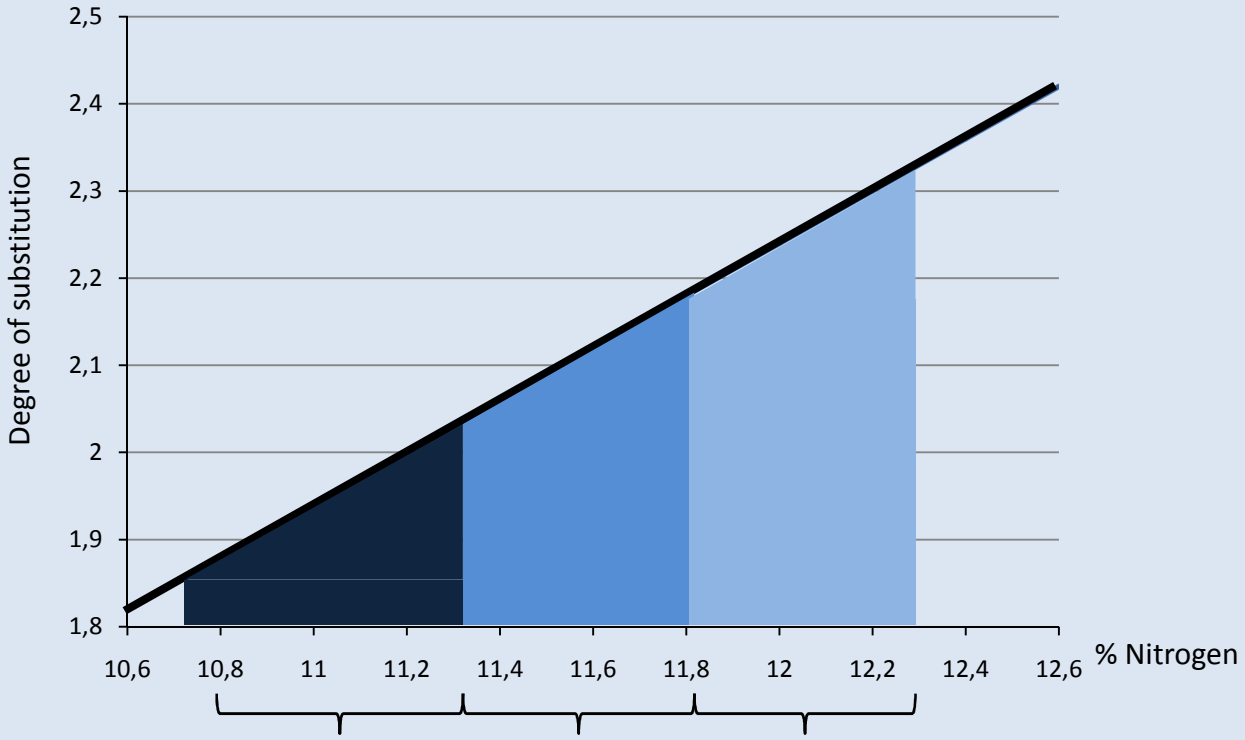
# Differencies

- Industrial NC covers the range 10.7 to 12.6 % Nitrogen
  - In energetic NC more than 80% of the cellulose-hydroxy groups are exchanged by nitro groups
  - Only 60 to 75 % of the cellulose-hydroxy groups are substituted by $NO_2$ in industrial NC



degree of substitution

# The N-content in industrial NC is always below 12.6 %

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# Characterization

According to DIN 53179 Industrial NC is characterized by

| | |
|---|---|
| E, A or M | **Degree of substitution** (=nitrogen content)<br>E = Ester soluble (11,8 – 12, 3 % N)<br>M = Ester/Alcohol Mix soluble (11,3 – 11,8 % N)<br>A = Alcohol soluble (10,7 – 11, 3 % N) |
| 4 to 35 | **Viscosity number**<br>(% of NC in 95% acetone/5% water to achieve a viscostiy of 400 ± 25 mPa*s measured by Höppler falling ball method) |
| Water, Ethanol, IPA, Butanol | **Damping agent** |
| 30 or 35 | **Concentration of damping agent** |

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**Examples:**

| | |
|---|---|
| **A 27 Eth 35** | **Medium viscosity alcohol soluble NC damped with 35 % Ethanol** |
| **E 9 IPA 30** | **High viscosity ester soluble NC damped with 30 % IPA** |

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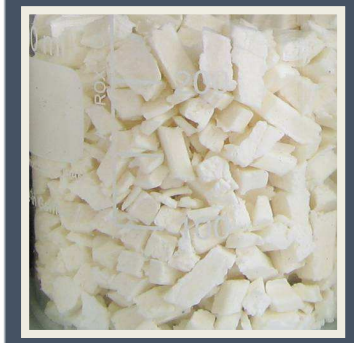
| 4 to 35 | **Viscosity number**<br>(% of NC in 95% acetone/5% water to achieve a viscostiy of 400 ± 25 mPa*s measured by Höppler falling ball method) |
| Plasticizer<br>ATBC, EPO, PU | **Damping agent** |
| **20** | **Concentration of plasticizer as damping agent** |



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H 22.5 ATBC 20

# Main criteria of industrial NC

## Solubility

**A-Types:** Alcohols, Ketones, Esters

**E-Types:** Esters, Ketones

**Both types are insoluble in hydrocarbons and water**

## Viscosity

**The viscosity plays a major role in lacquers and printing inks**

# Main criteria of industrial NC

## Solubility

**A-Types:** **Alcohols, Ketones, Esters**

**E-Types:** **Esters, Ketones**

**Both types are insoluble in hydrocarbons and water**

Ester soluble NC: Decorative coatings
Wood lacquer
Electrical varnisch

Alcohol soluble NC: Printing Inks

# Main criteria of industrial NC

## Viscosity

Beside the degree of substitution the viscosity of a NC solution is the second main factor to distinguish NC for industrial applications.

