Technology for Improving Efficiency of Fertilizer Applications

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Synergie GmbH

FERTASA
Soil Fertility and Plant Nutrition Symposium

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Synergie GmbH

Research & Development Center for Enhanced Efficiency Fertilizers and Biostimulants

Münster (Germany)

Gildenstrasse 36
48157 Münster
Germany
COMPO GmbH
48157 Münster
Germany

1956
Foundation COMPO
Münster, Germany

1986
Take over by
BASF AG

1998
Cooperation
Klassmann-Deilmann

2000
Take over by
K+S AG

2001
Acquisition
Algoflash, France

2004
Acquisition Meiners,
Germany (THG)

2005
Cooperation Syngenta,
Switzerland

2007
Acquisition Spiess-
Urania, Germany

2011
Takeover by Triton,
Germany

2012
Acquisition terrasan, Germany

2016
Integration by
Kingenta
Product categories

■ Potting soils
  High quality special potting soils for the individual needs of plants

■ Fertilizers
  A broad innovative range for a stronger and healthier growing of plants

■ Lawn seeds
  High quality lawn seed compositions, as well as mixture incl. seed substrate and fertilizer for new and to be repaired lawn plants

■ Plant protection
  Product against insecticides as aphids, against plant diseases and weeds

■ Biocides / Household insecticides
  To control harmful organisms
  (e.g. ants, bugs, rats etc.)
Kingenta Ecological Engineering Group

Linshu, Shandong Province, China

- Founded in 1998
- Revenues 18.7 Billion RMB (37.4 Billion Rand)
- 10,000 Employees
- Overseas Companies in USA, South America and Asia
- Products:
  - Compound NPKs
  - Controlled Release Fertilizers
  - Slow Release Fertilizers
  - Water Soluble Fertilizers
  - Efficiency Enhancers
  - Chelated Micronutrients
  - Biostimulants
14 Production sites in China
Content

• Stabilized Fertilizers
  • Nitrification Inhibitors
  • Urease Inhibitors

• Slow-Release Fertilizers (SRF)
  • IBDU
  • MU

• Controlled Release Fertilizers (CRF)
  • Polymer Coated
  • Sulfur Coated
  • Other Coatings

• Biostimulants
  • Humic Substances
  • Seaweed Extracts
  • Protein Hydrolysates (Amino Acids)
  • Microorganisms
  • Others
Specialty Fertilizers = Enhanced Efficiency

- NPK
- Water-Soluble-Fertilizers (WSF) incl. Foliar Fertilizers
- Stabilized Fertilizers
- Slow-Release Fertilizers (SRF)
- Controlled Release Fertilizers (CRF)
Biostimulants

- Humic Substances
- Seaweed and Herbal Extracts
- Protein Hydrolysates and other N-containing Substances
- Chitosan and other Polymers
- Inorganic Materials
- Beneficial Microorganisms
Nitrification Inhibitors (NI)

- Inhibit the transformation of ammonium into N-oxides (nitrate)
- Effect lasts for several weeks, depending on weather and soil conditions
- Most effective NI is DMPP
- Some important inhibitors:
  - DMPP (3,4-dimethylpyrazole-phosphate)
  - DCD (Dicyandiamide)
  - Nitrapyrin (N-Serve) (2-chloro-6-(trichloromethyl)-pyridine)
DMPP (3,4 Dimethylpyrazole phosphate)

Properties:

• White-beige powder
• Empirical formula: C₅H₁₁N₂O₄P
• CAS No.: 202842-98-6
• Molecular Mass: 194.13 g/mol
• Melting point: 167-169°C
• Solubility in water: 13.2%
• Solubility in H₃PO₄: 37-38%
Transformation of ammonium in the soil and effect of DMPP

Urea $\text{CH}_4(\text{N}_2\text{O})$  
UAN, AN, AS, ASN...

