High Throughput Approach for Agricultural Formulation Optimization

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The Dow Chemical Company
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High Throughput Research at Dow

Sample Preparation → Properties → Performance

Dow is a leading innovator in high throughput with an initial investment of > $100 million in the early 2000s

- Catalysis, synthesis and polymerization (new materials)
- Liquid formulations (agricultural, home and personal care, electronic materials)
- Coatings and adhesives (water-borne and reactive)
- Thermoset and thermoplastic formulation and application
Combinatorial Design of Experiments

Library Studio

Experimental Variables

Formulation Constraints

DOE: Understanding Reproducibility and Modeling Needs

Experimental Constraints

→ Design Parameters

← Formulation Components

← Equations

Plate 2

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Informatics Is Critical

Dow has various information research groups that work to develop and integrate the best hardware and software options for HTR.
Phase Diagrams

Experimental Design

Automated Liquid Handler

Phase Characterization

Ternary Phase Diagram

Output
- Number of phases
- Volume fraction of each phase
- Optical clarity of each phase

Visualization Software

Other Screens
Rheology, chemical/thermal stability, cleaning, solubility, cloud point, wetting, etc.
Phase Identification and Characterization Apparatus

- Heating/cooling programmable controller
- Mixing capabilities: Variable time/speed control
- Birefringence filters
- Digital imagery with side and back lighting
- Analyzes for optical clarity, color and uniformity
- 6-plate deck (~45 min/plate)
Temperature Scanning Turbiometry (TST)

- Samples are video recorded and software detects opacity changes
- Device ramps 48 samples through a temperature sweep using various min/max temperatures and adjustable heating rates
HTR Performance Evaluation Capabilities

- Solubility/compatibility
- Surface tension/CMC
- Foam generation and stability
- Wetting
- Solubilization
- Emulsion stability
- Rheology
- Freeze/thaw stability
- Optical clarity
- Application-specific screens
Agrochemical Formulation Development

When traditional formulation approaches are limited…

High throughput methods speed up new formulation development

• Reformulation to meet new regulatory requirements
• Aromatic solvent replacement
• Multi-active compatibility
• Tank mix compatibility
• Customized projects
Example: Reformulation of Emulsifiable Concentrate

40% AI
51% Solvent
9% Emulsifier

<table>
<thead>
<tr>
<th>NIS1</th>
<th>NIS2</th>
<th>6% NIS / 3% Anionic</th>
<th>4.5% NIS / 4.5% Anionic</th>
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<td>9</td>
<td>10</td>
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Example of a good emulsion:
Uniform opacity at different height levels

Example of a failed emulsion:
Different opacity at different height levels

CIPAC MT36
96 formulations in 45 min
Typical EW Formulation

<table>
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<tr>
<th>Items</th>
<th>Room Temp</th>
<th>0°C, 1wk</th>
<th>54°C, 2 wks</th>
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<tr>
<td>Active content (%)</td>
<td>30.31</td>
<td>30.30</td>
<td>30.18</td>
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<tr>
<td>Phase separation (%)</td>
<td>0</td>
<td>0</td>
<td>6.0 (water separation)</td>
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<tr>
<td>Viscosity (mPas)</td>
<td>186.7</td>
<td>147.5</td>
<td>124.2</td>
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<tr>
<td>Emulsion stability (diluted 200 times, 1h)</td>
<td>qualified</td>
<td>qualified</td>
<td>qualified</td>
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<tr>
<td>Persistent foaming (mL)</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Particle Size (d_{50}), µm</td>
<td>1.41</td>
<td>1.90</td>
<td>1.64</td>
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Stability of EW 30% Chlorpyrifos

- Polyether
- Phosphate ester
- DOW EO/PO copolymer
- DOW EO/PO butyl ether copolymer

- 54°C, 2 weeks
- 0°C, 1 week
- Initial
Summary

• High throughput formulation tools are utilized to **accelerate research** in a variety of application areas

• High throughput technique allows formulators to **cover more experiments** addressing unpredictability associated with active ingredients characteristics

• When traditional agrochemical formulation approaches fail, high throughput formulation strategies allow large scale, **systematic screening of additives in a short time period**
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