- Depending on final application industrial NC is available in a wide range of viscosities.
- Without any treatment nitration of cellulose leads to high viscous products (high molecular weight).
- During steam pressure boiling NC is stabilized and depolymerized
- Temperature and reaction time in the boiling process allows to adjust the desired viscoisty

  T = up to 140°C (2.8 bar)
  t = 20 min – 4 hours

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Specific Test Methods for Industrial NC

## Viscosity

Viscosity is determined
with a falling ball viscosimeter
by Höppler (ISO 14446).

X % of an ISO-Type X
(EU-Norm-Type) in a solution of
95 % acetone and 5 % water gives
a viscosity of 400 +- 25 mPa*s


**27% of A27 Eth.35**

**or**

**9 % of E 9 IPA30**

**in a solution of 95% acetone + 5% water**
**gives the same viscosity of 400 ± 25 mPa*s**

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## Viscosity

There are some other methods to determine viscosity and to characterize NC (esp. in USA and China)

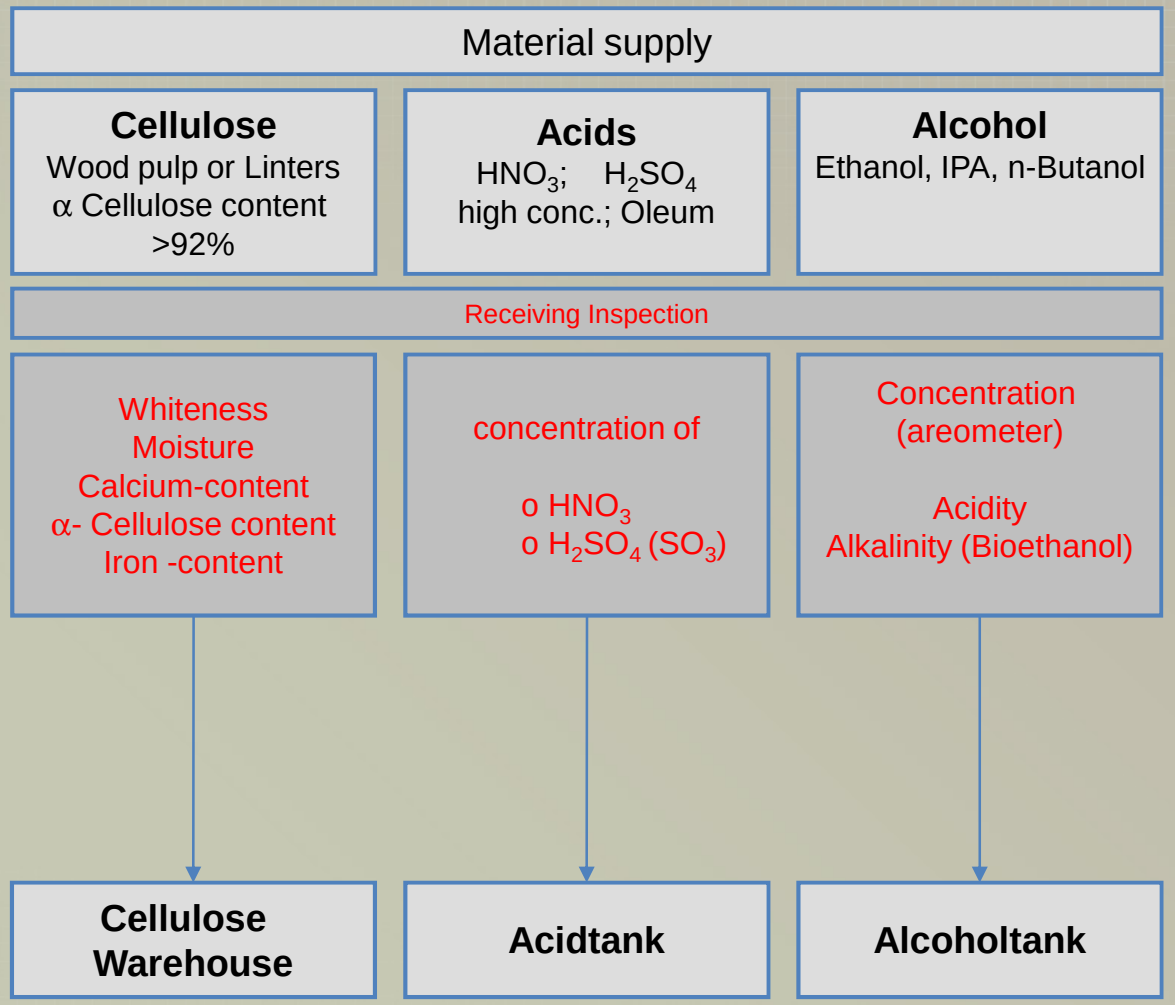
According to ASTM D 301-56 and D 1343-56
the viscosity is measured as falling time of a steel ball
(3/32 inch Ø) through a column filled with a 12.2 % NC solution
dissolved in a mixture of