Hydrolysis

Ammonium ($\text{NH}_4^+$)  $\rightarrow$  Nitrite ($\text{NO}_2^-$)  $\rightarrow$  Nitrate ($\text{NO}_3^-$)

Nitrification 1.step  Oxidation by Nitrosomonas  
Nitrification 2.step  Oxidation by Nitrobacter

leaching into the soil or groundwater
Transformation of ammonium in the soil and effect of DMPP

Urea CH$_4$(N$_2$O) → UAN, AN, AS, ASN…

Hydrolysis → Ammonium (NH$_4^+$) → Nitrite (NO$_2^-$) → Nitrate (NO$_3^-$)

Nitrification 1.step

Nitrification 2.step Oxidation by Nitrobacter

leaching into the soil or groundwater
### Transformation of ammonium in the soil and effect of DMPP

<table>
<thead>
<tr>
<th>Urea $\text{CH}_4(\text{N}_2\text{O})$</th>
<th>UAN, AN, AS, ASN…</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis</td>
<td></td>
</tr>
<tr>
<td>Ammonium $(\text{NH}_4^+)$</td>
<td>STOP</td>
</tr>
<tr>
<td>• Accumulation of $\text{NH}_4^+$</td>
<td></td>
</tr>
<tr>
<td>• No leaching into the soil or groundwater</td>
<td></td>
</tr>
</tbody>
</table>
## Effects of DMPP

### Inhibiting effects of DMPP and DCD
*(Residual NH$_4$-N relative to 8.7 mg NH$_4$-N as liquid pig manure)*

<table>
<thead>
<tr>
<th>Week</th>
<th>Control</th>
<th>DMPP</th>
<th>Control</th>
<th>DCD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>1</td>
<td>68</td>
<td>100</td>
<td>68</td>
<td>93</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>76</td>
<td>3</td>
<td>47</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>52</td>
<td>0</td>
<td>22</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>32</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>16</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Modified after Zerulla et al., 2001
Effects of DMPP

Effect of a stabilized ASN application on soil NH₄ and NO₃ contents over a period of 8 weeks

Modified after Zerulla et al., 2001
# Effects of DMPP

Leaching of NO$_3$ under a vegetable crop cover  
(as % of fertilized N)

<table>
<thead>
<tr>
<th>Days</th>
<th>ASN</th>
<th>ASN + DMPP</th>
<th>ASN + DCD</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>10.7</td>
<td>4.5</td>
<td>12.1</td>
</tr>
<tr>
<td>8</td>
<td>8.3</td>
<td>2.6</td>
<td>3.5</td>
</tr>
<tr>
<td>22</td>
<td>2.7</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Total</td>
<td>21.7</td>
<td>7.6</td>
<td>16.1</td>
</tr>
</tbody>
</table>

Modified after Zerulla et al., 2001
Effects of DMPP

DMPP reduces NO$_2$ emission under field conditions

Modified after Weiske et al. (2001)
Effects of DMPP

Our field trials in the Eastern parts of Germany on maize and cereals
Effects of DMPP

Effect of stabilized CAN and chitosan coating on maize yield

<table>
<thead>
<tr>
<th>Treatment</th>
<th>DM yield (t/ha)</th>
<th>DM (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>12.99</td>
<td>34.7</td>
</tr>
<tr>
<td>CAN</td>
<td>18.03</td>
<td>35.1</td>
</tr>
<tr>
<td>CAN + DMPP</td>
<td>18.21</td>
<td>34.7</td>
</tr>
<tr>
<td>CAN + DMPP + Chitosan</td>
<td>18.52</td>
<td>34.8</td>
</tr>
</tbody>
</table>
**Effects of DMPP**

Effect of stabilized CAN and chitosan coating on N-content and N-uptake of maize

<table>
<thead>
<tr>
<th>Treatment</th>
<th>N-Content in DM (%)</th>
<th>Nitrogen uptake (kg/ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.63</td>
<td>81.7</td>
</tr>
<tr>
<td>CAN</td>
<td>0.90</td>
<td>162.8</td>
</tr>
<tr>
<td>CAN + DMPP</td>
<td>0.93</td>
<td>168.7</td>
</tr>
<tr>
<td>CAN + DMPP + Chitosan</td>
<td>0.94</td>
<td>174.5</td>
</tr>
</tbody>
</table>
Stabilization Technique 1