25 % Ethanol
55 % Toluene
20 % Ethylacetate

Examples: RS ½ sec = E 23

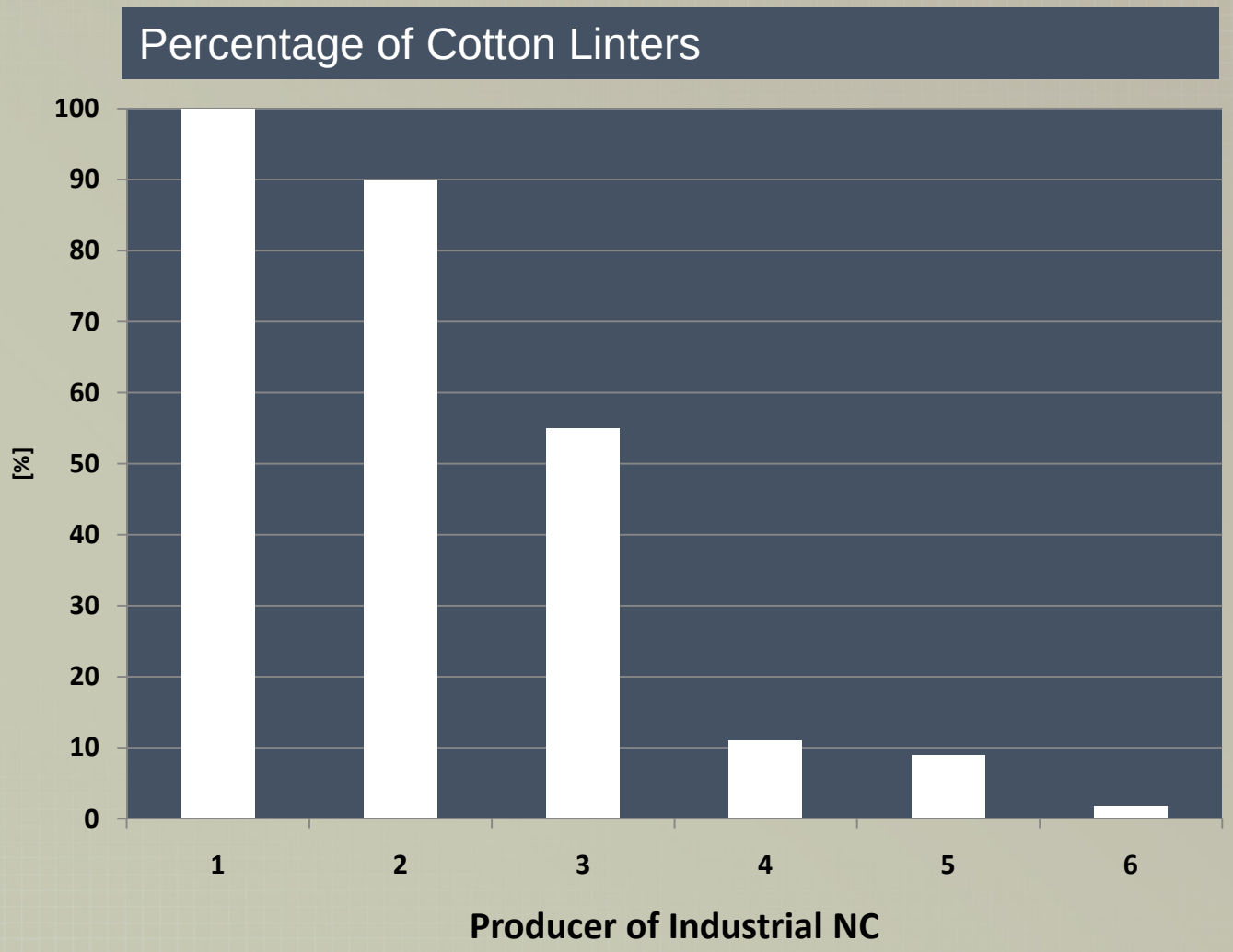
SS ¼ sec = A 27

# Rawmaterials



Raw Matrials

# Use of Cotton Linters

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## Receiving Inspection

| Cellulose | Acids | Alcohols |
|---|---|---|
| Whiteness | $HNO_3$ | Concentration (Density) |
| Moisture | $H_2SO_4$ ($SO_3$) | Acidity |
| Calcium-content | | Alkalinity (Bioalcohol) |
| α- **Cellulose content** | | |
| Iron –content | | |

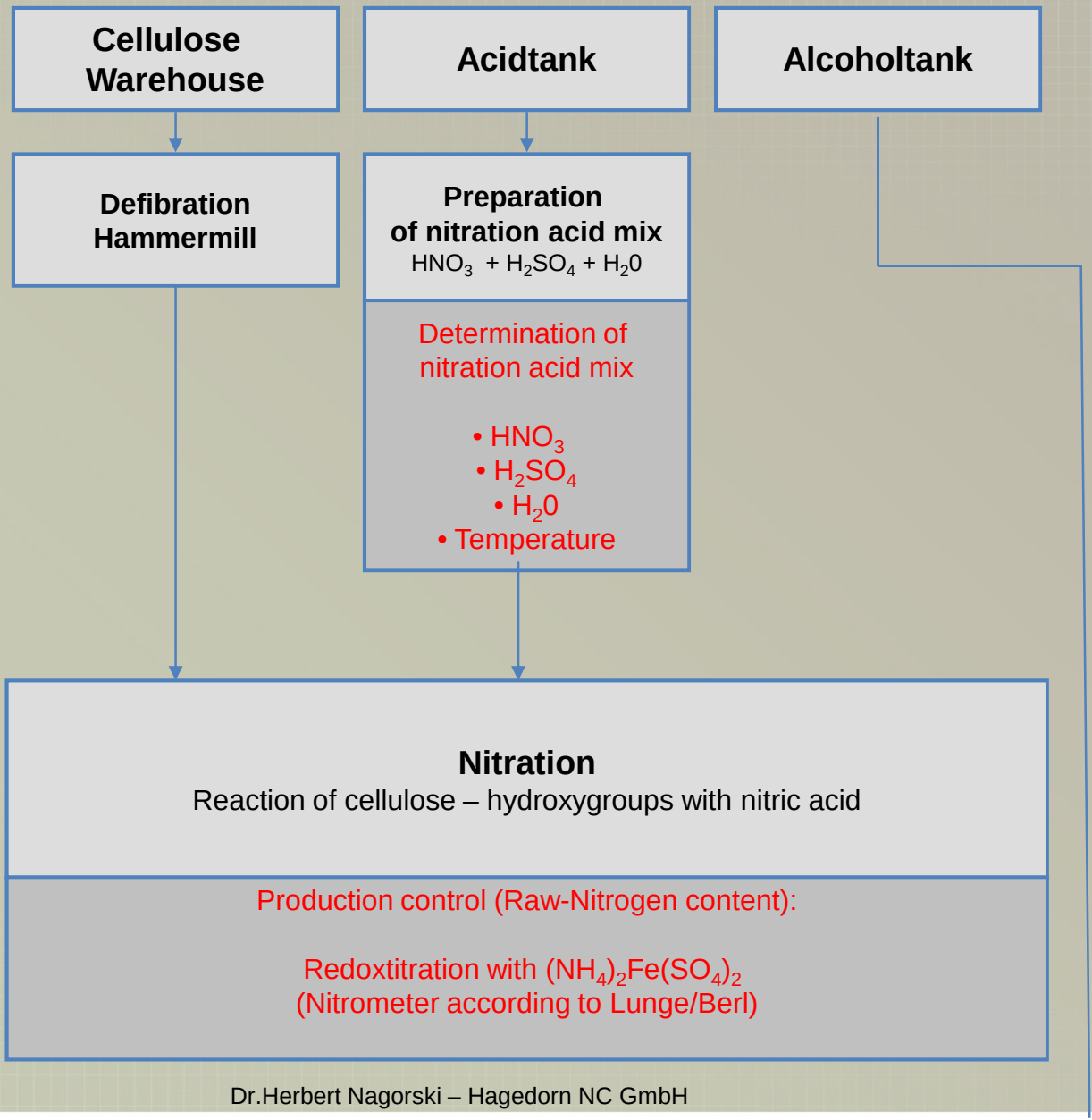
Most important test is the α - Cellulose content

# Suitability of Cellulose Types for Industrial NC

| Cellulose Type | Suited for |
|---|---|
| Cotton Linters | All Types of industrial NC |
| Wood Pulp > 95 % α - Cellulose | E-Grades, A-Grades* (*except some specific applications) |
| Wood Pulp > 92 % α - Cellulose | E-Grades |
| Wood Pulp < 92 % α - Cellulose | Not suited |

- Hemicellulose if present is nitrated as well
- Nitrated hemicellulose if not washed out sufficiently causes turbid NC – solutions

# Production set up and nitration



The process

## Posttreatment and Stabilization

**Centrifugation and washing**
Separation of excess nitration acid mix from the raw-nitrate

**Steam pressure boiling**
Stabilization and setting the viscosity
≤ 2.8 bar steam
≤ 140℃
0.5 – 4.0 h

**Washing**
Separation of residuals

Viscosity
Stability
Acidity
Optical appearance (in solution)
Nitrogen content

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# The process

**Mixing**
Homogenization of various lots

Viscosity
Optical properties
Evtl. Tests according to customer agreements
Accidity
Stability

**Damping**
With Water, Ethanol, IPA or Butanol (replacement of water)

Final Inspection

Colour
Haze
Viscosity (Internal-, Customer-, Iso-Method^)
Stability
Nitrogen Content
Alcohol solubility
Water content
Fibre length
Residual acid ($NO_3$/$SO_4$)
pH-Value

**Packing, Storage and Shipping**

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# Stability

Stability is one the most important properties of industrial NC

Tested from every lot produced in production and during final inspection .