Transform DMPP into an active liquid for the stabilization process

DMPP is a solid powder → Transform into a liquid → Add color → Liquid product for fertilizer solution and slurry

Stabilized WSF → Stabilized granular fertilizer → Stabilized urea
Stabilization Technique 2

“Stabilization” = To treat granular fertilizers or liquids with DMPP-containing solutions

“Do it yourself”
Stabilization Technique 3

General scheme of a stabilization unit

- Mixing drum
- Spraying nozzle
- Granulated fertilizer
- IBC with DMPP solution (ready to use)
- Heating jacket
Urease Inhibitors (UI)

- Blocking the transformation of urea to ammonium
- NBPT: (N-(N-Butyl) thiophosphoric triamide) discovered in 1980
- Binds to urease enzymes
- Over 400 different types of ureases known
- NBPT can bind to many of them
- Not crop specific but specific to groups of ureases
- Effect lasts for 14 days, then gradually decreases
N-(n-Butyl) thiophosphoric triamide (NBPT)

Properties:

- White crystalline powder
- Empirical formula: $\text{C}_4\text{H}_{14}\text{N}_3\text{PS}$
- CAS No.: 94317-64-3
- Molecular mass: 167.21 g/mol
- Melting point: 58-60°C
- Solubility in water: 4.3 g/l
- Higher solubility in organic solvents
**NBPT**

- Reduces \( \text{NH}_3 \) and \( \text{NO}_x \) emissions into the atmosphere
- Less \( \text{NO}_3 \) leaching into the ground water
- Better crop growth due to increased nitrogen efficiency

- Suitable for
  - Urea
  - UAN solutions
  - Organic N-fertilizers
Slow-Release Fertilizers

- Slow release fertilizers provide a steady supply of plant nutrients (mostly N) over an extended period of time
- SRF contain plant nutrients in a form that delays its initial availability
- Decomposition and release of nutrients through biological/chemical processes in the soil
- **Categories:**
  - Natural organic materials (bone flour, sheep wool...)
  - Synthetic organic fertilisers (based on urea)
    - *Ureaform (UF) / Methylene Urea (MU)
    - *Isobutylendiurea (IBDU) = Isodur®
    - *Crotonylidenurea (CDU) = Crotodur®
IBDU (Isobutyledendicurea)

- Is a defined molecule consisting of two urea molecules coupled by one isobutyraldehyde molecule
- N content: 32.2%
- N release time in soil: 2 to 4 months
- Minimum soil temperature: 8°C
- Sufficient soil humidity necessary, no release under drought conditions
- Release mainly governed by chemical hydrolysis, soil pH and particle size
- No intermediate or by-products
Insoluble in cold water, 100 % breakdown to plant available N depending on temperature and moisture.
MU (Methylene Urea), syn. UF (Urea Formaldehyde)

- Is not one defined molecule but a mixture of different condensed urea molecules
- N content: 38%
- UF represents the oldest slow release N form
- First developed in 1947, commercial production since 1955 in the USA
- Product of a chemical reaction of urea and formaldehyde
- Depending on process conditions the reaction results in a mix of molecules with different chains lengths
- N release time 8 to 12 weeks
- N release is influenced by soil temperature and moisture as well as on the biological activity of the soil
Urea + Formaldehyde

Monomethylolurea

Methylenediurea

Dimethylenetriurea + H₂O
Properties of the different UF fractions:

**Fraction 1: Cold water soluble (CWS) at 25°C**
- Product percentage in UF / MU fertilisers (38%N): ~ 13% N absolute
- Product percentage in IBDU fertilisers (32%N): ~ 4% N absolute