Detection of $NO_x$ that is evolved from 1 g dry NC heated for 2 h at 132 ℃ ⇨ Target ≤ 2,5 ml

| Typical values: | |
|---|---|
| A – Types | 1.0 – 1.5 ml |
| E – Types | 1.5 – 2.0 ml |

Stability acc. to Bergman Junk

# Determination of damping

The concentration of damping agent is determined by NIR spectroscopy

- Sample disk ( Ø = 138 mm; V = 150 ml)
- completely filled with NC (depending on NC-grade sample weight = 50 – 100 g)
- not only small sample amount

100 spectra taken within 45 sec

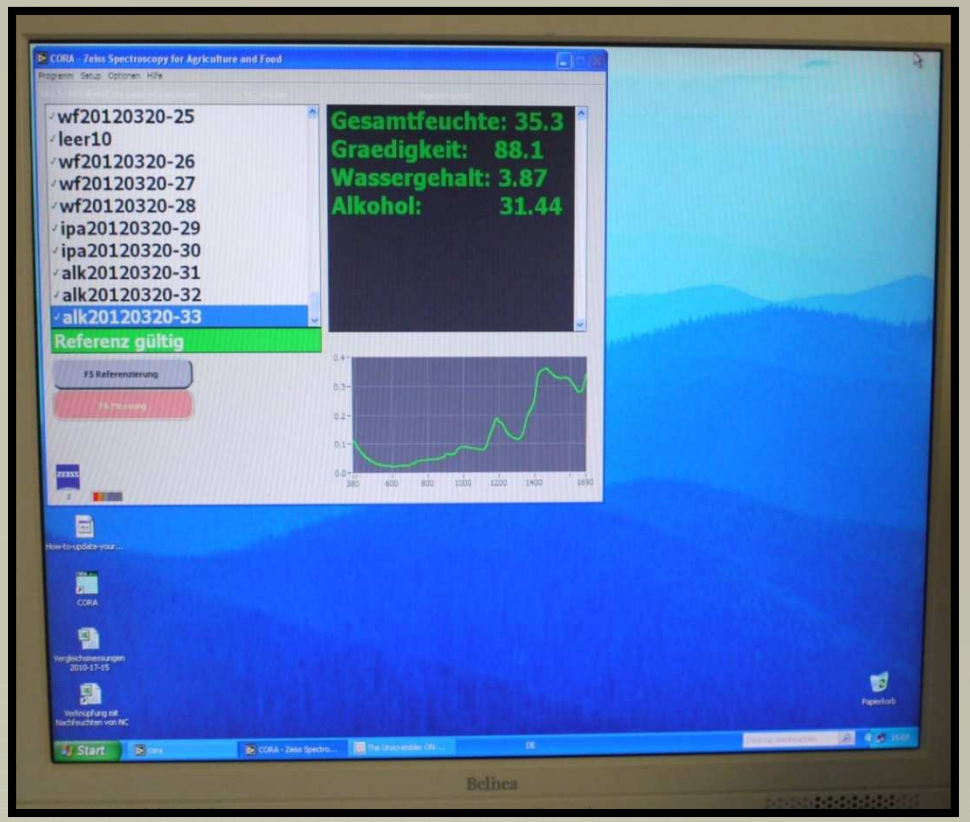
Random measurement of NC sample material

Specific Test Methods for Industrial NC

# Determination of damping

Simple and quick measurement of

- Total amount of damping agent
- Moisture content
- Alcohol content

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Production control

# Determination of damping

The NIR – method to determine the damping agent is not only used in the QC-Lab

The same method is applied in production controll with a simple, easy handling device


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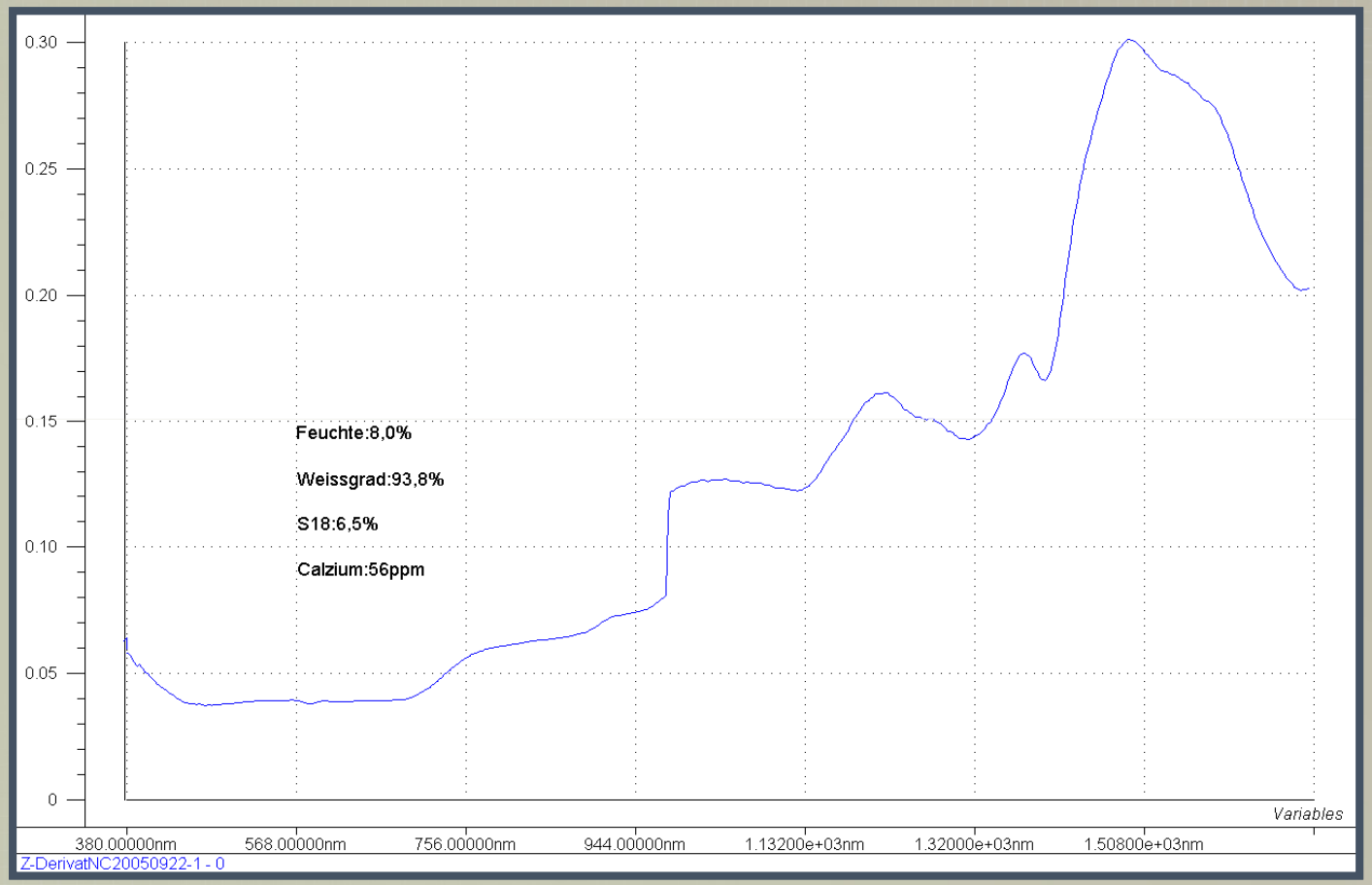
Specific Test Methods for Industrial NC

# NIR spectra of Cellulose

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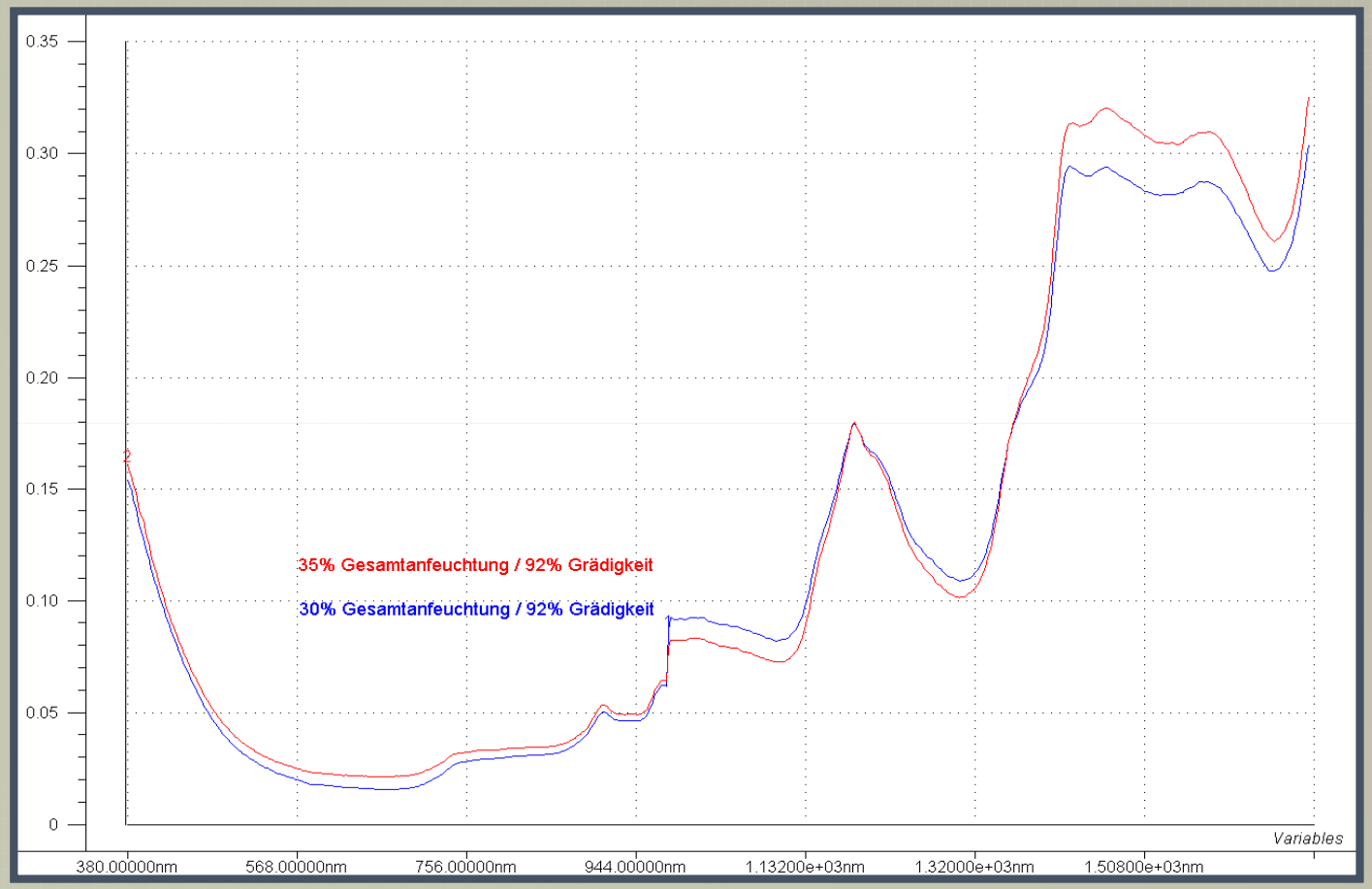
Calibration of this method is based on several hundred samples