**Fraction 2: Insoluble in cold water, soluble in hot water (HWS) at 100°C**
- Product percentage in UF / MU fertilisers (38%N): ~ 15 - 17% N absolute
- Product percentage in IBDU fertilisers (32%N): ~ 28% N absolute

**Fraction 3: Hot water insoluble (HWI)**
- Product percentage in UF / MU fertilisers (38%N): ~ 9 - 11% N absolute
- Product percentage in IBDU fertilisers (32%N): ~ < 1% N absolute
Properties of the different UF fractions:

Activity Index (AI)

= Indicator for the relative performance or quality of UF products.

The AI describes the share of the Cold Water Insoluble N (CWI, Fraction 2) relative to the Hot Water Insoluble N (HWI, Fraction 3). However the Cold Water Soluble N (CWS, Fraction 1) is not included in the AI and it has to be considered that CWS N has also to undergo certain biological degradation processes in the soil before being plant available.

The AI is only a valid parameter for UF, not for IBDU and CDU.

\[
Al = \frac{\% \text{CWI} - \% \text{HWI}}{\% \text{CWI}} \times 100
\]

The AI is varying between 40 and 80
Controlled Release Fertilizers

- Sulfur Coated Urea
- Polymer Coated Urea NPK
- Other coatings Urea NPK
- Blends
Release mechanism of CRFs

Granules are coated with a novel polymer coating based on organic materials that degrades naturally in time.

The granule attracts water and it penetrates the coating.

The nutrients dissolve in water to form a concentrated nutrient solution and are released to the soil by diffusion controlled by a steady-state equilibrium governed by temperature.
Release types of CRFs

From Trenkel, 2010
Longevity is strongly influenced by soil temperature

<table>
<thead>
<tr>
<th>Longevity in months (approximately)</th>
<th>Soil Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 °</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>11</td>
<td>9</td>
</tr>
<tr>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>20</td>
<td>18</td>
</tr>
</tbody>
</table>
Coating and longevity affect nutrient contents

<table>
<thead>
<tr>
<th>Product</th>
<th>Nutrient Contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>46-0-0</td>
</tr>
<tr>
<td>PCU 2M</td>
<td>44-0-0</td>
</tr>
<tr>
<td>PCU 6M</td>
<td>42-0-0</td>
</tr>
<tr>
<td>PCU 9M</td>
<td>41-0-0</td>
</tr>
</tbody>
</table>
**CRF - NPK and urea options**

<table>
<thead>
<tr>
<th>Formula</th>
<th>Longevity at 21°C</th>
<th>N</th>
<th>P₂O₅</th>
<th>K₂O</th>
<th>MgO</th>
<th>B</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Zn</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>15-09-15+2MgO+TE</td>
<td>3 Months</td>
<td>15</td>
<td>9</td>
<td>15</td>
<td>2</td>
<td>0,03</td>
<td>0,016</td>
<td>0,39</td>
<td>0,09</td>
<td>0,05</td>
<td>0,028</td>
</tr>
<tr>
<td>15-09-14+2MgO+TE</td>
<td>6 Months</td>
<td>15</td>
<td>9</td>
<td>14</td>
<td>2</td>
<td>0,02</td>
<td>0,016</td>
<td>0,39</td>
<td>0,09</td>
<td>0,05</td>
<td>0,027</td>
</tr>
<tr>
<td>15-08-14+2MgO+TE</td>
<td>9 Months</td>
<td>15</td>
<td>8</td>
<td>14</td>
<td>2</td>
<td>0,02</td>
<td>0,016</td>
<td>0,37</td>
<td>0,09</td>
<td>0,05</td>
<td>0,027</td>
</tr>
<tr>
<td>14-09-14+2MgO+TE</td>
<td>12 Months</td>
<td>14</td>
<td>9</td>
<td>14</td>
<td>2</td>
<td>0,02</td>
<td>0,016</td>
<td>0,37</td>
<td>0,09</td>
<td>0,05</td>
<td>0,027</td>
</tr>
<tr>
<td>14-13-13</td>
<td>6 Months</td>
<td>14</td>
<td>13</td>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13-14-13</td>
<td>9 Months</td>
<td>13</td>
<td>14</td>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43-0-0</td>
<td>3 Months</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>43</td>
</tr>
<tr>
<td>42-0-0</td>
<td>6 Months</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>42</td>
</tr>
<tr>
<td>NPK*</td>
<td>3 - 18 Months</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Measuring nutrient release patterns in the lab