Specific Test Methods for Industrial NC

# NIR spectra of Ethanol damped NC

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# Acidity of NC

10 g of wet NC suspended in 100 ml of water

Addition of a few drops of Methylorange

Red solution = NC is still acidic

Yellow solution = NC is neutral

pH-Value

5 g of wet NC suspended in 50 ml water

After 10 min of separation the water is measured with pH dipstick

# Fibre length

- 10 g dry NC in measuring cylinder filled up with water to a Volume of 250 ml
- After one hour the volume of the separated NC is recorded
- The fibre length is calculated as ml/10g

# Solubility in Alcohol

- 0,5 g dry NC dissolved in 75 ml Ethanol (94 %)
- Rotation for 3h – separation of not dissolved NC for 3h
- 50 ml of the solution evaporated to 25 ml Volume
- Precipitation of the dissolved NC by adding some water.
- Evaporation to dry weigth

Specific Test Methods for Industrial NC

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# Optical Properties (final inspection QC-Lab)

Measuring the optical properties is difficult if the final application is not sufficiently known.

To determine optical properties two standards are in use

**Alcohol soluble NC** in a mixture of

- Ethylacetate
- Butylacetate
- Butanol
- Toluene

**Ester soluble NC** in a mixture of

- Ethylacetate
- Glycol
- Ethanol
- Toluene

**There are a number of customer specific tests according to the desired application**

Example:
After Addtion of Isocyanate the solution has to stay clear for at least 8h

Specific Test Methods for Industrial NC

# Optical Properties (final inspection QC-Lab)

Evaluation of optical appearance of

- Colour Index according to Hazen (APHA) and/or Gardner
- Turbidity (Measurement with Ratio/XR Device against a Standard ( 4000 Te(F))
- Visible Fibres
  Amount and Length of visible fibres
- Clarity of the solution
- Visible particles
  visible particles (white/black), knots, impurities

All optical properties are determined in solution not on NC as produced

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# Optical Properties

Difference between Standard and Cosmetic Quality

# Plasticizer

If plasticizer is used for damping

the plasticizer is isolated by extraction

Benefits & Disadvantages

# Basics

Ester soluble NC: Decorative coatings
Wood lacquer
Electrical varnisch

Alcohol soluble NC: Printing Inks

Film properties:

High viscosity NC: film forming
relatively flexible

Low viscosity NC: hard, brittle

+ transparent, nearly odourless
+ sealing resistant (200-220℃ / 392 – 428℉)
+ Resistant against fats, oils, acids, water
+ good grinding behaviour for pigments
+ fast drying

- low adhesion on polyolefin films
- compatability with other binder systems

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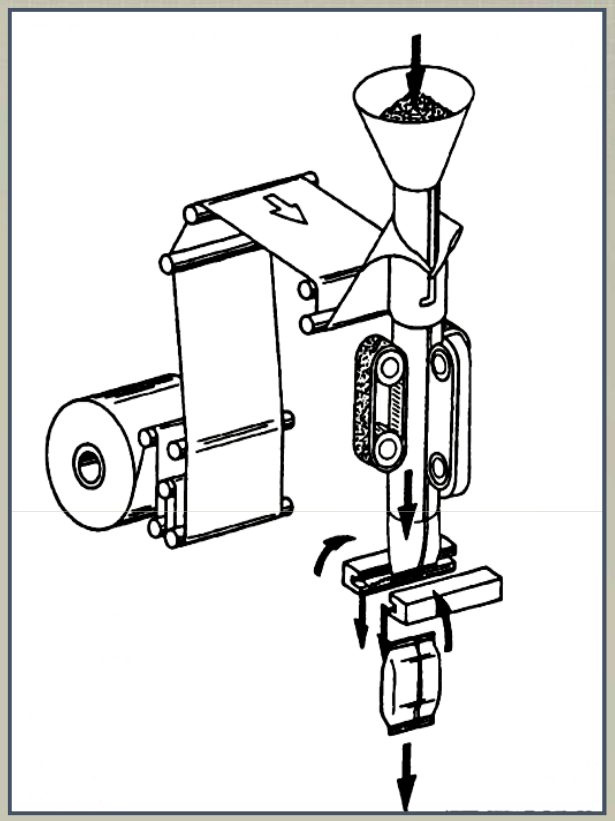
# Sealing resistance



NC printing inks withstand sealing temperatures up to 220℃ for short times


But NC should not be used for Inks applied in packaging for sterilization (>100 ℃; > 30 min = retort packaging)

Printing Inks

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# Evaluation of binder characteristics

Film forming
optical evaluation of smoothness , Gloss

Drying time
Time to reach constant weight

Blocking

Compatibilty with other binder system

Weatherbility

Lightstability (Xenon-Test)