Ozores-Hampton and Carson (2013)
N-release of coated urea measured in water at different temperatures (21 and 35°C)
N-release measured in water (25°C) and as weight loss in the greenhouse

Mayer (2010)
Comparison of Surplus Costs

<table>
<thead>
<tr>
<th>EEF Type</th>
<th>Duration of effect</th>
<th>Surplus costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>UI Stabilized</td>
<td>2 – 4 weeks</td>
<td>+ 40 €/t</td>
</tr>
<tr>
<td>NI Stabilized</td>
<td>4 – 8 weeks</td>
<td>+ 45 €/t</td>
</tr>
<tr>
<td>SCU</td>
<td>2 – 9 months</td>
<td>+ 150 €/t</td>
</tr>
<tr>
<td>PSCU</td>
<td>2 – 16 months</td>
<td>+ 250 €/t</td>
</tr>
<tr>
<td>PCU</td>
<td>2 – 16 months</td>
<td>+ 350 €/t</td>
</tr>
<tr>
<td>PCF</td>
<td>2 – 16 months</td>
<td>+ 800 €/t</td>
</tr>
</tbody>
</table>
CRFs

- Best way to control nutrient release from fertilizers
- Traditional use in nurseries and floriculture
- For field crops, fruit trees and vegetables blends are recommended (price)
- Release curves of different nutrients (NKP) are not identical
- Longevity depends on soil temperature
- High quality differences between producers in terms of release patterns and coating properties
Biostimulants

Improve

• Nutrient uptake
• Nutrient efficiency
• Tolerance to abiotic stress
• Crop quality
Biostimulants

- Humic Substances
- Seaweed and Herbal Extracts
- Protein Hydrolysates and other N-containing Substances
- Chitosan and other Polymers
- Inorganic Materials
- Beneficial Microorganisms
**PASP - Polyaspartate**

A polymer of aspartate subunits. Aspartate is an amino acid

- PASP act as phosphate efficiency enhancer, because they bind to P fixating cations such as Ca, Mg and Fe (same mode of action as for Avail)
- PASP is a strong chelator for cationic micro nutrients, keeping them available for the uptake by roots
- PASP induces better root growth and more root hairs
- PASP can help roots to store moisture
- Reports indicate that PASP increases the efficiency of applied fertilizers resulting in earlier emergence, faster growth and higher yield
PASP-Trial results

Soil PASP application increases crop yield
77.3% positive response

Application rate: 750 g/ha
PASP-Trial results

Foliar PASP application increased trace element content in maize

![Graph showing the increase in trace element content in maize with PASP application.](image-url)
Trends in Enhanced Efficiency Fertilizer Techniques

• Intensified use of stabilized and other enhanced efficiency fertilizers because of stringent legal regulations

• Consumer trend towards organic food

• Combinations of active ingredients and biostimulants

• Precision Agriculture

• Land is scarce: Higher productivity per area unit is a future task without alternative
Summary

• Different techniques for Enhanced Efficiency Fertilizers (EEF) have been developed and are fully viable

• The most advanced technologies are:
  • Nitrification/Urease Inhibitors (Stabilized Fertilizers)
  • Slow-Release-Fertilizers (IDBU, MU)
  • Controlled-Release-Fertilizers (S- or Polymer-coated)

• Biostimulants start to play a role as efficiency enhancers
谢谢！
Xièxiè!

Thank You!

Dankie!