For all these test the NC solution is applied on specific paper or on glass plates in defined thicknesses

# Evaluation of film properties

starts with preparation of a test ink, which is than applied to standard packaging substrates

- Bi-oriented polypropylene (OPP)
- Polyester
- Metallized OPP
- Aluminum
- Polyamid

Evaluation is made for

- Adhesion
- Scotch Tape Test
- Blocking

## Criteria for the use of printing inks

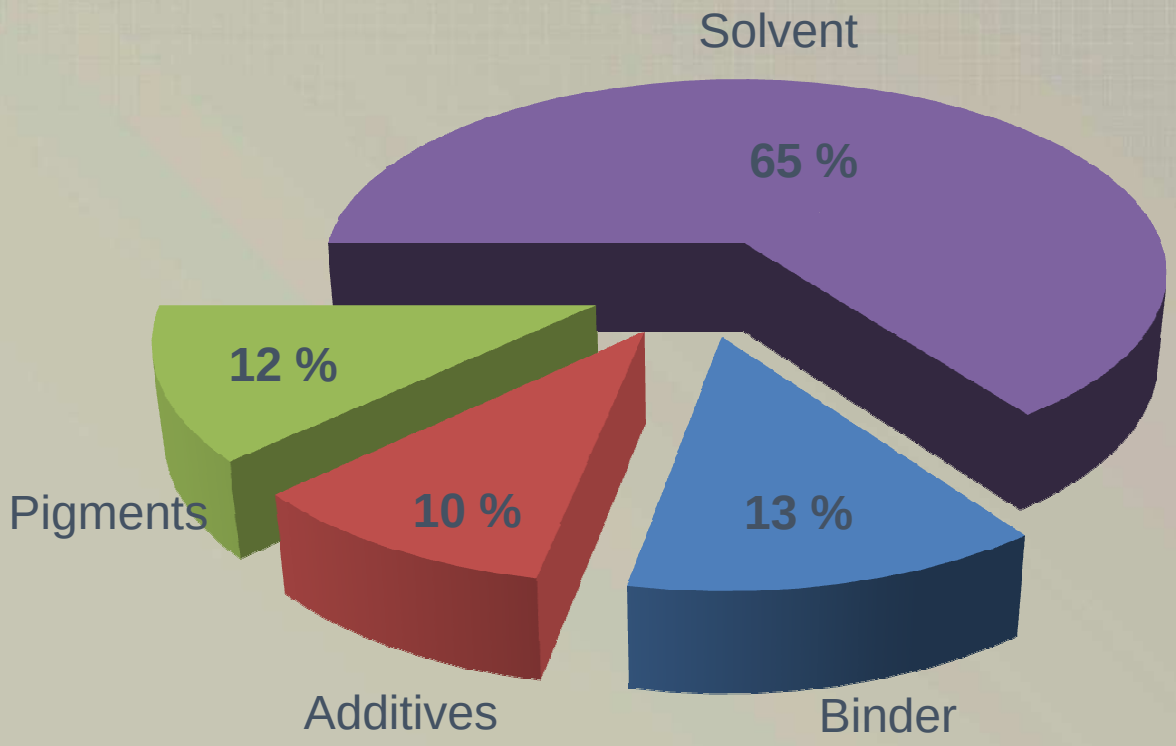
- Medium to high viscous NC types for transparent, non-coloured coatings

→ *low application weight due to high viscosity, flexible films*

- *Low viscous NC types for pigmented printing*

→ *higher application weight*
*more binder to fix pigments*
*rigid-brittle layers, (Use of Co-binder or plasticizer necessary)*

# Composition of printing inks




| | |
|---|---|
| Dry weight of Ink | = 3 – 6 g/m² |
| Binder | = 1 – 2 g/m² |
| Pigment | = 1 – 2 g/m² |

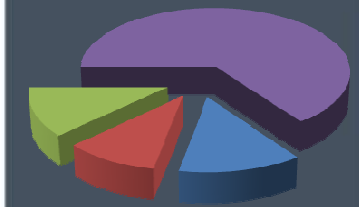
# Effekt of viscosity on pigment concentration

| Comparison of two different inks made of low / high viscosity NC | | |
|---|---|---|
| | **NC – Ink with AH 27** | **NC – Ink with AH 9** |
| Wet weight of ink | 9 – 18 g/m² | 3 – 6 g/m² |
| Dry weight of ink | 3 – 6 g/m² | 1 – 3 g/m² |
| Binder (NC) | 1 – 2 g/m² | 0.3 – 0.7 g/m² |
| Pigment | 1 – 2 g/m² | 0.3 – 0.7 g/m² |

- Both inks have the same viscosity
- Inks made from high viscosity NC lead to lower dry weight on the subtrate = lower pigment concentration (g/m²)

➡ Colour strength is reduced using high viscosity nitrocellulose

Low viscosity NC is preferred in printing inks
Due to hardness of low viscosity NC layers, printing inks usually contain plasticizer and/or cobinder



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# Contact

Hagedorn-NC GmbH
Dr. Herbert Nagorski
General Manager Technology
Emsufer 4
49808 Lingen
Fon ++49 (0) 591-9148-25
Fax ++49 (0) 591-9148-41
herbert.nagorski@hagedorn.de

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